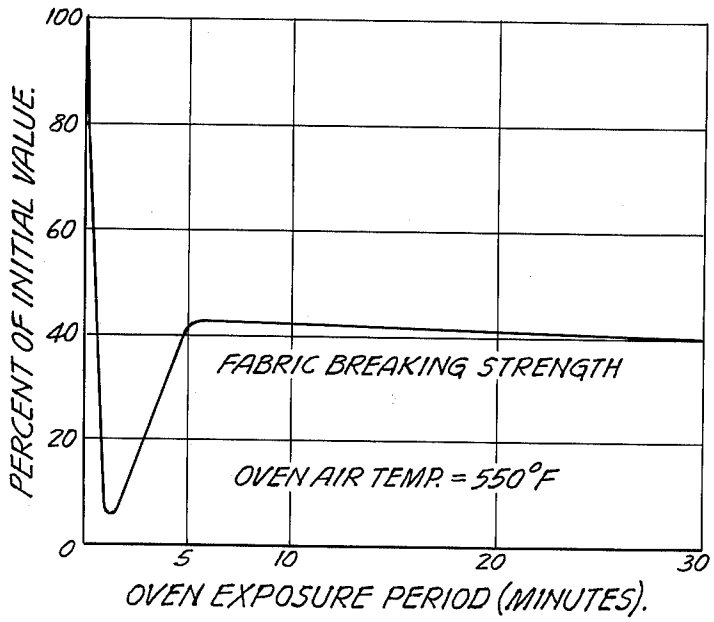
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HEAT-RESISTANT BLACK FIBERS AND FABRICS DERIVED FROM RAYON

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GRAPH SHOWS TYPICAL NEARLY COMPLETE LOSS OF STRENGTH FOLLOWED BY SUBSTANTIAL REGAIN IN CONVERTING WOVEN RAYON FABRIC (IMPREGNATED WITH NITROGENOUS SALT) INTO A CORRESPONDING USEFUL FLEXIBLE BLACK ORGANIC FABRIC WHICH IS HEAT RESISTANT AND INSULATIVE AND WHOSE FIBERS CONTAIN COMBINED NITROGEN AND 50-65% CARBON.

(THIS PRODUCT IS CAPABLE OF BEING RAPIDLY CARBONIZED TO CORRESPONDING USEFUL ELECTRICALLY CONDUCTIVE FABRICS).

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HEAT-RESISTANT BLACK FIBERS AND FABRICS DERIVED FROM RAYON

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This application is a continuation-in-part of my copending application S.N. 22,129, filed April 14, 1960 (now abandoned).

This invention relates to new and useful man-made organic fibers, and fabrics thereof, which have good flexibility and tensile strength and that are per se black, inert, thermally stable, flame-resistant and resistant to intense heat. They have good thermal and electrical insulating properties.

These novel fibrous materials are produced by a thermo chemical transformation of corresponding rayon (regenerated cellulose) fabrics and fibers, which retain fiber identity but are changed to a flexible black state having a different chemical composition and radically different chemical and physical properties. In this process the rayon precursor, impregnated with a nitrogenous salt, is heated for a short time to a final temperature of at least 450° F., as more fully disclosed hereafter.

A woven rayon cloth when thus transformed to this black state, has substantially the same pliancy as the original rayon cloth and a yarn tensile strength (breaking strength) at least 20% as great; and may have up to about 40% or more of the original tensile strength. It has substantially the same physical structure and appearance except for its lustrous jet black color. The fabric has good abrasion resistance and it does not blacken the fingers when stroked.

The original polymeric cellulose molecules of the rayon fibers are not only changed by pyrolysis but by accompanying chemical compounding reaction whereby from about 3% up to about 6% by weight of nitrogen atoms (apparently carbon-bonded) become chemically combined in the stable polymeric oxygen-containing carbon-compound molecules of the black product fibers. This insulative fiber product is non-carbonized, is not charred, is free from elemental carbon, and it is non-tarry. The carbon content as determined by analysis is in the range of about 50 to 65%. The thermochemical transformation is rapid, requiring not over about 30 minutes at oven temperatures which are in the range of about 450 to 900° F.; and a total oven exposure of about 10 minutes or less can be employed under suitable conditions. Thus the process of manufacture is quite different from those that have been employed in producing partially-carbonized fibers, and carbon fibers, by lengthy heating of cellulose fibers at gradually increased temperatures. (The present product can be carbonized without loss of fiber identity to make electrically conductive fiber material of 70 to 99+% carbon content as described in a later section, but the intervening present description relates solely to the preparation and properties of the aforesaid insulative type of black fiber material containing up to 65% carbon.)

The accompanying drawing graphically illustrates a typical transformation and shows the surprising changes in fabric strength during the oven heating; the salt-impregnated fabric at first losing nearly all of its strength, and then regaining enough strength to provide a usefully flexible and strong black fabric product. The fabric treatment in this case is similar to that described hereafter in the illustrative "example."

A water-soluble nitrogenous salt reactant is employed

but no product material, other than the transformed fibers per se, is responsible for the aforesaid properties of the present product. The product retains its essential properties even though subjected to prolonged or repeated boiling in water (which leaches out any soluble residues present), and even though subjected to hot concentrated sulfuric acid. Chemical analysis shows that these after-treatments of the black fabrics and fibers may result in some increase in the weight percentage of nitrogen, but do not decrease this percentage, demonstrating that the nitrogen is strongly chemically combined in the fiber molecules and that the presence of extraneous substances is not responsible for the characteristic features.

Examination of thin cross-sectional slices of the black fiber under the microscope, with transmission illumination by white light, shows a substantially uniform amber color over the entire section; making clear that the entire fiber is substantially homogenous and has been transformed. The slice is translucent and no carbon or other particles are observed. The lustrous jet black opaque appearance of the fabrics and fibers is due to substantially complete absorption of all visible wave lengths of incident light by fibers which are smooth-surfaced and which are translucent in the sense just mentioned (permitting incident light to penetrate and be absorbed in the body of the fiber).

This invention provides woven and nonwoven fabrics, yarns, staple fibers, and continuous filaments, of useful strength and flexibility, which are flame-resistant and are resistant to high temperatures, and which are good electrical and heat insulators. They do not become fragile upon prolonged or repeated exposure to temperatures as high as 600° F., and even higher, and can tolerate short exposures to temperatures higher than 1000° F. without becoming fragile. A blowtorch flame does not cause combustion even when applied until the fabric has finally disintegrated and vaporized.

A dramatic demonstration of uniqueness was provided by fastening a piece of the black woven cloth (prepared as in the subsequent "example") in a hoop-shaped frame so as to provide an unsupported cup. A half-pound of molten steel (temperature of about 2700° F.) was poured into this cloth cup and allowed to cool to room temperature. The cloth did not burn or disintegrate and retained sufficient strength and flexibility to support the cast chunk of steel at all stages. Another demonstration was to fill such a black cloth cup with a pound of lead pieces and heat the bottom with a Bunsen burner flame (which contacted the cloth) so as to melt the lead and then further heat the molten pool of lead at 800° F. for half an hour. In these demonstrations the cloth was not tightly woven; nevertheless, there was no leakage of the molten metal, showing that it did not wet the fibers.

