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(54) FLOC FOR ELECTROSTATIC HAIR TRANSPLANTATION.

(57) A floc for electrostatic hair transplantation wherein the entire surface (inclusive of the front and rear end faces) of a short fiber is covered substantially or completely (not more than 3 % of non-coated portions) with an electrically conductive polymer layer (preferred thickness: 0.01 to 0.1 μm on an average), a production method thereof, and an electrostatic hair transplantation product using the former. A preferred polymer layer comprises a polymer or a copolymer using pyrrole, N-methylpyrrole, aniline or thiophene as a monomer. Chargeability and separability of this floc are not affected by surrounding moisture and satisfactory flying force can be stably provided during an electrostatic hair transplantation process. Accordingly, the floc can be utilized repeatedly for electrostatic hair transplantation in a dry environment under any hair transplantation systems, and post-conditioning, etc. that has conventionally been necessary, can be eliminated. The resulting hair transplantation product has a uniform density of transplanted hairs and is free from entanglement of fibers.

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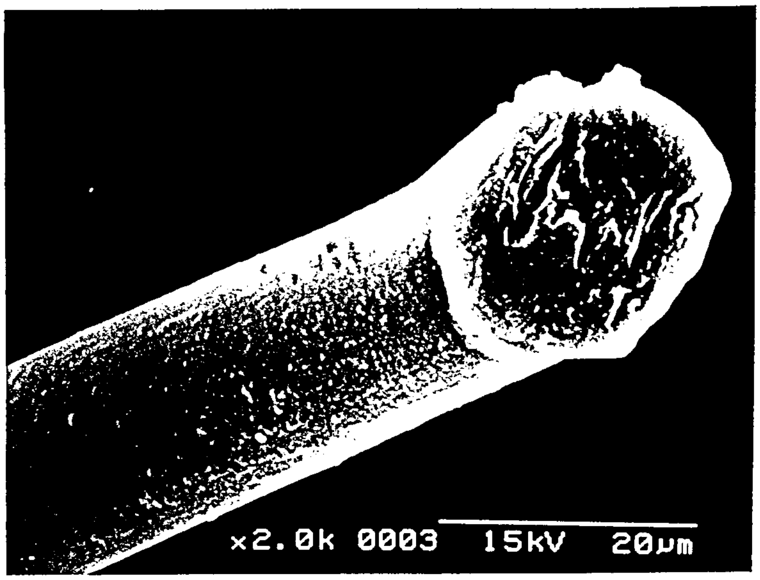
FIG. 2



Technical Field

The present invention relates to flock to be used for electrostatic pile planting, and more specifically, it relates to flock for electrostatic pile planting which may be used repeatedly in the process of electrostatic pile planting in a constantly dry environment, since it requires no moisture regulation during the process of electrostatic pile planting.

The present invention further relates to a method for the production of such flock, and to electrostatically pile-planted goods on the surfaces of which the (originally electrically conductive) flock is planted.

Background Art

Generally, electrostatic pile planting refers to the technique of causing shortly cut flock to move by an electrostatic attracting force in an electric field formed by the application of a high voltage and planting it onto a substrate which has been pre-coated with an adhesive, and the flock used in this technique is usually any of a variety of natural, regenerated or synthetic short fibers cut to a length of about 0.5-5 mm.

However, simply cutting the fibers to the required length does not result in a sufficient electric charge even in a high-voltage electric field, and thus, provides no moving force. Further, fibers tend to entangle with each other, resulting in poor separability (manageability). In order to obtain better chargeability, separability and so on of the fibers to improve the moving force, therefore, the treatment so-called pre-coating in flocking has conventionally been effected on the cut fibers.

The methods for the pre-coating in flocking conventionally and commonly been carried out include a method wherein the cut fibers are treated with tannin, tartar emetic and the like to maintain the electrical conductivity of their surfaces by means of the water retention characteristics of the tannin compounds formed on their surfaces, and a method wherein a surfactant, sodium silicate, colloidal silica or the like is adhered to the cut fibers to maintain the electrical conductivity of their surfaces by means of the water of crystallization contained in said materials. The former method is adopted mainly in Europe, and the latter in Japan.

In general, fibers with an electric leakage resistance value on their surfaces within the range of 10^5 to 10^8 Ω/cm are considered to be suitable flock for electrostatic pile planting on which sufficient moving forth is conferred.

Nevertheless, even with such pre-coating in flocking, it is not necessarily guaranteed that the above-mentioned condition of the leakage value will always be satisfied during the electrostatic pile planting, and therefore, there has usually been taken the measure wherein the electric leakage resistance value of the flock surface is set, before the planting, in the above-mentioned range by regulating the moisture in the flock precisely to 20-25 % (after conditioning) and, then, the planting process is carried out.

However, because of the reasons that the function of conventional flocking-property improvers used for the precoating in flocking is easily affected by moisture therein and that the electrical conductivity of the fiber surfaces coated therewith fluctuates rather acutely depending on the change of the humidity of the surroundings, said measure is disadvantageous in requiring delicate after conditioning which makes it difficult to carry on stable operation throughout the year. In the case of hydrophobic fibers such as polyester fibers, aromatic polyamide fibers and the like, it is particularly difficult to control their moisture, and thus their quality has not been consistent.

Furthermore, in the case of continuous electrostatic pile planting, wherein the flock not used in planting onto a substrate is collected and re-used in planting after removing impurities, there has been a drawback in requiring afresh regulation of the moisture in the flock for re-using it in the next planting, as the flock unused and collected after the first planting by a cyclone or the like is in extremely dry condition even if the humidity of the flock had been set for the first planting at an optimum level of about 80%.

An additional problem with the continuous electrostatic pile planting is that, while flock is repeatedly re-used for electrostatic pile planting, the flock to be used comes to have a non-uniform composition consisting of a mixture of pieces having various degrees of moisture, and this sometimes causes eventual heterogeneous electrostatic pile planting.

