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METHOD OF MAKING CARBONIZED CELLULOSE FIBERS FOR INCORPORATION IN ELECTRICALLY CONDUCTIVE PAPER

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No Drawing. Continuation-in-part of application Ser. No. 528,375, Feb. 18, 1966. This application June 16, 1969, Ser. No. 833,667

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ABSTRACT OF THE DISCLOSURE

Natural cellulosic fibers are separated by forming an aqueous slurry of them, and the separated fibers are contacted with an organic compound to de-bond them from each other. Organic compound may be an alcohol or ketone, preferably one which boils below 130° C., or it may be a quaternary ammonium compound having an alkyl group containing at least 12 carbon atoms, or two alkyl groups containing at least 10 carbon atoms each. The de-bonded fibers are subjected to a carbonizing temperature of at least 550° C. in the absence of oxygen to make them electrically conductive. The fibers have a length-to-thickness ratio of at least 20:1, and a length of between one and five millimeters.

This application is a continuation-in-part of copending application Ser. No. 528,375, filed Feb. 18, 1966, and now abandoned.

This invention relates generally to the manufacture of paper, and has particular reference to paper having electric conductivity.

It is a general object of the invention to provide an improved procedure whereby standard paper-making techniques and machinery can be employed to produce, on a practicable commercial scale, paper having electric conductivity of a magnitude useful for a number of industrial purposes.

As pointed out in Pat. No. 3,148,107, the inclusion in paper of particulate conductive material, such as carbon, tends to degrade the mechanical properties of the paper and to impart undesirable dark coloration and smudginess. The patent referred to describes a procedure in which metal-coated fibers, such as silver-coated glass fibers, are incorporated in a paper web to establish an effective network of conductive paths through the paper.

It is an object of the present invention to provide a procedure of simpler, less expensive character for producing a paper having electric conductivity similarly attained by a small percentage of conductive fibers uniformly distributed through the sheet. The improved procedure obviates the necessity for employing special non-cellulosic fibers such as glass, and special metallizing procedures for coating these fibers to the required degree. It affords the possibility of employing natural cellulosic fibers for the purpose, the fibers being rendered conductive solely by a carbonization treatment.

For the achievement of the desired objective I first provide a supply of discrete carboniferous fibers having a a high ratio of length to thickness. A length to thickness ratio of at least 20:1 is required to achieve any commercially useful result, and a ratio of at least 50:1 is needed if the percentage of carbonized fibers in the sheet is to be held to a desirably low value. Moreover, unless the fibers are of substantial length (about a millimeter or more) the sought-for multiple conductive paths through the paper sheet cannot be produced in the desired manner. On the other hand, fibers of excessive length snarl and knot. Carbonized natural fibers of length greater than 5

millimeters are difficult to keep dispersed in conventional paper-making. As a practical matter, whole and unbroken fibers a few millimeters long are best suited to the purposes of this invention, because it is difficult to break longer fibers, and particularly tangled masses of longer fibers, into shorter fibers of uniform length.

Unsuccessful attempts have heretofore been made to provide such carbonized cellulose fibers. Wood pulp of the kind that is customarily employed for paper making is commercially available in the form of "dry lap" pulp, which is a dried matted-together board-like product; it can also be obtained in baled "flash-dried" condition; and it is also furnished in the form of an aqueous slurry. In the case of the slurry, its dehydration (in order to make the fibers available for carbonization) results in the formation of the well-known hydrogen bonds which bind the fibers into an inseparable state. In the case of the dry lap product, the fibers are already bonded together to a degree which makes it impossible, either by dry milling or by repulping and drying, to derive dry fibers sufficiently whole and discrete for the intended carbonization. Even fibers commercially available in "flash-dried" condition have been found to embody large numbers of hard bonded units which do not separate after being carbonized. Of course, the bonded units or lumps of fibers can be separated by sufficient beating. However, beating to the extent necessary to separate the fibers causes the fibers to be broken into lengths much too short to produce conductivity in the manner sought.