The extreme inertness of this novel material is further indicated by the fact that no solvent for it has yet been found. Rayon fibers will completely solvate and dissolve in an acid solution of calcium thiocyanate, but the converted black fibers are not affected. Moreover, rayon fibers are completely digested by 60% H_2SO_4 at room temperature, whereas the converted black fibers are not affected even at steam bath temperature, and in fact are resistant to attack by 70% H_2SO_4 at steam bath temperature for periods in excess of 24 hours. The present black fibers are only moderately attacked by 20% NaOH solution after 24 hours on a steam bath; although the washed and dried fibers are found to have become embrittled and to have lost much of their strength. Surprisingly, the original flexibility of these caustic treated fibers can be revived by washing with dilute sulfuric acid solution.

These unique properties suggest various practical uses. For instance: Heat-resistant insulative articles of wear-

ing apparel, aprons and gloves for metallurgical and foundry workers and for fire fighters. Fire barrier drapes. Also, fire-resistant insulating sleeves and wrapping tapes for electrical conductors and cables and for piping and conduits. Also, fire-resistant fibrous insulating batts. Fibers in flock form can be used for providing heat-resistant flocked coatings. Fabrics, yarns and continuous filaments can be used to advantage in fiber-reinforced plastics subject to high temperatures; including "ablation" types, and types which should not include any metal or metal atoms, or leave an ash residue upon decomposition and vaporization. Also as backings or reinforcing fibers in high-temperature types of insulating tapes and adhesive tapes, including pressure-sensitive adhesive tapes. Also, inert acid-resistant filter cloths for filtering very hot gases, liquids and even molten metals. The present yarns have better heat resistance than industrial asbestos yarns; and the fabrics have better thermal insulating properties than asbestos fabrics.

The following described process is employed in making the insulative black fiber products of this invention from rayon textile fiber starting materials, which can be in the form of cloth (woven, knitted or felted); nonwoven fibrous batts, felts, fabrics or tissues formed of staple fibers; yarns, roving, continuous filament tows, etc., whose structural identity can be retained throughout the process. (The term "rayon," as here used, is employed in the modern sense as designating man-made regenerated-cellulose filaments and the textile fibers, yarns and fabrics made therefrom. Such filaments and fibers may range in size from about 5 to about 30 microns in diameter. The term does not include cellulose acetate fibers and fabrics; but it does include high tenacity regenerated cellulose fibers made by saponifying (hydrolyzing) oriented cellulose acetate fibers, as illustrated by "Fortisan" cellulose fibers, yarns and fabrics.) An important economic feature is that these rayon fibers and fabrics are readily and inexpensively available from the textile industry, and that the process is relatively simple, rapid and economical and needs no unusual or elaborate equipment. Thus the woven cloth products can be manufactured directly and inexpensively from woven rayon cloths of the same physical structure. Cotton and other natural cellulosic fiber materials are not equivalent and cannot be employed.

The rayon starting material in continuous web, yarn, roving or tow form can be processed in continuous fashion from start to finish, which is preferable in factory production although batch procedures can be used when making up small lots or in experimenting.

The basic steps are:

(1) The fibrous rayon starting material (preferably in continuous web, yarn, roving or tow form) is scoured to remove sizings and other contaminants if present; suitable procedures being well known in the textile industry. For instance, starch sizings on warp yarns can be removed by washing with soap or detergent solution, or by enzymatic action; and oil lubricants with a volatile solvent such as mineral spirits. A final scouring to remove residual contaminants may be desirable, such as with ammonia water (e.g., 28% ammonium hydroxide solution) or with 4% sodium hypochlorite solution. The scoured fabric may be dried at about 125° F. The scouring step may obviously be omitted when the rayon yarn or other rayon starting material is in a sufficiently clean state as received from the supplier. The clean dry rayon starting material is impregnated throughout with an aqueous solution of a nonoxidant water-soluble salt of a strong acid and nitrogenous base, such that the saturated fibrous material, after squeezing to a damp state to remove excess liquid and to ensure that all fibers are treated, contains the salt in a sufficient proportion to render the fibers, even when dried, nonflammable and able to undergo the subsequent thermochemical transformation to provide product fibers containing at least 3% by weight of combined nitrogen. A salt solution concentration of about 10 to 30% gives best results. Ammonium sulfate, ammonium sulfamate, dibasic ammonium phosphate, ammonium chloride, and methyl and ethyl amine salts of phosphoric acids, and various mixtures thereof, are presently preferred salts. These nitrogenous phosphate salts result in at least 0.5% by weight of carbon-bonded phosphorus atoms, as well as carbon-bonded nitrogen atoms, being incorporated in the polymeric molecules of the product fibers. Boric acid (or equivalent boron compound) may also be included so as to result in product fibers that include at least 0.5% by weight of carbon-bonded boron atoms which enhance fiber stability at high temperatures. A pickup of salt (dry basis by weight) of about 10 to 30% appears to give best results. Immersion for about 5 minutes in a near boiling salt solution is preferably employed to facilitate impregnation of the fibers, excess solution then being removed to give about a 100% wet pickup of salt solution.

(2) The damp salt-treated fibrous material is then heated until dry, preferably at about 140 to 250° F. The dry rayon fibers are thus impregnated (and not merely coated) with the salt owing to the permeability of the fiber structure to such aqueous salt solutions. If this treatment has caused bundling and sticking together of fibers, further processing will be improved by flexing, rubbing, tumbling the salt-impregnated material to loosen and free the individual fibers so they will be fully exposed to the atmosphere during heating.

(3) The dry salt-impregnated rayon fibers are next heated in an oven at an elevated temperature and for a time which is short but is sufficient to bring about the desired transformation of the fibers to the previously described strong and flexible nitrogen-containing black state. Air is not excluded. On the contrary, heating in the presence of air (or equivalent oxygen-containing atmosphere) is essential to the production of the presently desired product fibers. Convenient use can be made of a vertical tower-type of air-circulating oven for continuous manufacture. The preferred general temperature range is about 450 to 600° F. when a plain air atmosphere is employed. If the temperature is too high for the existing conditions and period of exposure, an uncontrollable exothermic reaction develops and the fibers or fabric will glow red and yield a brittle product. The optimum temperature-time combination can be determined by trial-and-error under any given set of manufacturing conditions. The air flow should be regulated to avoid a destructive exothermic reaction ("exotherm"); a decrease in the rate at which air enters the oven resulting in a lower concentration of oxygen in contact with the hot fibers due to the diluting action of decomposition vapors emitted from the fibers. Optimum temperatures when a circulating air oven is employed are usually in the range of about 500 to 550° F., and corresponding optimum times in the inverse range of about 30 to 5 minutes. The most desirable heating period is one that is long enough to develop the maximum tensile strength, beyond which point the tensile strength starts to diminish. The treatment of light rayon fabrics appears to be optimized at a combination of about 550° F. and five minutes. In the case of heavy close-woven cloths (such as one weighing about 20 oz. per square yard), it has been found desirable to conduct the heat treatment in successive stages at increasing temperatures to avoid a too-rapid temperature rise in the interior of the fabric (resulting from the exothermic nature of the reaction and the poor heat conductivity of the fibers), as by heating for successive ten minute periods at approximately 475° F., 500° F. and 525° F. All of these temperatures refer to the temperature of the air in proximity to the fibrous material, which enters the oven at a much lower temperature and builds up in temperature in response both to the external heating and to the internal heating produced by the exothermic chemical reaction in the fibers.