On the other hand, electrostatic pile planting apparatuses equipped with humidity-regulating devices have recently been developed. However, the disadvantage here is that the conditions, such as the moisture regain of the flock as raw material and the humidity of surrounding environment, sometimes fluctuate for one reason or another, and such apparatuses can not satisfactorily cope with such fluctuation, and thus, they have the drawback in their practical operation that it is not always easy to regulate the moisture of the flock constantly within the optimum range. For example, the moving force of the flock will decrease greatly if the condition of the flock becomes too dry, while, if the flock becomes unnecessarily wet, the flock pieces will entagle with each other to become tacky and, at times, to take doughy form, which notably reduces the separability.

The inconveniences and disadvantages described above all derive from the performance of the conventional flocking-property improvers the function of which is not exhibited at all in absolute-dry or almost absolute-dry conditions and is sufficiently exhibited for the first time under the conditions of humidication within a specific range.

Moreover, the conventional flocking-property improvers are not only a factor or instigation of such inconveniences and disadvantages, but they also have drawbacks in that, in the case of tannin and the like, color fastness is low and, in the case of sodium silicate and the like, the planted fibers exhibit a stiff appearance, the adhesion strength of the adhesive used is weakened, and the aging of the fibers is accelerated. In addition, in the latter case, there has been the problem of the production of so-called white dust consisting of silicate dust and so on during the electrostatic pile planting process. White dust is sometimes harmful to human health when absorbed upon inhalation, and it can only be removed under severe conditions of high-temperature, highly concentrated alkali treatment, for example, treatment with a 5 % aqueous solution of sodium hydroxide at 60 °C for 30 minutes.

Now, it has been found by the inventors of the present invention, as a result of intensive investigations, that by substantially or completely coating the entire surfaces of flock fibers including both ends thereof with an electrically conductive polymer layer comprising polypyrrole or the like, the average thickness of said layer being from 0.01 to 0.1 μm, it is possible to obtain flock for electrostatic pile planting the chargeability and separability of which are constantly maintained to a favorable degree with no substantial influence of the surrounding moisture, thereby providing satisfactory moving force during the electrostatic pile planting, which allows continuous electrostatic pile planting smoothly and consistently in a dry environment.

Disclosure of the Invention

It is an object of the present invention to provide flock for electrostatic pile planting which enables said planting to be always stably carried out in a dry environment, and may thus be repeatedly used for said planting.

It is another object of the present invention to provide flock for electrostatic pile planting which completely eliminates the need for moisture regulation of flock during the electrostatic pile planting conventionally been employed, by allowing the continuous electrostatic pile planting in a dry environment as mentioned above.

Therefore, the present invention provides flock for electrostatic pile planting which, by eliminating the need for mositure regulation, renders unnecessary the humidity-regulating devices in electrostatic pile planting apparatuses and the step, as pre-treatment, of regulating the moisture of flock as raw material.

It is a further object of the present invention to provide a method for the production of flock for electrostatic pile planting by which the flock for said planting may be reliably and easily produced.

It is a still further object of the present invention to provide electrostatically pile-planted goods on which thus produced electrically conductive flock is planted, in particular, those on which said flock is planted uniformly without irregularities and stably with no twisting or the like, which eventually have a high electrical conductivity.

The present invention relates to flock for electrostatic pile planting which is characterized in that the entire surfaces including the ends of short fibers are substantially or completely coated with an electrically conductive polymer layer. Preferably, the ratio of the portion of the flock surface which is not coated with said layer to the entire surface is 3 % or less.

Therefore, by the coating with the electrically conductive polymer layer, the electric leakage resistance value of the surface of the flock according to the present invention is preferably adjusted within a range of 10^5 to 10^8 Ω/cm.

The short fibers consist of natural, semi-synthetic or synthetic fibers, and the aspect ratio thereof is preferably within the range of 1:30 to 1:100. The short fibers may also be colored ones.

As a preferred embodiment, the electrically conductive polymer layer is a polymer layer or copolymer layer formed by polymerizing one or more monomers selected from the group consisting of pyrrole, N-methylpyrrole, aniline, thiophene and thiophene-3-sulfonic acid, and the particularly preferred is a polymer layer obtained by polymerizing pyrrole as a monomer.

The thickness of the electrically conductive polymer layer is preferably or necessarily within a range of 0.01 μm to 0.1 μm, as an average. A more desirable thickness is 0.01 μm to 0.03 μm as an average when the short fibers are permeable fibers, and 0.02 μm to 0.05 μm as an average when they are non-permeable fibers.

The present invention further relates to a method for the production of flock for electrostatic pile planting, which comprises allowing the polymerization reaction of monomer(s) in a treating liquid containing short fibers (or long fibers), using a chemical oxidative polymerization agent as catalyst, together with a dopant and/or a surface tension reducing agent which are optionally be added, and coating the surfaces of the fibers in said liquid with the resultant electrically conductive polymer, and, in the case of long fibers, cutting the coated long fibers to short fibers.

The present invention also relates to electrostatically pile-planted goods produced using the above-mentioned flock as raw material, in accordance with the up-type electrostatic pile planting method, the down-type electrostatic pile planting method, the up/down-type electrostatic pile planting method, or the side-type electrostatic pile planting method, or by means of a electrostatic pile planting apparatus of fluidizing tank type.

Brief Description of the Drawings

Fig. 1 is a microphotograph showing the tip of a piece, enlarged by an electron microscope, of the conventional flock for electrostatic pile planting consisting of polyester fibers which have undergone the pre-coating in flocking with sodium silicate. The length of the white line in the lower right-hand section of the photograph is 50 μm.

Fig. 2 is a microphotograph showing the tip of a piece, enlarged by an electron microscope, of the flock for electrostatic pile planting according to the present invention consisting of polyester fibers (fineness: 1.5 deniers) the entire surface of which, including the ends, have been completely coated with a pyrrole polymer layer. The length of the white line in the lower right-hand section of the photograph is 20 um.