It is an object of this invention to solve this problem and to provide a commercially feasible method for producing whole carbonized cellulose fibers of adequate length and length to thickness ratio to serve as an additive of the character described in an otherwise conventional paper making procedure. The invention provides carbonized cellulose fibers adapted to become uniformly distributed through a paper sheet and to impart, even at very low percentages by weight, substantial and useful conductivity to the paper, without deleterious alteration of color or undesirable weakening of tensile strength.

The invention is predicated upon (1) a special preliminary de-bonding of cellulose fibers, and (2) a subsequent carbonization.

The de-bonding may be achieved in various ways. One procedure involves replacement of the aqueous phase of a fibrous slurry with a non-aqueous medium and the subsequent withdrawal of such medium. The non-aqueous medium may be an alcohol or a ketone. Another procedure involves the addition, to an aqueous fibrous slurry, of a cationic compound adapted to prevent interbonding of the fibers when they are recovered. The cationic compound may be a suitable quaternary ammonium compound.

Examples of de-bonding procedures follow:

EXAMPLE I

A mass of commercially furnished unbleached hardwood ("dry lap") pulp was dispersed in water by gentle stirring. The slurry was then filtered in a vacuum filter, and the filter cake flushed with acetone to replace most of the water in the cake. The acetone was pulled through the pad of pulp by the vacuum. The pulp was then removed from the filter and completely immersed in a vessel containing acetone. After stirring the slurry was again subjected to the action of a vacuum filter, and the filtered pad of material was then dried in an oven until it became soft and fluffy. Microscopic inspection disclosed that the fibers were uninjured and completely separate. They were then subjected to a carbonizing treatment (hereinafter to be described) at a temperature of 800° C. When the carbonized fibers were subsequently dispersed in water they separated freely, and further microscopic

examination revealed that they were intact and wholly disconnected from one another.

EXAMPLE II

Unbleached hardwood ("dry lap") pulp was dispersed in water by gentle stirring. The slurry was then filtered in a vacuum filter, and the filter cake was flushed several times with methyl ethyl ketone. The pulp was removed from the filter and suspended in methyl ethyl ketone, then filtered to remove the bulk of the ketone, and dried in an oven. The pulp was light and fluffy, and after being carbonized at 800° C. the pulp dispersed readily in water to yield long individual fibers.

EXAMPLE III

The procedure of Example II was followed, except methyl isobutyl ketone was used in place of methyl ethyl ketone. The results were the same.

EXAMPLE IV

Unbleached hardwood pulp was dispersed in water, and then filtered in a vacuum filter. The filter pad was flushed with ethanol to replace most of the water in the pad. The pulp was removed from the filter and suspended in ethanol and filtered, dried in an oven, and carbonized at 800° C. When stirred in water, the pulp broke up into individual carbonized fibers.

EXAMPLE V

The procedure of Example IV was followed, except propanol was used in place of ethanol. The results were the same.

EXAMPLE VI

The procedure of Example IV was followed, except butanol was used in place of ethanol, and the filter pad was flushed several times with butanol. The results were the same.

The debonding process of the type illustrated by Examples I–VI can be carried out with any water-miscible or partially miscible ketone or alcohol having a polarity lower than water. However, since the present procedure for making carbonized fibers involves drying the pulp in an oven, after it has been flushed with one of these solvents, for practical reasons it is preferred that the ketone or alcohol used having a boiling point below about 130° C. In this way, the pulp can be dried in a short time at a relatively low temperature.

Further examples of de-bonding follow:

EXAMPLE VII

As a control, dry esparto pulp was dispersed in water by stirring, formed into a paper sheet, and allowed to air-dry overnight at room temperature. A portion of the sheet was then carbonized at 700–750° C., made into an aqueous slurry, and agitated. The fibers were found by microscopic inspection to be present in the form of wholly unsuitable black lumps, and as bundles of broken fibers.