Higher oven temperatures (up to about 900° F.) and correspondingly shorter heating periods (down to one

minute or even less) can be utilized by introducing into the oven an atmosphere of lower oxygen content than plain air (which contains 23% oxygen by weight). This provides a further expedient for effectively regulating conditions so as to avoid an uncontrolled or excessive ("run away") exothermic reaction. Thus use can be made of air diluted with steam, nitrogen or ammonia so as to have an oxygen content which is substantially less than 23% and which may be as low as about 5% by weight. Or use can be made of an equivalent artificial atmosphere comprised of a mixture of oxygen with steam or ammonia, a preferred example being a mixture of 93% ammonia and 7% oxygen (by volume). Air diluted with nitrogen or ammonia to an oxygen content of approximately 5 to 10% by weight is a preferred example for use at oven temperatures of about 700° F. or somewhat higher and exposure periods of about two minutes, and conversion can be followed by cooling in air to room temperature. It is also possible to use an equivalent two-stage oven process in which the salt-impregnated fibrous rayon material is converted to a black nitrogen-containing state in an oxygen-free atmosphere (e.g., a steam, nitrogen or ammonia atmosphere), at a temperature which may be as high as about 900° F., and is then further heated in air or other oxygen-containing atmosphere to complete the conversion to the desired final state (apparently by freeing the fibers of an easily-oxidizable decomposition product); resulting in lustrous black fibers free from by-product contaminants. It is also possible to employ a very short conversion period of less than one minute at temperature as high as the order of 900° F. when conditions are adjusted so that the hot fibers only contact an atmosphere of low oxygen content, and the converted material is then immediately exposed to a non-oxidizing atmosphere to prevent harmful oxidation action.

During the first part of this thermochemical operation, the nitrogenous-salt-impregnated fibers become degraded to a weak though self-supporting state, apparently by the decomposition and ring-cleavage that the cellulose molecules are undergoing; resulting in the liberation of water and other gases. As the reaction progresses beyond this point, the fibers regain strength and flexibility until a maximum is achieved at a tensile strength which may be as high as 40% or more of that of the original rayon fibers. (This time-temperature conversion effect is illustrated in the graph of the drawing.) During this strength-regaining stage, the decomposed molecules are reforming into a new type of polymeric fiber molecule, containing up to about 6% by weight of combined carbon-bonded nitrogen atoms. Analysis of intermediate samples indicates that inclusion of carbon-bonded nitrogen atoms in the fiber molecules is coincident with increase of fiber strength after passing the minimum strength point. The maximum weight loss is reached after the point of minimum strength has been reached. When the peak strength point has been reached there will have been a loss of approximately three molecules of water per cellulose unit and a negligible loss of carbon. Shrinkage of a woven cloth may be about 10%. Continued heating beyond this point causes evolution of both water and carbon dioxide.

(4) The black insulative nitrogen-containing fibrous product, after cooling, may be washed to remove soluble materials that are present (and which might adversely affect desired properties of the product for particular usages). This washed and dried end product, prepared under substantially optimum conditions, has a weight which is approximately two-thirds that of the corresponding original rayon fibers (dry basis). It is hygroscopic as illustrated by the fact that it can absorb up to about 20% of its weight of water when exposed to an atmosphere of 100% relative humidity at 72° F. Fabrics and fibers which have been conditioned by exposure to a humid atmosphere are more flexible and stronger than those that are extremely dry.

These insulative products (washed or not) are suitable for sale and for many uses without further thermal or chemical treatment. They have good strength and flexibility, the tensile strength being at least 20% (and preferably at least about 40%) that of the original rayon starting material. The corresponding tenacity-retention percentages are higher since tenacity values in grams per denier involve the fiber weight per unit length, and the black fibers weigh less than the original rayon fibers from which they are made. Tenacity values of fibers and yarns of 0.4 gram per denier and higher, and even above 1.0 gram per denier, can be obtained. Woven products having a tensile strength of at least 20 lbs. per inch width can be made. Products of highest strength are made from fibrous saponified oriented cellulose acetate ("Fortisan") starting materials.

Elemental analyses for carbon, hydrogen and nitrogen, of various washed and dried sample products prepared under various conditions in the temperature range of 450 to 600° F., and using various nitrogenous salts, have shown the presence of these elements in approximately the following ranges (percentage by weight) :

	Percent
Carbon	54 to 61
Hydrogen	3.4 to 4.0
Nitrogen	3.1 to 5.8

Phosphorus, sulfur, chlorine, and boron were also found by analysis of these products when made using phosphate, sulfate or chloride salts, or boric acid, respectively; in small proportions ranging up to as high as about 2.5%. The balance in each case was oxygen (in the range of about 30 to 35%). In comparison, pure cellulose (dry basis) has a composition of 44.4% carbon, 6.2% hydrogen and 49.4% oxygen. The washed and dried end products commonly weigh 60 to 67% as much as the rayon starting material from which made. These facts demonstrate the radical chemical transformation undergone by the cellulose molecules; and also the continued "organic" nature of the fibers. X-ray diffraction studies of this black fiber product show that the original crystalline structure of the rayon cellulose fibers is lost.

Returning to the nitrogenous salt used for impregnating the fibrous rayon starting material, a number of examples were previously mentioned in describing stage (1) of the process. All nonoxidant ammonium and amine salts of strong acids render the fibers sufficiently nonflammable and appear to be effective in producing the described thermo-chemical transformation, provided that they are at least least moderately water-soluble so that aqueous treating solutions of at least 10% salt concentration can be made up. The term "water-soluble" is used herein in this sense. Examples of these strong acids are sulfmaic. sulfuric, phosphoric, hydrochloric, trichlororacetic and trifluoroacetic acids. Examples of the amines are the mono-, di-, and trimethyl and ethyl amines; hydrazine, aniline, morpholine, pyridine, and ethylene diamine. A variety of salt combinations of each of these acids and amines have been successfully tested as treating salts so as to demonstrate the general point, although obviously they are not equal in respect to economic and practical considerations. Ammonium nitrate, ammonium persulfate and amonium perchlorate are examples of salts which are recognized and used as oxidants, and which are inoperable in the present process because of the strong oxidizing action on the hot carbonaceous fibers that promotes combustion or a strong exothermic reaction which prevents formation of the desired flexible product fibers. Suitable and preferred ammonium salts have previously been listed.