Fig. 3 is a microphotorgaph showing the tip of a pre-colored filament, enlarged by an electron microscope, of the same polyester fiber as shown in Fig. 2 (but on the surfaces of which no pyrrole polymer layer is formed). The length of the white line in the lower right-hand section of the photograph is 20 μm.

Best Mode for carrying out the Invention

The flock according to the present invention is substantially or completely coated with an electrically conductive polymer layer on the circumferential faces along the entire length of the fibers and at both front and back ends thereof, thereby enabling the electric leakage resistance value of its surface to be adjusted within a range of 10^5 to 10^8 Ω/cm.

Preferably, the ratio of the portion of the flock surface not coated with the electrically conductive polymer layer to the entire surface is 3 % or less.

The fibers may be of natural, regenerated (semi-synthetic) or synthetic type, and convenient fibers include aromatic polyamide fibers (trade names: Kevlar, Nomex, Konex, etc.), other polyamide fibers (6-nylon, 6,6-nylon, 4,6-nylon, etc.), regular polyester fibers, cation dyeable polyester fibers, acrylic fibers, vinylon fibers, regenerated cellulose fibers (rayon), wool fibers, cotton fibers, flax fibers, and polyethylene, polypropylene as well as other composite spun fibers, and so on. Further, the fibers may be colored, and there may be used so-called pre-colored fibers which have been colored during the spinning stage with pigments incorporated.

As raw material fibers for the flock for electrostatic pile planting, the above-mentioned fibers having the properties of a denier value of about 1 to 65 d, a fiber length of about 0.3 to 6.0 mm, and an aspect ratio of 1:30 to 1:100 are preferable. With the fibers having an aspect ratio greater than 1:100, uniform electrostatic pile planting may not be achieved at times. The larger the diameter of the fibers to be used, the greater the aspect ratio may be, but it is necessary to select fibers having a smaller aspect ratio in the case of fibers with a small diameter. Generally, fibers with a fiber length (mm) of 0.3 times the denier value are said to be most suitable as raw material fibers for flock for electrostatic pile planting.

The electrically conductive polymer layer may be a layer of a polymer or copolymer prepared by the polymerization of, for instance, pyrrole, N-methylpyrrole, aniline, thiophene, thiophene-3-sulfonic acid or a derivative thereof as a monomer, but any polymer layer may be used so long as it confers the above-mentioned electrical conductivity.

The monomers to be used to form said electrically conductive polymer layer may include, for instance, aniline and aniline derivatives such as o-chloroaniline, m-chloroaniline, p-chloroaniline, o-methoxyaniline, m-methoxyaniline, p-methoxyaniline, o-ethoxyaniline, m-ethoxyaniline, p-ethoxyaniline, o-methylaniline, m-methylaniline and p-methylaniline; thiophene and thiophene derivatives such as 3-methylthiophene and 3-

methoxythiophene; and pyrroles including various substituted pyrroles such as, 3,5-substituted pyrroles like 3,5-dimethylpyrrole, 3,4-substituted pyrroles like methyl 4-methylpyrrole-3-carboxylate, N-substituted pyrrole like N-methylpyrrole, as well as 3-substituted pyrrole like 3-methylpyrrole and 3-octylpyrrole.

A preferred electrically conductive polymer layer is a polymer layer or copolymer layer prepared by the polymerization of pyrrole, N-methylpyrrole, aniline, thiophene or thiophene-3-sulfonic acid as a monomer. Particularly preferred one, from the viewpoint of adhesion strength to fibers, degree of electrical conductivity, processing properties and so on, is a polymer layer obtainable by the polymerization of pyrrole as a monomer.

The thickness of the electrically conductive layer may basically be optional, so long as the layer exhibits the above-mentioned electrical conductivity and appropriate separability, etc. Nonetheless, where the thickness of the electrically conductive polymer layer is less than 0.01 µm as an average, it is difficult to form an electrically conductive polymer layer with uniform thickness owing to the influence of the coarseness of the surfaces of the fibers themselves, often resulting in conferring insufficient electrical conductivity to flock for obtaining satisfactory moving force. On the other hand, where the thickness of the polymer layer is over 0.1 µm as an average, the fastness to crocking of said layer is reduced and, as the thickness becomes greater, the resistance value becomes smaller than required and the electrical conductivity becomes larger, even if the required electrical conductivity is secured, and in consequence, sparks are generated during electrostatic pile planting by the proximity or contact of the flock pieces, that sometimes causes clearly recognizable irregularity in the pile density on the surfaces of the pile-planted goods.

Therefore, the thickness as an average of the electrically conductive polymer layer is preferably or necessarily within the range of 0.01 µm to 0.1 µm. Since the layer is such a ultra-thin film, there is no major impairment in the original appearance, flexibility, etc. of the fibers, by the presence of the layer. For instance, when such flock is used in a weatherstrip on an automobile window glass, the weatherstrip with a stable rubbing resistance value is obtainable, since the original elasticity of the fibers is retained because of the extremely rare hardening of the fibers.

For the formation of an electrically conductive polymer layer with a thickness within the above-mentioned range onto the surfaces of fibers, the monomer to be used for the preparation of the polymer should be added in a proportion of about 0.3 % to about 1.0 % relative to the weight of the fibers, though the amount may vary slightly depending on the type of the fibers. For example, if pyrrole, a type of monomer, is added in a weight ratio of 0.75 % to polyester fibers (specific gravity: 1.34) of 3 denier and 0.8 mm in length, a pyrrole polymer layer with an average thickness of 0.044 µm (calculated value) is formed on the surfaces around and both ends of the fibers.