EXAMPLE VIII

One gram of tetraethyl ammonium chloride was mixed with three liters of deionized water, and then 25 grams of dry esparto pulp was dispersed in the mixture. The pulp was then made into a sheet, the formed sheet lightly blotted, and allowed to air-dry overnight at room temperature. The dry sheet was torn into little pieces and carbonized at 700–750° C.

One fifth gram of the carbonized sheet was dispersed in 300 milliliters of deionized water by agitating for 30 seconds. Several drops containing the suspended fiber were placed on white blotter paper and also on a glass microscope slide. Microscopic inspection of the fibers showed them to be very similar to the control sample.

EXAMPLE IX

The procedure of Example VIIII was followed, except tetrabutyl ammonium chloride was substituted for tetra-

ethyl ammonium chloride. The results were substantially the same.

EXAMPLE X

The procedure of Example VIII was followed, except 1.5 grams of alkyl trimethyl ammonium chloride, sold under the trademark "Arquad 12–33" by Armour Industrial Chemical Company, Chicago, Ill., was the quaternary ammonium compound used. Microscopic inspection of the carbonized fibers dispersed in water showed more individual fibers than the control, and some lumps.

EXAMPLE XI

The procedure of Example X was followed, except 3.0 grams of Arquad 12–33 was used. The results were about the same as in Example X.

EXAMPLE XII

The procedure of Example VIII was followed except 1.0 gram of alkyl trimethyl ammonium chloride, sold under the trademark "Arquad 18–50" by Armour, was substituted for tetraethyl ammonium chloride. Microscopic inspection of the carbonized fibers dispersed in water showed a negligible increase in individual fibers compared to the results of Examples X and XI.

EXAMPLE XIII

The procedure of Example VIII was followed, except 0.66 gram of dialkyl dimethyl ammonium chloride, sold under the trademark "Arquad 2HT–75" by Armour, was the quaternary ammonium compound used. A noticeable increase in the number of individual carbonized fibers, and reduction of clumps, was observed.

EXAMPLE XIV

The procedure of Example VIII was followed, except that the quaternary ammonium compound used was polyoxyethylene (2) cocomethyl ammonium chloride, sold under the trademark "Ethoquad C/12" by Armour; 0.5 gram of this compound was used. The results were about the same as in Example X.

EXAMPLE XV

The procedure of Example XIV was followed, except using 1.0 gram of a compound sold under the trademark "Ethoquad C/25" instead of Ethoquad C/12. Whereas Ethoquad C/12 has an approximate molecular weight of 353 (74–76% quaternary), Ethoquad C/25 has an approximate molecular weight of 925 (95% minimum quaternary). The results were about the same as Example XIV.

EXAMPLE XVI

The procedure of Example VIII was followed, but 0.5 gram of didecyldimethyl ammonium chloride was used as the quaternary ammonium compound. This compound, which could not be found commercially, was prepared from didecylmethyl amine and methyl chloride. Microscopic examination of the carbonized fibers showed many more individual fibers than in case of Examples X and XI, but not as many as in Example XIII.

EXAMPLE XVII

The procedure of Example VIII was followed, except that 0.5 gram of a mixed 1-(2-hydroxyethyl)-2-heptadecenyl and heptadecadienyl-1-(4-chlorobutyl)-2-imidazolium chloride, sold under the trademark "Nalquat G–9–12" by National Aluminate Corporation of Chicago, Ill., was the quaternary ammonium compound used. Microscopic inspection revealed that the carbonized fibers were whole and unbroken and completely separate from one another.

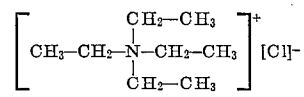
EXAMPLE XVIII

The procedure of Example VIII was followed, except that unbleached hardwood pulp was used instead of esparto pulp, and 0.625 gram of a quaternary ammonium

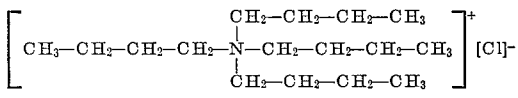
compound sold under the trademark "Avitex" by E. I. du Pont de Nemours, of Wilmington, Del., was used instead of tetraethyl ammoniunm chloride. The carbonized fibers were found to be whole and unbroken and completely separate from one another.