The nitrogenous phosphate salts are noteworthy because the high degree of flameproofing and fireproofing they impart. This is important in preventing combustion or glowing during the manufacture of the black product at the higher temperatures which are preferably

employed in order to permit of a short thermochemical treatment period. It also prevents the finished product from glowing or after-glowing when subjected to intense heat or to a flame as may sometimes otherwise happen. The beneficial effect of using a phosphate salt is retained even though the black product has been thoroughly washed. The nitrogenous sulfate and sulfamate salts also provide good glow resistance. It has already been noted that in such cases a small amount of phosphorous or sulfur (or both if both types of salt are used) is found upon elemental analysis of the washed and dried product. The inclusion of boric acid (or equivalent boron compound) in the salt composition to provide 0.5 to 2.5% boron content in the product also inhibits combustion and glowing, and results in carbon-bonded boron atoms becoming incorporated in the product fibers, which enhance stability at high temperatures. An alternative way of imparting high after-glow resistance is by impregnating the black product with a phosphate salt solution (for instance, a 10% aqueous solution of dibasic ammonium phosphate) and then drying; although this does not provide a product that is free of water-soluble material. However, for some usages this is unimportant.

EXAMPLE

A mixture of nitrogenous salts, including a phosphate salt, and also including boric acid, can be used quite satisfactorily; as illustrated by the following 20% concentration treating solution that has proved very effective:

	Part by weight
Ammonium sulfamate	10
Dibasic amonium phosphate	4
Dicyandiamide	2
Boric acid	4
Water	80

A woven rayon cloth which was treated with this salt solution, dried, and subjected to heating for 5 minutes at 550° F., in the manner previously described, yielded an excellent black cloth having the following elemental analyses before and after washing:

Element (percent by weight)	Before Washing	After Washing
Carbon	51.4	56.0
Hydrogen	3.9	3.8
Nitrogen	5.37	5.52
Sulfur	3.5	2.6
Phosphorous	2.07	0.35
Boron	0.8	0.8
Oxygen (by difference)	33.0	30.9

The dried salt-treated cloth weighed 120% as much as the untreated rayon starting cloth; the converted black cloth weighed 68% as much; and after thorough washing in distilled water, and drying, it weighed 60% as much. (Percentages by weigh on dry basis.) Despite the transformation, involving a 40% loss of weight, the yarns of the ultimate black cloth product had a tensile strength about 40% as great as that of the yarns of the original rayon cloth; and this cloth had a good drape and hand (handle), a resilient snap, and good tear resistance.

As previously noted, the graph of the accompanying drawing illustrates a typical strength-time curve for this transformation. A comparison of the tenacity strengths and thermal stabilities of insulative organic black yarns made by the present process with those of industrial asbestos yarns, is of interest. These abestos yarns contained 20% by weight of cotton fibers, which had been included to provide an asbestos yarn of adequate coherency and strength for general industrial usage (such asbestos yarns being sold in the U.S.A. as "Underwriters Grade"). The black yarn of the present invention had an initial tenacity value of 0.94 gram per denier which was reduced to 0.46 upon five hours baking in an oven at 500° F. The asbestos yarn had an initial tenacity value of 0.31 which was reduced to 0.10 upon similar baking for five hours at 500° F. Thus the black yarn after this baking had a higher tenacity than the unbaked asbestos yarn. In another comparison wherein samples were heated for 17 hours at 400° F., the tenacity value for the black yarn was reduced to 0.36 whereas the value for the abestos yarn was reduced to 0.16. These figures illustrate the surprising strength and thermal stability of the black organic fibers and yarns of this invention.

In another test sample pieces of a typical black woven fabric weighing 8 ounces per yard were exposed for different periods at different temperatures in an air atmosphere in a muffle furnace. The samples retained at least half their weight when heated for four hours at 600° F., 45 minutes at 800° F., or 30 minutes at 1000° F.; and retained about one-half the original warp-direction breaking strength when heated for four hours at 600° F. or two hours at 800° F. A piece exposed for four hours at 800° F. shrank down to less than one-fourth the original area with an 85% loss of weight, but retained fiber identity and was still self-sustaining with a warp-direction breaking strength of 2 lbs. per inch width. None of these samples became electrically conductive, thus showing that they do not become "carbonized" when heated in air.

Electrical arc-proofing tape

A valuable industrial use of the type of black insulative woven fabric described above is as a substitute for asbestos fabric in electrical arc-proofing and fireproofing tape constructions where the fabric carries a heavy coating on one side of a flame retardant elastomer (such as polychloroprene or a plasticized polyvinyl chloride). This tape is wrapped upon high voltage power cables in manholes, cable trays, switchboxes and substations, etc.

Electrical systems usually contain multiple power cables in a given area. The superior electric arc resistance and fireproofing of the present tape enables the blast and heat effects of a failing power cable to be better contained with less risk of other cables failing. For example, an arc can be contained until the automatic cut-off equipment (delay relay and circuit breaker) has functioned such that neighboring lead cable sheathes survive, unmelted and unharmed, contrary to what happens when cable sheath failure occurs prior to power cut-off. Thus a 200 ampere arc can be contained for at least 40 seconds. The tape as a whole is fireproof (self-extinguishing) and the woven fabric cannot melt, which is not true of glass and asbestos fabrics. During continued exposure to an arc the coating ablates and the fabric carbonizes and gradually erodes away. A lead cable sheath protected in this way can withstand a burning transformer oil flame without melting for much longer than when an asbestos tape wrap is used (lead melts at about 625° F. whereas such flame may subject the tape to a temperature of 1500° F. or higher). This tape is not affected by water, sewage or ultraviolet light and has excellent acid and chemical resistance.

The presently preferred tape construction is made as briefly described below:

The starting fabric comprises spun viscose-rayon yarns in a plain close weave having 22 warp yarns and 24 fill yarns per inch, a caliper thickness of 26 to 30 mils, and a weight of 12 ounces per square yard. The tensile breaking strengths in the warp and fill directions are 135 and 140 lbs. per inch width, respectively, and the corresponding average elongations are 17% and 28%, respectively. This cloth is impregnated with the treating solution whose formulation is given above in the "example" so as to have a salt-mixture pickup of 14 to 17% by weight (dry basis).

The dry salt-impregnated cloth is continuously heat-converted by passing through a vertical, direct, gas-fired tower with circulating air fan where it is subjected to

an air temperature in the range of 450 to 525° F. during a residence time of 12 to 15 minutes. The temperature and the air circulation are closely controlled to bring about strength-regain without a destructive exotherm, was previously discussed, thereby obtaining a strong, flexible, resilient, black woven cloth having a carbon content of 54 to 56% and also containing nitrogen, phosphorous and boron as well as oxygen and hydrogen; which cloth has tensile strengths in the warp and fill directions of at least about 45 lbs. and 26 lbs. per inch width, respectively.