Obviously, even if an equivalent amount of a monomer is used, the thickness of the electrically conductive polymer layer formed on the surfaces of the fibers will vary depending on the condition (coarseness) of the fiber surface, and the porosity, the composition, etc. of the fibers. For instance, in the case of non-permeable fibers such as polyester fiber and Aramid fiber, an electrically conductive polymer layer is formed with an average thickness almost equal to the thickness as calculated on the basis of the amount of the added monomer, while in the case of permeable fibers such as 6-nylon fiber, 6,6-nylon fiber and vinylon fiber, the layer is formed with an average thickness somewhat smaller than the thickness as calculated on the basis of the amount of the added monomer. Further, the thickness of the layer also varies depending on the dispersing condition and so on of the fibers in a treating liquid as described below.

Preferable thickness of the electrically conductive polymer layer is generally about 0.01 to 0.03 µm in the case of permeable fibers such as nylon fiber, vinylon fiber, cellulose fiber, and about 0.02 to 0.05 µm in the case of non-permeable fibers such as polyester fiber, aramid fiber and acrylic fiber.

Such electrically conductive polymer layer as described above, in general, is formed by carrying out polymerization reaction of a monomer in a treating liquid containing fibers, using an oxidative polymerization agent as catalyst, thereby the resulting electrically conductive polymer binds with the fibers in the liquid to coat their surfaces.

More specifically, therefore, the present invention relates to a process for the production of flock for electrostatic pile planting, which comprises allowing polymerization reaction of monomer(s) to proceed in a treating liquid containing short fibers (which may be colored), using a chemical oxidative polymerization agent as catalyst, together with a dopant and/or a surface tension reducing agent which are optionally added, thereby coating the surfaces of the fibers in the liquid with the resulting electrically conductive polymer.

The monomer and the chemical oxidative polymerization agent may be added to the liquid together or in the order of the monomer first and then the agent. Further, the agent as catalyst may be added all at once or in portions, or may be added continuously in a small amount.

The polymerization reaction of the monomer is preferably effected as slowly as possible. It is preferably effected under the condition of low temperature, at 2-35 °C, more preferably at 2-25 °C.

If the polymerization speed is quite fast, the reaction in the aqueous phase proceeds rapidly (in an instant), causing difficulty for the polymer to adhere to the surfaces of fibers, and as a result free polymer particles are formed in the water tank.

The polymerization reaction is carried out while stirring or circulating the treating liquid. When the solubility of the monomer decreases as the polymerization proceeds, the resulting polymer is selectively deposited or adhered to the surfaces of the fibers. As a result, the reaction is extremely quantitative.

In order to ensure satisfactory moving force of the flock in all of the electrostatic pile planting methods described below, all the surfaces, including the ends thereof, of the short fibers are required to be substantially coated with the electrically conductive polymer layer, preferably in a uniform thickness.

From this point of view, the flock according to the present invention is most preferably prepared by the polymerization reaction of the monomer for the pre-coating in flocking in a slurry-state treating liquid, while stirring or circulating it, to form an electrically conductive polymer layer on the surfaces of the fibers. In this case, it is particularly preferable that the fibers are present in the slurry-state treating liquid in a weight ratio to said slurry of 1:8-15. The stirring speed is not specifically restricted, but, owing to the necessity of preventing sedimentation of the flock, it should be higher in the case of using, for example, polyester fibers than in the case of using polyamide fibers.

The flock according to the present invention may also be prepared from long fibers by subjecting them to this so-called pre-coating in flocking and then cutting thus treated long fibers to a predetermined measurement to make short fibers.

For instance, if a circular tow is cut open into a linear shape and then cut to a predetermined measurement to make flock, the electrically conductive polymer layer will not be formed on the cut faces, namely, the ends of the flock. However, the area of the ends of the flock to the entire surface is about 0.3 to 1.2 %. In the case of polyamide fibers, vinylon fibers and the like, the monomer diffuses into the interior of the fibers, and in consequence, the perimeter or the entire surface of the ends of the obtained flock will sometimes be made electrically conductive, even if tow-like ones are subjected to the pre-coating in flocking and then cut. In such a case, the ratio of the area which has not been made electrically conductive to the entire surface of the flock become even smaller.

When the pre-coating in flocking is carried out for fibers in tow state, the convergence of the fibers becomes densest and, therefore, it is difficult to uniformly coat the fiber surface with the electrically conductive polymer layer, and besides, some loss will be caused when such fibers are cut to make flock. In view of the cost and other factors of the pre-coating in flocking, therefore, it is most preferable to cut long fibers and then carry out said pre-coating thereof in a treating liquid in the state of slurry.

Thus, the present invention also relates to a method for the production of flock for electrostatic pile planting, which comprises allowing polymerization reaction of monomer(s) to proceed in a treating liquid containing long fibers (which may be colored), using a chemical oxidative polymerization agent as catalyst, together with a dopant and/or a surface tension reducing agent which are optionally be added, thereby coating the surfaces of the fibers in the liquid with the resulting electrically conductive polymer, and then cutting the coated long fibers into short fibers.

In both of the method wherein short fibers are used and the method wherein long fibers are used, monomers selected from pyrrole, N-methylpyrrole, aniline, thiophene and thiophene-3-sulfonic acid are preferably used alone or in combination of two or more. Pyrrole is the most preferred.

As the chemical oxidative polymerization agent as catalyst, any substance which accelerates the polymerization of the above-mentioned monomers may be used in general. Such substances may be, for instance, persulfuric acid as well as persulfates such as ammonium persulfate, potassium persulfate and sodium persulfate; ferric salts such as ferric chloride, ferric perchloride, ferric sulfate, ferric nitrate, ferric periodate, ferric citrate and ferric p-toluenesulfonate; permanganic acid as well as permanganates such as potassium permanganate; chromates such as chrome trioxide; halogens such as chlorine, bromine and iodine; peroxides such as hydrogen peroxide and benzoyl peroxide; and metal chlorides such as copper chloride. Water-soluble ferric salts are particularly preferred.

The chemical oxidative polymerization agent to be used may be any of the above-mentioned compounds, alone or in an appropriate combination, and is used normally in a ratio of about 1 to 3 moles per mole of the monomer.