Consideration of the chemical structures of the quaternary ammonium compounds referred to in Examples VIII–XVIII indicates that only compounds having at least one relatively long chain alkyl group show any debonding action.

The structure of tetraethyl ammonium chloride (Example VIII) is as follows:

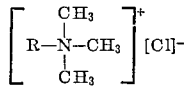


The structure of tetrabutyl ammonium chloride (Example IX) is as follows:



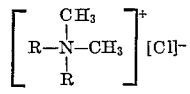
Thus, it will be seen that a compound with as many as four carbon atoms in each of its alkyl groups has no debonding effect.

Arquad 12–33 (Examples X and XI) and Arquad 18–50 (Example XII) have the following general structure:



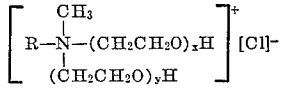
The Arquad series of compounds are each actually composed of several compounds, each compound having the general structure set forth above, and "R" being an alkyl group. The primary constituent (about 90%) of Arquad 12–33 has a dodecyl R group including a 12 carbon chain. The primary constituent (about 93%) of Arquad 18–50 has an octadecyl R group including an 18 carbon chain.

Arquad 2HT–75 (Example XIII) has the following general structure:



The primary constituent (about 75%) of this compound has two octadecyl R groups each containing an 18 carbon chain.

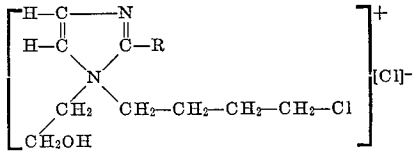
The general structure of Ethoquad C/12 (Example XIV) and Ethoquad C/225 (Example XV) is as follows:



"R" is an alkyl group derived from coco fatty acid. In Ethoquad C/12, the R group includes a 12 to 18 carbon chain, and in Ethoquad C/25, the R group includes a 12 to 18 carbon chain.

The general structure of didecyldimethyl ammonium chloride (Example XVI) is the same as that of Arquad 2HT–75, and each R group includes a 10 carbon chain.

The general structure of Nalquat G–9–12 is believed to be as follows:



R is an alkyl group comprising a 17 carbon chain.

The structure of Avitex is unknown, but from its relatively high molecular weight, it certainly includes at least one alkyl group having at least 12 carbon atoms.

The desired de-bonding action produced by a quaternary ammonium compound is believed to occur because the compound has a cationic component adapted to attach itself to the dispersed cellulose fibers, and a long carbon chain alkyl group which envelops or coats the fibers to prevent their interbonding. The examples show that significant de-bonding is produced only with quaternary ammonium compounds having at least one alkyl group containing at least 12 carbon atoms, e.g., Arquad 12–33, or at least two alkyl groups containing at least 10 carbon atoms, e.g., didecyldimethyl ammonium chloride. It appears that the longer the carbon chain of the alkyl group or alkyl groups, the better the de-bonding action.

The amount of quaternary ammonium compound needed is so small that the compound disappears entirely during the drying and carbonizing procedures. In the examples, from 2%–4% by weight of the fibrous material was employed. However, even lesser amounts may be used, although the desired prevention of fiber bonding does not manifest itself to an adequate degree if an amount less than about 1.0% is employed.

With respect to the carbonizing process, it has been found that adequate conductivity can be achieved if the cellulose fibers are subjected to temperature above 550° C. in the absence of air. Any suitable enclosed vessel can be employed, provided it has a vent adapted to allow the escape of the voluminous gases that are given off by the cellulose in the early stages of the carbonization. Enclosure of such a vessel in an electrically heated muffle furnace has been found satisfactory. Exposure to heat for a period of at least four hours was found to be desirable. At temperatures below about 550° C. no appreciable conductivity was achieved. At temperatures above this, however, e.g. at about 900° C., the carbonization reduces resistivity to a negligibly small value and the carbonized fibers become admirably suited for the intended purpose.