This black cloth (without washing or other intermediate processing) is subsequently reverse-roll coated on one side with a polyvinyl chloride plastisol, having a viscosity in the range of 140,000 to 170,000 cps., in a coating weight of 40 to 45 ounces per square yard, followed by passing through a horizontal oven having a temperature of about 350° F. with residence time of 4 to 5 minutes. This plastisol is a dispersion of polyvinyl chloride in a suitable liquid plasticizer composition. Heating the coating causes the plasticizer to dissolve in the polyvinyl chloride which fuses to result, upon cooling, in a uniform nontacky elastomeric layer, covering and anchored in the fibrous cloth structure on one side. The coated fabric is then slit and wound into rolls of desired width and length for sale (e.g., 1½" or 3" width and 20 ft. length).

This arc-proofing tape product has a weight of about 56 ounces per square yard, a thickness of 50 to 65 mils, warp and fill thread counts of 26 and 25 per inch, respectively, and tensile strengths in the warp and fill directions of 45 lbs. and 20 lbs. per inch width, respectively.

The tape is normally wrapped upon the cable sheath in either a half-overlapped spiral manner or in a two-layer butt-wrapped manner, the PVC coating facing either inwardly or outwardly. It can easily be held in place by spiral wrapping or banding, as with a glass-cloth type of pressure-sensitive electrical adhesive tape.

In a test which strikingly demonstrated superior utility, a horizontal length of 3 inch diameter lead cable sheath was wrapped with this tape in the half-overlapped spiral manner. An electric arc of 370 amperes and 44 volts was generated below the wrapped cable and was directed against it by means of a stream of nitrogen. The arc flame temperature was of the order of 18,000° F. Yet after a 22 second exposure the wrapped lead sheath was unmelted and unharmed. In a comparison test where the cable sheath was given a conventional asbestos tape wrap, after only 6 seconds the asbestos had melted and a sizeable hole developed which extended completely through both the asbestos and the lead sheath.

In another comparison, wrapped lead cable sheaths were exposed to the flame from a can of burning transformer oil placed therebelow. The estimated temperature was in the range of 1,500 to 1,800° F. The present tape allowed no melting of the lead for 17 minutes. A conventional asbestos tape wrap permitted severe melting in 15 minutes.

Conductive carbonized fiber products

An important use of the aforesaid black nitrogen-containing organic nonconductive fiber materials of this invention (which contain about 50 to 65% carbon) is in making partially carbonized to highly carbonized electrically conductive fiber materials in which fiber identity is retained and fiber tenacities of at least 0.3 gram per denier can be obtained with adequate flexibility. Woven fabrics, knitted fabrics, braided fabrics, nonwoven fabrics, yarns, rovings, and continuous filament tows can all be converted by continuous procedures without loss of fiber identity. The fibers are smooth, lustrous and black.

This conversion can be effected by rapid heating (not over 30 minutes being needed and less than 5 minutes being usual) in a nonoxidizing environment at a temperature in the range of about 500 to 2600° C. (about 950 to 4700° F.) or higher. The higher the final peak temperature the higher the carbon content and the higher the electrical conductivity. That various nonoxidizing environmental atmospheres can be employed since they need not have a particular chemical composition, has been shown by experiments using steam, nitrogen, hydrogen, molten metals or a vacuum. The use of nitrogen is preferred for practical and economic reasons. The functional atmosphere in contact with the hot fibers will include nonoxidizing vapors emitted from the nitrogen-containing fibers during the pyrolytic conversion. The volatile products are largely evolved during the first 10 seconds and consist mainly of water, carbon dioxide, carbon monoxide, hydrogen cyanide, and decomposition products of the salts. Carbonization can also be effected by envelopment in a nonoxidizing flame.

These carbonized fibers contain carbon in proportions ranging from about 70% to higher than 99% (i.e., to 99+%), and range in electrical conductivity from semiconductors to good conductors (the fiber resistivities ranging in order of magnitude from 10^{-4} to 10^{10} ohm-cm.). Strong flexible woven fabrics having thicknesses ranging from 15 to 25 mils and dry weights ranging from 3.1 to 6.6 oz. per. sq. yard, with carbon percentages ranging from 71 to 90%, were found to have fiber resistivities ranging from 10^{10} to 0.1 ohm-cm. (the voltage/current ratio being measured by using the well-known four probe method). These fabrics showed moisture regain percentages ranging from 8 to 35% (by weight) when dried and then exposed at 72° F. to air of 50% relative humidity; the regain being still greater at higher humidities. Woven carbon fabrics, carbonized to a final temperature of 1400° C. (2550° F.) or higher, can be formed with carbon contents of 95% or higher and correspondingly lower resistivities. These have moisture regain values of less than 12%. Highly flexible and stretchable knitted carbon fabrics can be made. Depending upon the treatment, the temperature coefficient of resistivity may be positive or negative. In general, the higher the carbon content the smaller the temperature coefficient.

Fibers and fabrics containing from about 70% up to 90% carbon may be referred to as "paritally carbonized," and those containing above 90% carbon may be referred to as "carbon" fibers and fabrics. All such fibers and fabrics may be designated as conductive carbonaceous fibers or fabrics.

These fibers are predominately amorphous and even those of highest carbon content (99+% carbon) are not "graphitized" carbon, and are not "graphite" carbon fibers per se, although some degree of polycrystalline graphitic type structure may be present as shown by X-ray diffraction patterns.

These carbonized fibers and fabrics, owing to the nature of the novel black nitrogen-containing organic fibrous material that is subjected to the carbonizing process and to the retention of combined nitrogen in the carbon structure, and also owing to the rapidity of the process, are significantly different than those reported by other workers which are made by heating of cotton or other cellulose fiber material up to high temperatures requiring carefully controlled heating in the absence of air at all stages or requiring a gradual elevation of temperature over a period of several hours or more. (Thus see U.S. Patent No. 3,011,981 issued Dec. 5, 1961, and British spec. No. 965,622 published Aug. 6, 1964.) Carbonized cellulose fibers and fabrics have been "graphitized" to a highly graphitic carbon state by prolonged heating in an oxygen-free atmosphere up to a final temperature which has to be of the order of 2700° C. or higher, preferably at least 3000° C. (Thus see U.S. Patent No. 3,107,152 issued Oct. 15, 1963, and the article by Schmidt and Jones in Chemical Engineering Progress, issue of Oct. 1962, at pp. 42–50.)

A description has previously been given herein of a demonstration in which molten steel (temperature of about 2700° F.) was poured into a cup formed of a black insulative woven cloth made by the process of this invention, and was allowed to cool to room temperature, the cloth retaining strength and flexibility. The cloth in proximity to the molten steel was thus rapidly heated to a temperature which could be nearly as high as the steel temperature, while out of contact with the air and in contact with a nonoxidizing fluid medium. The molten steel was a nonoxidizing fluid and decomposition vapors generated by the suddenly pyrolyzed fibers would flush out air in contact with contiguous fibers. Inspection and analysis of fabrics treated in this way showed that a fibrous layer is thus carbonized to a conductive state in proximity to the steel; this layer comprising flexible black fiber with carbon contents ranging from approximately 70% to 80% and higher (depending upon the relative temperature to which subjected) and electrical resistivities correspondingly ranging from about 10^{10} to about 10^{-2} ohm-cm.