In the polymerization of the above-mentioned monomers, a dopant may also be used optionally for the purpose of enhancing the electrical conductivity of the fibers. The dopant is preferably used under the condition of pH 1-5, more preferably pH 1-3.

Suitable dopants may include, for example, p-toluenesulfonic acid, benzenesulfonic acid, monochlorobenzenesulfonic acid, dichlorobenzenesulfonic acid, trichlorobenzenesulfonic acid, naphthalenesulfonic acid, isopropylnaphthalenesulfonic acid, dodecylbenzenesulfonic acid, naphthalenedisulfonic acid, naphthalenetrisulfonic acid, sulfosalicylic acid and other aromatic sulfonic acids; perchloric acid, hydrochloric acid, sulfuric acid, nitric acid and trifluorosulfonic acid. An aromatic sulfonic acid or an alkali metal salt thereof is particularly preferred.

To the treating liquid, a surface tension reducing agent may further be added for the formation of a uniform film of the electrically conductive polymer on the fiber surface.

The surface tension reducing agent may be a surfactant, and in addition, it may be an organic solvent or anti-forming agent of silicon-type, acetylene glycol-type or of fluorine-type. Surfactants are used to improve the wettability of the fiber surface, and alcohols are additionally added so as to improve the wettability of fiber surface upon mixture with water.

The above-mentioned surfactants may include, for example, anionic surfactants such as sodium alkyl sulfates, sodium alkylbenzenesulfonates, sodium alkylsulfosuccinates, sodium polyoxyalkylenesulfonates and sodium alkylnaphthalenesulfonates; and nonionic surfactants such as polyethylene glycol/polypropylene glycol block copolymers, polyethylene glycol alkyl ethers and polyethylene glycol alkylphenyl ethers.

The above-mentioned organic solvents may include, for example, alcohols such as methanol, ethanol, isopropyl alcohol, n-propyl alcohol, n-butanol, isobutanol and isoamyl alcohol; as well as dimethylformamide, tetrahydrofuran, dioxane, acetonitrile, cyclohexanone, methyl ethyl ketone and acetone.

Generally, the amount of the surface tension reducing agent to be added may be a minute amount to a small amount, and for example, an amount of about 0.01 % to about 2 % to the total weight of the treating liquid is sufficient in the case of a surfactant, and about 0.1 % to about 5.0 % in the case of an alcohol.

The polymerization of the above-mentioned monomer conveniently proceeds under the pH condition ranging 1-4, in said range the desired electrically conductive polymer being obtained efficiently.

The fibers are washed with water after the completion of the polymerization, and, on that occasion, a small amount of a softening agent, smoothing agent or the like, such as stearic acid amide, may be added if necessary to prevent the entanglement of flock pieces and to improve their conveyability by a screw or the like in the feeding path from the storage tank in the electrostatic pile planting apparatus.

Where non-colored polyester fibers are used as raw material fibers, it is preferable to wash and remove, prior to the formation of the electrically conductive polymer layer, the surfactant or oily substances which extrude from inside the fibers into the treating liquid for the polymerization reaction.

Further, the pre-coating in flocking (the formation of the electrically conductive polymer layer) according to the present invention, may be carried out after the coloring or before the coloring. However, since alkali coloring of polyester fibers causes dedoping and, thus, reduces the electrical conductivity, said coloring, if carried out, should be carried out before the above-mentioned pre-coating, and it is preferable to wash the colored fibers with an acid by way of precaution. Likewise, alkali coloring after said pre-coating should be carried out under acidic condition.

By using pre-colored fibers or by coloring fibers, flock with a variety of color tones is obtainable due to blending of the color phase of the dye used and the color phase of the electrically conductive polymer.

The dyes to be used may vary depending on the fiber, but may include, for example, acidic dyes, metal complex dyes such as chrome complex dye, dispersion dyes, cationic dyes and reactive dyes.

In the case of polyester fibers, specifically, coloring with a dispersion dye requires reductive washing, which accelerates dedoping of the electrically conductive polymer, and thus, the pre-coating in flocking should be carried out after the coloring. As to other fibers, such as polyamide fibers and acrylic fibers, no reductive washing is required.

The fibers are dried after said pre-coating, and for the drying of flock, it is most preferable to use the fluidiz- ing tank-type drying method in which slurry-state flock or flock after dehydrated from the slurry-state by centrifugal separation is dried by contact with a hot air flow in a fluidizing tank, so as to minimize the entanglement of flock pieces. The drying according to this method may be carried out under the conditions of a temperature about 120-180 °C and a residence time in the tank of 0.1-5 seconds, for more favorable operation. When the drying is effected under such conditions, the flock according to the present invention having the moisture of about 1-5 % is easily obtainable. In contrast, in the case of the drying method in which the flock bagged after dehydration by centrifugal separation is placed in a rotating drum and heated by hot-air circulation, it requires a long drying time and has the drawback of worsening manageability of the flock, and thus, it is not preferable.

The flock according the present invention is produced through the steps as described above. The moisture regain of said flock is usually about 1 to 5 %, close to the official regain, which is distinctively lower than the moisture regain of 20 to 25 % (value for flock after-conditioned and planted) of the conventional flock. Thus, the flock is lighter, and the transportation and handling thereof is facilitated. Since the electrically conductive polymer layer is substantially not affected by moisture, the moisture regain remains almost unchanged at about 1 to 5 % even if the surrounding air is of a high humidity, and thus, the flock of the present invention is constantly maintained in almost absolute dry state. As a result, the color fastness of the flock is improved and the transportation costs are reduced.

For easy understanding of the flock according to the present invention, the various properties of the typical one are given below.