The invention may be carried out with a variety of natural cellulosic fibrous materials, including hardwood pulp, softwood pulp, grass and cereal straw, sugal cane bagasse, sisal, hemp, and esparto. The fibers should be no more than 5 millimeters long and preferably straight. Fibers appreciably shorter than 1 mm. do not have a length-to-thickness ratio of adequate magnitude to establish the over all conductivity sought to be attained; fibers that are too long (e.g., flax) have a tendency to become tangled and thus impair the uniformity of distribution required. For these reasons the hardwood pulps are preferred, since the fibers are relatively fine, straight, and smooth. The grasses, especially esparto, afford fibers which are excellently suited for the purposes of the invention. The term "pulp" as used in the appended claims is intended to signify any of the commercially available products commonly employed for paper making, whether in dried or semi-dried state of in aqueous dispersion.

Examples of the complete paper-making procedure follows:

EXAMPLE XIX

As a control, an additive consisting of a highly conductive carbon black (Vulcan XC72R Furnace Black) was added to a slurry of beaten softwood pulp in an amount equal to 35% by weight, of the fibrous material. A paper was formed of this slurry by usual paper-making techniques and was found to have a basis weight of 20 pounds (500 rectangular sheets 20 inches wide and 30 inches long), a tensile strength of 1045 grams per inch, and a resistivity of 1100 ohms per square. The resistivity referred to was in the plane of the sheet, as are all the other resistivities hereafter to be mentioned, unless otherwise specified. The conductivity was in a commercially useful range, but the paper was black, having a brightness measuring 5% on a photovolt tester, and smudgy.

EXAMPLE XX

A paper-making stock was prepared comprising one-half bleached softwood pulp and one-half bleached hard-

wood pulp. To this pulp was added de-bonded and carbonized esparto fibers, as hereinbefore described, in an amount equal to 4.3% of the total weight of all the fibers. (The weight percentages hereinafter referred to are similarly based). A paper was made by usual techniques having a basis weight of 22 pounds. The paper had a tensile strength of 6400 grams per inch, was light gray in color, having a brightness of 43% on a photovolt tester, and a resistivity of 450 megohms per square. This degree of conductivity is of use, for example, in certain electrostatic printing processes.

EXAMPLE XXI

Esparto fibers were de-bonded and carbonized as hereinbefore described, and were added to a slurry of ordinary cellulosic paper-making fibers in an amount equal to 6%, by weight. A paper was formed by usual techniques, having a basis weight of 11½ pounds. Its conductivity in the plane of the sheet was found to be no greater than that of ordinary paper (i.e., paper of the same basis weight but without the added carbonized fibers), but in the transverse direction, i.e., through the sheet (about 0.0025 inch), its resistivity was only 9000 ohms as compared with 10 megohms or more for the conventional paper containing no conductive fibers. For certain industrial uses, this grade of conductivity is of useful magnitude.

EXAMPLE XXII

An electrically conductive paper was formed of conventional softwood pulp to which carbonized de-bonded esparto fibers had been added in an amount equal to 10%. The paper had a basis weight of 11 pounds, a tensile strength of 1130 grams per inch, and a resistivity of 480 ohms per square.

It is to be noted that the tensile strength was greater than that of the carbon-filled paper of Example XIX even though the basis weight was considerably less, and coupled with this added strength characteristic was an increase in conductivity. Moreover, the paper was of far more sightly character, being medium gray in color (brightness of 32%) and it was not at all smudgy.

EXAMPLE XXIII

A paper similar to that of Example XXI was made, employing 10% of carbonized de-bonded hardwood fibers. The basis weight was 11 pounds, the tensile strength 1210 grams per inch, and the resistivity 730 ohms per square. The color was medium gray. The usefulness and desirable qualities of the paper were comparable to those of Example XXI.