It is this unique phenomenon involving rapid carbonization of the precursor heat-resistant black nitrogen-containing organic fibers, which is utilized in making the carbonized conductive fibers, with which this section of the specification is concerned.

Continuous factory or laboratory production of uniform material can be achieved by passing the earlier-described nonconductive type of nitrogen-containing black fabric, yarn, roving or tow through a horizontal furnace having electrical radiant heating elements located above and below the moving material, the latter efficiently absorbing the radiant energy because of its blackness. Air is flushed out by introduction of a nonoxidizing gas such as nitrogen. During operation of the process, pyrolysis results in nonoxidizing vapors being emitted from the hot fibers and providing a nonoxidizing furnace atmosphere. This can be augmented by addition of nitrogen if necessary or desirable to maintain a nonoxidizing environment.

When a final peak temperature of about 800° C. (about 1500° F.)or higher is used, successive heating in two or more furnace zones may be preferred, each zone being provided by a successive furnace section equipped to provide a higher temperature level. Conveniently, each furnace section can be about two feet in length when feed rates of 1 to 10 feet per minute are used. Nitrogen or other monoxidizing gas is introduced, and the exhaust is regulated, such as to maintain a nonoxidizing atmosphere in each furnace section. Thus a four zone furnace with maximum temperature of 1400° C. can be provided by means of successive zones operated at 600°, 800°, 1000° and 1400° C.; with exposure in each zone being from about 10 to 120 seconds depending upon the rate of travel of the fibrous material. A minimum of tension should be used. Nonwoven staple fiber fabrics or batts which are weak can be transported on a carrier web. This furnace can easily be operated as a one, two or three zone furnace when desired. Temperatures are measured with thermocouples located close to the travelling fibrous material or by an optical pyrometer. The longer furnace exposures (at the slower travel rates) give a lower weight yield but the fibrous material is stronger and more flexible. Products of highest strength result when the final temperature exceeds 1000° C. (1800° F.) and the carbon content exceeds 80%. These show a moisture regain of less than 20% by weight when a dry sample is exposed to ambient air of 50% relative humidity. The electrical resistivity of dry fibers of above 80% carbon content is less than 0.5 ohm-cm.

The carbon content and specific properties of any given carbonized product depend not only on the final furnace temperature, and exposure timing, but on the nature and composition of the particular nonconductive black organic precursor fibrous starting material that is converted. When the original rayon fibers are of the "Fortisan" type, the ultimate carbonized fibers are stronger than when ordinary high tenacity viscose rayon fibers are used, fiber and yarn tenacities of 1.5 grams/denier and higher being obtainable. Black precursor fibers containing 0.5 to 2.5% by weight of combined boron (presumably carbon-bonded boron atoms diffused through the carbon structure) are more resistant to carbonizing temperatures and the product fibers have a lower carbon content for any given final furnace temperature than do those which do not contain boron.

A black cloth (not washed) prepared in the manner previously described in the "example," wherein the rayon fibers were impregnated with the specified salt mixture which included boric acid, was carbonized to a final temperature of 1400° C. (2550° F.). The carbon cloth product was strong and flexible and had a fiber resistivity of about 5×10^{-3} ohm-cm. A complete elemental analysis gave the following composition:

	Weight percent
Carbon	90.8
Nitrogen	1.8
Boron	1.5
Hydrogen	0.8
Phosphorous	0.9
Sodium	0.2
Sulfur	0.1
Oxygen (by diff.)	3.9

A sample of such carbon cloth was tested by exposure at 2000° F. in air for one minute. There was no material loss of strength in the warp direction and the dimensions decreased by only 4% although there was a weight loss of 30%.

The highest attained carbon content was 98% even when using a final furnace temperature of 2450° C. (4440° F.), and fibers of this type contained approximately 0.3% nitrogen, 1.5% boron and a trace of phosphorous (about 300 p.p.m. by spectral analysis). These latter fibers had a resistivity of about 3.5×10^{-4} omh-cm. and had a positive temperature coefficient of resistivity. Thus these fibers have a substantially greater conductivity than has been reported for essentially pure graphite carbon fibers. The fact that these highly carbonized fibers retain a substantial total content of nitrogen, phosphorous and boron is responsible for unique properties.

In contrast, rayon fabrics and fibers which had been impregnated solely with ammonium sulfate or ammonium chloride and converted to the nonconductive black state, when sequentially carbonized to a final temperature of about 1400° C. (2550° F.), yielded carbon fabrics and fibers containing 95 to 98% carbon. The ammonium chloride impregnated type yielded carbon fabrics and fibers containing over 99% carbon using a final temperature as low as 1650° C. (3000° F.) (30 minute exposure); or using a final temperature of 2200° C. (4000° F.) with a total carbonizing period of less than 5 minutes.

In the latter case fibers having carbon percentages as high as 99.5 to 99.9% can be obtained. These carbon fibers retain a trace of combined nitrogen in the structure and a low order of graphitic carbon development. The resistivity temperature coefficient is small (about 3×10^{-4} per ° C.) and negative when the carbon content is in the 99.4+% range. Fibers of this type are suitable for use as highly stable power resistors, and for use in highly stable conductive papers to be employed as resistors and as electrical heating elements that will not greatly vary in resistance with use and at different temperatures. Cellulosic papers containing about 5 to 50% by weight of dispersed carbon fibers can be readily and economically produced.

An illustrative cellulosic paper containing uniformly intermingled dispersed carbon fibers of this type, and alpha cellulose fibers, in a 1 to 3 ratio by weight, had a tensile strength of 11 lbs. per inch width, and a specific

resistivity of 0.2 ohm–cm. which only varied by 6% in the temperature range of 23 to 130° C. With a 1 to 10 ratio, another paper had a resistivity of 24 ohm–cm.

A specific example of a preferred cellulosic heating element paper is one composed of 83% cellulose fibers, 10% asbestos fibers, and 7% of 0.8 denier carbon fibers (99.5+% carbon) of ¼ inch length, by weight. This paper in a weight of 135 lbs. per thousand square yards (corresponding to a 45 pound basis weight), having a caliper thickness of 5 mils, has a resistance of about 110 ohms per square. A radiant heating panel 3 ft. by 4 ft. in area in which a sheet of this paper provides the heating element, the power at a nominal 120 volts being directly applied across metal strip electrodes contacting opposite edge margins of the sheet, has a nominal 750 watt rating, and a warm "safe-to-touch" surface temperature. This paper is also useful in providing an internal electrically heated layer in warming trays.

A single continuous manufacturing operation can be employed, using a multi-zone electrically heated furnace, for continuously transforming the initial dried salt-impregnated unpyrolyzed rayon fabric, yarn, roving or tow, to the final carbonized conductive product form, without cooling or separate handling of the intermediate nonconductive black organic material. In this case the latter intermediate product in its hot state quickly enters a nonoxidizing environment and is promptly carbonized; hence efficient use can be made of types of intermediate black fiber products which do not have as good glow-resistance and heat stability as do those which contain carbon-bonded boron or phosphorous (or both).