Filament fineness D:	Approx. 1-65 deniers
Fiber length:	0.3-6 mm
Aspect ratio:	Approx. 1:30-1:100
Surface electric leakage value:	Set to 10^5-10^8 Ω/cm (based on the measuring method of the Japan Flock Industrial Association)
Moisture content:	Approx. 1-5 %
Thickness of electrically conductive polymer layer:	Approx. 0.01-0.1 µm
Amount M of raw monomer(s) for the electrically conductive polymer:	0.3-1.0 % (weight ratio to the fibers)
The conductivity of the purified water used for the coating with electrically conductive polymer layer:	5 µS or less
D/M ratio:	2.5-250

In determining the amount (in weight ratio to the fibers) of the raw material monomer, the area of both ends of the raw material fibers may essentially be ignored, since it is as small as 1-3 % relative to the entire surface area due to the large aspect ratio of said fibers. In consequence, if commonly used raw material fibers with a fineness of 1-65 deniers and a fiber length of 0.3-6 mm, are used, it is preferable to use them in the amount obtainable according to the following equation:

$$D/M = 2.5x \qquad \text{(i)}$$

wherein x is ranging from 1 to 100.

Therefore, the preferable range of the D/M ratio is about 2-4 for the raw material fibers of 3 deniers, about 10-20 for the raw material fibers of 15 deniers, and about 150-250 for the raw material fibers of 65 deniers. The above equation particularly applies in the case of polyester fibers, nylon fibers, acrylic fibers and so on.

The flock according to the present invention may be used in the electrostatic pile planting in the conventional manner, enabling the production of a wide variety of electrostatically pile-planted goods. The method of electrostatic pile planting is not particularly restricted, and there may be employed any of the up-type electrostatic pile planting method (a method in which the flock is placed on a lower electrode and the material to be planted is arranged at an upper electrode, and a voltage is applied between the upper and lower electrodes to cause the flock to move upward), the down-type electrostatic pile planting method (a method in which the material to be planted is arranged at a lower electrode and a linear or lattice-shaped upper electrode is used, and while a voltage is applied between the upper and lower electrodes, the flock is allowed to fall down through the lattice holes of the upper electrode, thereby it move downward) and the side-type electrostatic pile planting method (a method in which the material to be planted is arranged in connection with electrode on a side of the electric field, and the flock is discharged from a hopper into the electric field while applying voltage, thereby it is caused to move first downward and then sideward). Further, pile planted goods, such as automobile interior parts, may be produced from the flock according to the present invention by means of a fluidizing tank-type electrostatic pile planting apparatus (an apparatus wherein there is employed as supply tank a fluidizing tank so constructed that a porous sheet is placed therein and vibrations are applied thereto, and it may be of up/down-type, side-type, etc.)

Thus, the present invention further relates to the electrically pile-planted goods which are prepared by electrically planting the above-mentioned flock as raw material on the surface to be planted of substrates according to the up-type, down-type or side-type electrostatic pile planting method or by means of the fluidizing tank-type electrostatic pile planting apparatus.

In addition, it is also possible to enhance the electrical conductivity of the flock of the pile planted goods by carrying out, after the completion of the electrostatic pile planting, an appropriate doping treatment, for instance immersion in a solution having an acid concentration of 0.01-1 mol/L and preferably at a temperature of 10-90 °C, to apply a dopant to the flock.

According to the present invention, the surface electric leakage resistance value of the flock may easily be adjusted within the range accepted to be suitable for electrostatic pile planting because the flock surface is substantially coated with the electrically conductive polymer layer, and the exhibition of such antistatic function enables to use this flock, which is obtained in almost absolute dry state, in electrostatic pile planting.

Most importantly, since the flock itself becomes not easily affected by moisture owing to the properties of the coated layer of the electrically conductive polymer, the good antistatic function is maintained almost constantly irrespective of the humidity condition (wet or dry) of the surrounding air. As a result, the moving force satisfactory for the electrostatic pile planting according to any of the methods, including the up-type and the down-type, without carrying out the after-conditioning which is conventionally required.

Further, according to the present invention, particularly in the case of the flock of which entire surface, including not only the circumferential face but also both front and rear ends, is covered with the electrically conductive polymer layer, it is possible to make it more reliable to plant the flock at a right angle to the surface of the substrate to be pile-planted, and that enables to reduce the ratio of producing defective goods and to produce pile-planted goods with higher quality. It is thought that, in the electrostatic pile planting, the application of a high voltage creates the positive charge at one end of the flock and the negative charge at the other end to produce clearer polarization and, therefore, the flock is planted at a right angle to the substrate surface to be pile-planted.

Furthermore, according to the present invention, because of the characteristic property of the electrically conductive polymer layer which is not easily affected by moisture, the separability (manageability) of the flock does not receive any such adverse affect as to cause problems by the raising and falling of the moisture and humidity of the surroundings. Therefore, it does not cause any such inconveniences as the tacky flock surface, the formation of doughy masses resulting from twisting and entanglement of the flock pieces, and the generation of sparks resulting from the contact between the flock pieces.

In short, according to the present invention, a satisfactory moving force is always obtainable during the electrostatic pile planting process because the electrical conductivity and the separability of the flock may stably be maintained within the aimed range and conditions with no substantial influence by the surrounding moisture, and thus, stable electrostatic pile planting may be carried out by any pile planting method. In particular, according to the present invention, the flock is in almost absolute dry state and, accordingly, it may be used repeatedly in the electrostatic pile planting in a dry environment, thus enabling the continuous electrostatic pile planting to be carried out smoothly and stably.

In consequence, for the reason that the continuous electrostatic pile planting in a dry environment is made possible, the present invention does not require at all the regulation of moisture in the flock (the after-conditioning) which has been carried out in the conventional electrostatic pile planting, and besides, it renders such measures as the humidity-regulating device in the electrostatic pile planting device and the step, as pre-treatment, for regulating moisture in the flock as raw material, unnecessary.

Moreover, by using the flock according to the present invention, high quality electrostatically pile-planted goods are provided with the pile planted neatly and in an upright position to the substrate surface, in an even distribution with no dense or thin parts, and without any defects such as twisting and entanglement.