EXAMPLE XXIV

To achieve similar results in a paper even lighter in color, an additive was employed consisting of 8% of de-bonded carbonized softwood fibers and 12% of titanium dioxide, these percentages being based, by weight, on the fibrous material in the main paper-making slurry. The paper resulting from the use of this slurry had a basis weight of 12 pounds and a resistivity of 2000 ohms per square. The paper had a brightness measuring 48% on a photovolt tester.

EXAMPLE XXV

A paper similar to that of Example XXIV was formed of the same slurry, except that the amount of de-bonded carbonized fiber was increased to 13%. The basis weight of the paper produced was 12 pounds, its brightness was 36%, measured as before, and its resistivity was reduced to 380 ohms per square.

EXAMPLE XXVI

A paper-making stock was prepared of unbleached softwood, and to this stock was added de-bonded and carbonized hardwood fibers in an amount equal to 25% by weight. The paper had a basis weight of 8 pounds, a resistivity of 400 ohms per square, and a tensile strength of 1800 grams per inch. Note that the conductivity of this sheet is more than double the conductivity of the control sheet (Example XIX) although its basis weight is only 40% of the basis weight of the control sheet.

From these examples, it will be seen that the percentages of carbonized fibers may be retained at low values and still afford a uniformly distributed network of minute conductive path through the paper. Generally speaking, the percentage should be as low as possible, compatible with the nature and ultimate purpose of the paper to be produced. However, a percentage of carbonized fibers less than 4% produces no conductivity currently useful for practical applications. The maximum percentage of carbonized fibers which can be used is limited primarily by the tensile strength required of the paper for the particular use, since the tensile strength decreases as the percentage of carbonized fibers increases. This is indicated by the following example.

EXAMPLE XXVII

A paper-making stock was prepared comprising 40% bleached softwood pulp and 60% de-bonded and carbonized esparto fibers. A paper sheet was made having a basis weight of 12 pounds. The sheet had a resistance of 140 ohms per square, and a tensile strength of 612 grams per inch.

The advantages of the improved conductive paper include the fact that it remains conductive even under conditions of low humidity. Also, it remains porous and permeable to water vapor.

The invention has been shown and described in preferred form only, and by way of example, and many variations may be made in the invention which will still be comprised within its spirit. It is understood, therefore, that the invention is not limited to any specific form or embodiment.

What is claimed is:

1. A method of producing electrically conductive fibers capable of being uniformly distributed in a paper-making slurry, so that an electrically conductive paper sheet can be formed from said slurry, the method comprising the steps of forming an aqueous slurry of natural cellulosic fibers to separate the fibers from one another, adding to the slurry a de-bonding amount of a quaternary ammonium compound, said quaternary ammonium compound having at least one alkyl group containing a chain of at least 12 carbon atoms, or at least two alkyl groups each containing a chain of at least 10 carbon atoms, thereafter drying the fibers, and subjecting them to a carbonizing temperature of at least 550° C. in the absence of oxygen to form electrically conductive fibers.

2. A method as defined in claim 1 wherein the fibers have a length-to-thickness ratio of at least 20:1 and a length of between one and five millimeters.

3. A method as defined in claim 1 wherein the quaternary ammonium compound is added to the aqueous slurry in an amount equal to at least 2.0% by weight of the fibers.

4. A method of producing electrically conductive fibers capable of being uniformly distributed in a paper-making slurry, so that an electrically conductive paper sheet can be formed from said slurry, the method comprising the steps of forming an aqueous slurry of natural cellulosic fibers to separate the fibers from one another, draining the water from said slurry, and thereafter but before the fibers dry, contacting the fibers with an organic compound consisting of a water-miscible or partially miscible ketone or alcohol having a polarity lower than water, thereafter drying the fibers, and subjecting them to a carbonizing temperature of at least 550° C. in the absence of oxygen to form electrically conductive fibers.

5. A method as defined in claim 4 wherein the ketones and alcohols have a boiling point below about 130° C.

6. A method as defined in claim 4 wherein the fibers have a length-to-thickness ratio of at least 20:1 and a length of between one and five millimeters.

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