Of particular interest in this connection is the conversion of rayon fabric, yarn, roving or tow which is impregnated solely with ammonium chloride. Using a four zone furnace of the type previously described but with zone temperatures of 350, 600, 800 and 1400° C. (660, 1110, 1470 and 2550° F.), and with nitrogen supplied only to the last three zones, dried salt-impregnated viscose rayon woven fabrics were passed therethrough at a windup rate of 3 feet per minute to obtain, upon cooling, strong flexible woven carbon fiber products containing approximately 97.1% carbon and 1.2% nitrogen with a warp yarn tenacity of at least 0.3 gram/denier. The yield was about 25% (that is, the final carbon fabric weighed one-fourth as much as the original untreated rayon fabric).

A very rapid continuous process can be employed for directly converting filament rayon tow (previously impregnated with ammonium chloride, dried and flexed) into carbon filament tow of 99.5+% carbon which can be chopped to provide flexible conductive staple carbon fibers. Use is made of a horizontal carbon tube furnace having two heating zones in series, each about 18 inches long and 2 inches in diameter and separated 18 inches for ease of operation and control. Nitrogen is introduced countercurrently to properly control the atmospheric environment of the hot filaments as they pass through the tube. Exhaust hoods remove fumes emitted from the ends. The first zone is maintained at a temperature which increases from about 800° C. to about 1400° C. in the travel direction. The second zone is maintained at 2200° C. The tow is drawn through at a rate such that it enters at 6 feet per minute and exits at 3 feet per minute (due to 50% shrinkage and 75% weight loss). It thus remains in the furnace for one minute, the exposure at 2200° C. being for ½ minute. In this arrangement sufficient air is drawn into the first furnace tube zone by the entering filament tow to provide adequate oxygen for the initial conversion to the black nitrogen-containing nonconductive organic fiber state, such conversion being at a very rapid rate (less than 20 seconds) because of the high temperature. This high temperature does not cause a destructive glow or exotherm since the black filaments are immediately carbonized in a nonoxidizing atmosphere in the first zone up to a carbon content of about 97%. The resultant hot carbon filament tow is then promptly and quickly further carbonized in the second zone so as to acquire a 99.5+% carbon content, after which the carbon tow is cooled to room temperature.

The flexible conductive carbon fibers of staple length (⅛" to 2" in length) that can be chopped from this latter product have many fields of utility. These fibers are non-hygroscopic. The resistivity at room temperature of typical fibers of 10 microns diameter (0.8 denier) is 2 to 3×10^{-3} ohm-cm. They have a low negative coefficient of resistivity (about 3×10^{-4} per ° C.). The conductivity involves "N-type" mobility. These fibers are highly stabe to prolonged exposure to high temperatures even in the presence of air. They can be incorporated in various papers, nonwoven fibrous fabrics, films, coatings, laminates and molded articles to provide desired electrical, thermal and physical properties. (As in making the previously mentioned electrical heating papers, for instance.)

The various aforesaid types of carbonized fibers, which are smooth but have micropores, can be modified, whether in fabric or free fiber form, by providing a thin film, coating or deposit which can be strongly bonded by virtue of the microporous fiber surface structure, despite chemical inertness of the fiber. Thus a deposit of pyrolytic graphite, a carbide formation, an oxide coating, a silica or silicate coating, a metallic film or coating, a coating of a high-temperature-resistant polymer (which may be polymerized in situ), a sizing or priming coating to enhance bonding to a further coating or to a varnish or resin in which embedded, are illustrations.

Further uses of conductive fiber products

As already indicated, the carbonized products disclosed above have many and unique fields of utility owing to the variety of combinations and ranges of properties made available.

The fibrous materials of low conductivity (resistivities in the range of 10^3 to 10^{10} ohm-cm.) have high negative temperature coefficients of resistivity, suggesting use in thermistors and temperature-responsive switching devices. Packed pulverized fibers of this type have high pressure coefficients of resistivity (as much as 10,000 to 1 over the range of 10 kilobars to atmospheric), suggesting use in pressure transducers.

On the other hand, carbon fiber products of over 90% carbon content combine good electrical conductivity with excellent thermal stability, including stability to lengthy exposure to high temperatures even in the presence of air. Thus woven and knitted fabrics can be used as flexible and conformable electrical heating elements for laboratory ware. An advantage over the use of metal heating wires embodied in a heat-resistant fabric of some sort is that such wires need to be of fine gauge and are relatively fragile, and such fabric constructions are not as flexible and conformable as those made possible by use of conductive carbon fibers.

The various types of conductive fibers that can be produced provide for a wide choice of properties in making up papers, nonwoven fabrics, films, coatings and laminates, containing such fibers in various proportions to provide desired electrical and other properties.

These carbon fabrics and fibers can be combined with high-temperature-resistant resins to provide dense void-free molded or compressed conductive solid articles and laminates of great thermal stability. For example, a woven viscose rayon fabric impregnated with ammonium chloride, which was heated in an oven for 5 minutes at 550° F. and subsequently carbonized to a final temperature of about 1320° C. (2400° F.), provided a flexible carbon fabric having a carbon content of 97% and a nitrogen content of 1.6%, a tenacity in the warp direction of 0.37 gram per denier, and a fiber resistivity of 5×10^{-3} ohm-cm. This cloth was impregnated with a

thermosetting phenolic laminating varnish which is commercially available and specifically designed and sold for high temperature applications (e.g., "Resinox" SC–1008 phenolic resin varnish sold by Monsanto Chemical Co.) so as to have a resin pickup of 35% when dried. Sufficient layers of this pre-impregnated cloth were laminated together to form a composite one inch thick. This was then compressed for one hour under a pressure of 1000 p.s.i. at a temperature of 350° F. The resultant cured sheet was ½ inch thick and was hard, dense and rigid and had a high electrical conductivity and a relatively low temperature coefficient of resistivity. These properties suggest electrical use for making potentiometer elements, etc. This sheeting had a relatively low thermal conductivity, low thermoexpansibility, high thermal shock strength. Samples exhibited low erosion and ablation rates even at plasma jet temperatures (of the order of 18,000° F.) without spalling or violent decomposition. The eroded surface seemed to glaze and fuse itself. Ablation and erosion resistance appeared to be superior to corresponding graphite fabric structures, presumably owing to the lower thermal conductivity of the present carbon fibers and to the differences in their microstructure and chemical composition as compared to the "graphite fibers" of the so-called graphite fabrics that are commercially available.

Molded parts can be made by charging the mold with chopped fabric or chopped tow fibers pre-impregnated with a thermoset resin such as a high-temperature-resistant phenolic or modified phenolic resin. The bulk charge and the mold can be preheated to enhance the flow in the mold.