Examples

The examples below further illustrates the present invention in greater detail.

Example 1:

Cut 6,6-nylon fibers (fineness: 3 deniers, fiber length: 0.5 mm) were colored with a metal complex dye: Kayakalan Black (a product of Nihon Kayaku K.K.) under the conditions of 95 °C for 60 minutes, and then well washed with water. Pyrrole monomer was used in an amount of 0.63 % in weight ratio relative to the fibers, and the polymerization thereof was carried out continuously in water at 5 °C for 240 minutes, using ammonium persulfate as catalyst, while stirring together with the colored 6,6-nylon fibers in the water. Then, the 6,6-nylon fibers were well washed with water and subsequently dried to the moisture of 2.5 %.

The surface electric leakage resistance value of the resulting flock was measured to be 3×10^6 Ω/cm.

Using this flock, the electrostatic pile planting was carried out (applied voltage: 50-80 kV) in accordance with 3 types of methods: the up-type, the down-type and the fluidizing tank-type. In all of these methods, the moving force of the flock was sufficiently high and the planting onto a 2/1 transverse fabric (polyester/cotton = 65/35, thickness: 0.15 mm) is uniform and good.

Example 2:

Cut acrylic fibers (fineness: 1.3 deniers, fiber length: 0.4 mm) were well pre-washed with water to remove the surfactant, oils and the like, and put into water, to which 0.35 % (weight ratio relative to the fibers) of N-methylpyrrole and 0.3 % (weight ratio relative to the fibers) of pyrrole were then added as monomers, and the polymerization was carried out continuously at 5 °C for 200 minutes, using ferric chloride as catalyst. Then, the acrylic fibers were well washed and dried to the moisture of 2.5 %.

The surface electric leakage resistance value of the resulting flock was measured to be 7 x 10^7 Ω/cm.

Using this flock, the electrostatic pile planting was carried out under the conditions analogous to Example 1, and good moving force and satisfactory results were obtained in any of the planting methods, as in Example 1.

Example 3:

Cut 6-nylon fibers (fineness: 1.5 deniers, fiber length: 0.5 mm) were colored with a milling-type dye: Kayanol Milling Black (a product of Nihon Kayaku K.K.) under the conditions of 90 °C for 60 minutes, and then well washed with water. Aniline p-toluenesulfonate was used as a monomer in an amount of 1.0 % in weight ratio relative to the fibers, the polymerization thereof was carried out continuously in water at 5 °C for an adequate period of time,using potassium persulfate as catalyst, while stirring together with the colored 6-nylong fibers in the water. Then, the 6-nylon fibers were well washed with water and dried to the moisture of 3.5 %.

The surface electric leakage resistance value of the resulting flock was measured to be 1 x 10^8 Ω/cm.

Using this flock, the electrostatic pile planting was carried out under the conditions analogous to Example 1, and good moving force and satisfactory results were obtained in any of the planting methods, as in Example 1.

Example 4:

Cut para-aromatic polyamide fibers (fineness: 2.0 deniers, fiber length: 0.5 mm) and 0.5 %, in weight ratio relative to the fibers, of pyrrole monomer were put into water, and the polymerization was carried out continuously at 3 °C for 240 minutes, while stirring, using ammonium persulfate as catalyst. Then, the fibers were well washed and dried to the moisture of 1.0 %.

The resulting flock was dark green, and its surface electric leakage resistance value was measured to be 3 x 10^7 Ω/cm.

Using this flock, the electrostatic pile planting was carried out under the conditions analogous to Example 1, and good moving force and satisfactory results were obtained in any of the planting methods, as in Example 1.

Comparative Example 1:

Polyethylene terephthalate fibers (fineness: 15 deniers, fiber length: 2.1 mm) were colored with a dispersion dye: Kayalon Polyester Black (a product of Nihon Kayaku K.K.) under the conditions of 130 °C for 60 minutes, and were then washed reductively with a mixed hydrosulfite/sodium hydroxide solution at 60 °C for 20 minutes. Then, the pre-coating in flocking was carried out in the conventional manner using sodium silicate to prepare flock for pile planting.

Using a fluidizing tank-type electrostatic pile planting apparatus, the moisture regain of the flock was adjusted to 0.5 %, 3.0 % and 18 %, and the planting (applied voltage: 60 kV) was carried out onto the same substrate as the one in Example 1. In the case of moisture regains of 0.5 % and 3.0 %, only insufficient moving force was obtained and uniform planting could not be achieved. In the case of moisture regain of 18 %, though planting is effected to some extent, it was not possible to carry out the continuous planting by repeating the collection and re-using of the flock.

The results of the electrostatic pile planting tests conducted in the above examples are summarized and shown in Table 1.

Table 1

	Flock	Moisture regain	Planting method	Applied voltage	Results
No. 1	Example 1	2.5 %	Up	60 kV	◎
No. 2	Example 1	2.5 %	Down	60 kV	◎
No. 3	Example 1	2.5 %		60 kV	◎
No. 4	Example 2	2.5 %	Up	60 kV	◎
No. 5	Example 2	2.5 %	Down	60 kV	◎
No. 6	Example 2	2.5 %		60 kV	◎
No. 7	Example 3	3.5 %	Up	60 kV	◎
No. 8	Example 3	3.5 %	Down	60 kV	◎
No. 9	Example 3	3.5 %		60 kV	◎
No. 10	Example 4	1.0 %	Up	60 kV	◎
No. 11	Example 4	1.0 %	Down	60 kV	◎
No. 12	Example 4	1.0 %		60 kV	◎
No. 13		0.5 %		60 kV	x
No. 14		3.0 %		60 kV	x
No. 15		18 %		60 kV	o

Notes:

" ◎ " indicates that the flock obtained sufficient moving force and the planting was uniform and very good.

" o " indicates that the flock obtained necessary moving force and the planting was good while the continuous planting was not possible.