Ablative and other characteristics can be modified by incorporating inorganic fillers, such as metal oxides (e.g., zirconium dioxide or other refractory oxide), metal powders and flakes, etc., in the varnish or resin impregnant. Properties can also be modified by inclusion of fibers of other types such as graphite fibers, glass fibers, silica fibers, metal fibers, aluminum oxide fibers, aluminum silicate fibers, fluorocarbon fibers, etc.

Liquid epoxy molding and coating compositions containing dispersed carbon fibers can be provided which are capable of being cured in situ to provide either flexible or hard conductive molded parts and coatings.

Woven fabrics, nonwoven fabrics, and carbon wool can be used in unusual and demanding filter and adsorption applications which capitalize on their chemical inertness, adsorptive properties, or thermal properties, or combinations thereof.

Pressure-sensitive adhesive coating compositions containing dispersed conductive carbonized fibers can be coated out to form, upon drying, a normally and aggressively tacky, viscoelastic, fiber-reinforced conductive adhesive coating upon either a permanent base or backing, or a temporary removable support having a release surface to permit of transferring the adhesive layer to another surface. Electrical conductivities over a wide range are possible by selection of proportions and type of fiber. Carbonized continuous filament strands can be embedded in lineally aligned fashion in pressure-sensitive adhesive tape structures (for example, in the viscoelastic adhesive layer) to provide a desired degree of electrical conductivity. Thus lineal conductivity through the carbonized filaments can be provided in a tape which is otherwise insulative.

Adhesive tapes having electrically conducting backings can be produced by using conductive carbonized woven, knitted, braided or nonwoven fabric backings which may or may not be impregnated or coated with rubbers, varnishes, etc. Knitted fabrics permit of tapes which are stretchable and conformable in both directions. Conductive papers containing carbon fibers can also be used to provide conductive paper-backed adhesive tapes. High-temperature-resistant pressure-sensitive adhesive tapes can be made using high-temperature-resistant pressure-sensitive adhesive, such as certain silicone adhesives.

I claim:

1. A process of manufacturing black, non-conducting, inert, heat-resistant, non-carbonized organic fabrics and fibers of good flexibility and strength, by a controlled thermochemical transformation of corresponding fibrous regenerated cellulose starting material without loss of fiber identity, which comprises impregnating the fibers of the starting material with a water-soluble salt of strong acid and nitrogenous base that is capable of rendering the fibers nonflammable, and heating the salt-impregnated fibrous material in a dry state for at least about 5 minutes at an effective temperature of at least about 450° F., the temperature and time of such heating being regulated so as to cause the fibrous material to pass through a stage of low fiber strength and then regain a higher strength equal to at least 20% of the original strength, such that a black fibrous product having the above-mentioned characteristics is produced.

2. A process according to claim 1 wherein a water-soluble nitrogenous phosphate salt is employed and wherein the black fibrous product is thoroughly washed to remove soluble residues, so as to provide a flexible flame-resistant black fibrous product which is free from after-glow upon intense heating, the fibers having a chemical composition including approximately 54 to 61% carbon, 3.4 to 4.0% hydrogen and 3.1 to 5.8% nitrogen.

3. New and useful black organic fibrous material made by the process of claim 1.

4. New and useful black organic fibrous material made by the process of claim 2.

5. A process of thermochemically converting regenerated-cellulose fiber starting material to corresponding black insulative organic fiber material, which comprises impregnating clean starting material with an aqueous solution of a salt composition consisting essentially of at least one nonoxidant water-soluble salt of a strong acid and a nitrogenous base, the pickup of salt being about 10 to 30% of the fiber weight, drying, and heating the dry salt-impregnated fiber material for a short time and in the presence of air at a temperature of at least about 450° F., the conditions being controlled so as to cause the fiber material to pass through a pyrolytic stage producing low fiber strength and then to regain at least 20% of the original strength, such as to result in a flexible black insulative fiber material having a fiber carbon content in the range of about 50 to 65% and nitrogen content of at least about 3%, the heating process being terminated before degradation to weak brittle fibers occurs.

6. A process according to claim 5 wherein said salt composition includes a nitrogenous phosphate salt sufficient to impart at least 0.5% phosphorous to the composition of the product fibers.

7. A process according to claim 5 wherein said salt compoistion includes a boron compound adapted to impart at least 0.5% boron to the composition of the product fibers.

8. A process according to claim 5 wherein said salt composition includes a nitrogenous phosphate salt and a boron compound adapted to impart at least 0.5% phosphorous and 0.5% boron to the composition of the product fibers.

9. New and useful black organic fibrous material made by the process of claim 5.

10. Black insulative woven fabrics made from corresponding woven rayon fabrics by the process of claim 5.

11. New and useful black organic fibrous material made by the process of claim 6.

12. New and useful black organic fibrous material made by the process of claim 7.

13. New and useful black organic fibrous material made by the process of claim 8.

14. A process of thermochemically converting regenerated-cellulose fiber starting material to corresponding

black insulative organic fiber material and then carbonizing the latter to provide corresponding conductive fiber material, which comprises impregnating clean starting material with an aqueous solution of a salt composition consisting essentially of at least one nonoxidant water-soluble salt of a strong acid and a nitrogenous base capable of imparting to the insulative product fibers a nitrogen content of at least 3%, drying, heating the dry salt-impregnated fiber material for a short time and in the presence of air at a temperature in the range of about 450 to 900° F., the conditions being controlled so as to cause the fiber material to pass through a pyrolytic stage producing low fiber strength and then to regain at least 20% of the original strength, resulting in flexible black insulative fiber material having a carbon content in the range of about 50 to 65%, and subsequently carbonizing this fiber material by rapid heating in a nonoxidizing environment to a final temperature of at least 950° F. to produce electrically conductive nitrogen-containing fibers having a carbon content of at least 70%.

15. New and useful electrically conductive nitrogen-containing carbonaceous fiber material made by the process of claim 14.

16. New and useful electrically conductive nitrogen-containing carbon fiber material having a carbon content above 99%, made by the process of claim 14.

17. A process of thermochemically converting regenerated-cellulose fiber starting material to corresponding conductive carbon fiber material without loss of fiber identity, which comprises impregnating clean starting material with an aqueous ammonium chloride solution such that there is a pickup of ammonium chloride of about 10 to 30% of the fiber weight, drying, heating the dry impregnated material for a short time and in the presence of air at a temperature of at least 450° F., the conditions being controlled so as to produce a flexible black nitrogen-containing organic fiber material, and subsequently carbonizing this nitrogen-containing fiber material by rapid heating in a nonoxidizing environment to a final temperature high enough to provide electrically conductive nitrogen-containing carbon fibers containing at least 95% carbon.

18. New and useful electrically conductive carbon fiber material made by the process of claim 17.

19. An electrically conductive cellulosic paper characterized by containing at least about 5% by weight of dispersed conductive carbon fibers made by the process of claim 17.

References Cited by the Examiner

UNITED STATES PATENTS

2,390,903	12/1945	Von Glahn	8—140 X

FOREIGN PATENTS

634,690	3/1950	Great Britain.
750,262	6/1956	Great Britain.

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