" x " indicates that the flock did not obtain necessary moving force and the planting was not good.

Example 5:

1 kg of polyester fibers cut to a predetermined length (fineness: 3.0 deniers, fiber length: 0.8 mm) and 8.3 g of pyrrole monomer (0.83 % in weight ratio to the fibers) were introduced into water, and polymerization was carried out continuously for 3 hours at a liquid temperature of 3 °C, while stirring, using 50.2g of ferric chloride as catalyst. Then, the polyester fibers were well washed, and dried at 160 °C in accordance with the fluidizing tank drying method.

The electric leakage resistance value of the resulting flock was 4.0 x 10^5 Ω/cm, and the moisture regain was 1.5 %.

Using this flock, electrostatic pile planting was carried out (applied voltage: 50-80 kV) by means of an up-type, a down-type, a fluidizing tank- side-type, and a fluidizing tank-up/down-type planting apparatuses, and the flock showed a sufficiently high moving force and high quality electrostatically pile-planted goods were obtained in any of the planting methods, without any particular after conditioning.

Figs. 1-3 are microphotographs showing the tips of the flock pieces or the like in the above examples, enlarged by an electron microscope. The length of the white line in the lower right-hand section of the photograph is 50 µm (Fig. 1) or 20 µm (Figs. 2 and 3).

Fig. 1 shows the conventional flock for electrostatic pile planting, comprising polyester fiber which has been subjected to the pre-coating in flocking with sodium silicate, Fig. 2 shows the flock according to the present invention corresponding to Example 5, comprising polyester fiber (fineness: 1.5 deniers) the entire surface of which is coated with a pyrrole polymer layer, and Fig. 3 shows a pre-colored filament (no pyrrole polymer layer is formed on its surface) of the polyester fiber which is the raw material for the flock in Fig. 2.

Example 6:

Following the method described in Example 1 in Japanese Patent Laid-open No. Hei 3-163709, 6,6-nylon continuous fibers (fineness: 3 deniers) were rolled up onto a bobbin, which was then placed in a tank together with a treating liquid consisting of 20 liters of water, 13.4 g of pyrrole and 64.9 g of ferric chloride, and said liquid was repeatedly passed through the bobbin and through the gaps between fibers to give them electrical conductivity, thereby obtaining long fibers having the surface electric leakage resistance value of 1.0 x 10^6 Ω/cm.

Then, the long 6,6-nylon fibers thus treated were cut to 0. 5 mm, and planted electrostatically in the same manner and conditions as those in Example 1. The flock obtained sufficient moving force and the continuous planting was possible, although there were recognized on the planted goods a few fibers not planted at a right angle to the substrate surface.

Industrial applicability

The flock according to the present invention may be used in electrostatic pile planting in general, and are suitable for the production of various kinds of electrostatically pile-planted goods for a wide range of uses, including interior materials for construction (wallpapers, curtains, carpets, mats, etc.), footwear (Japanese sandals, clog thongs, etc.), daily goods (decorative covers, decorative cords, jewel cases, stationery, etc.), goods for automobiles (dashboards, sun visors, weather-strips, flocky yarn for car sheets, etc.), air conditioner/heaters, warmers with quilts on them, foot warmers, etc.), clothing (hats, jackets, gloves, etc.) and electronic devices (brush rolls, etc.).

Claims

1. Flock for electrostatic pile planting, characterized in that the entire surfaces including the ends of short fibers are substantially or completely coated with an electrically conductive polymer layer.

2. Flock according to claim 1, characterized in that the ratio of the portion of the surface of the flock which is not coated with the electrically conductive polymer layer to the entire surface is 3 % or less.

3. Flock according to claim 1 or 2, characterized in that the short fibers are colored.

4. Flock according to any one of claims 1 to 3, characterized in that the thickness of the electrically conductive polymer layer is within the range of from 0.01 µm to 0.1 µm as an average.

5. Flock according to any one of claims 1 to 4, characterized in that the electrically conductive polymer layer is a polymer layer or a copolymer layer formed by polymerizing one or more monomers selected from the group consisting of pyrrole, N-methylpyrrole, aniline, thiophene and thiophene-3-sulfonic acid.

6. Flock according to claim 5, characterized in that the electrically conductive polymer layer is a polymer layer obtainable by polymerizing pyrrole as a monomer.

7. Flock according to any one of claims 1 to 4, characterized in that the thickness of the electrically conductive polymer layer is about 0.01 µm to 0.03 µm as an average when the short fibers are permeable fibers, and about 0.02 µm to 0.05 µm as an average when they are non-permeable fibers.

8. Flock according to any one of claims 1 to 7, characterized in that the short fibers comprise natural, semi-synthetic or synthetic fibers, and the aspect ratio of the fibers is within the range of 1:3 to 1:100.

9. Flock according to any one of claims 1 to 8, characterized in that the surface electric leakage resistance of the flock is within the range of 10^5 Ω/cm to 10^8 Ω/cm.

10. A method of producing the flock for electrostatic pile planting according to claim 1 or 2, comprising allowing polymerization reaction of monomer(s) to proceed in a treating liquid containing short fibers, using a chemical oxidative polymerization agent as catalyst, together with a dopant and/or a surface tension reducing agent which are optionally added, thereby coating the surfaces of the fibers in the treating liquid with resulting electrically conductive polymer layer.

11. A method of producing the flock for electrostatic pile planting according to claim 1 or 2, comprising allowing polymerization reaction of monomer(s) to proceed in a treating liquid containing long fibers, using a chemical oxidative polymerization agent as catalyst, together with a dopant and/or a surface tension reducing agent which are optionally added, thereby coating the surfaces of the fibers in the treating liquid with the resultant electrically conductive polymer layer, and then cutting thus coated long fibers to short fibers.

12. A method according to claim 10 or 11, wherein one or more monomers selected from the group consisting of pyrrole, N-methylpyrrole, aniline, thiophene and thiophene-3-sulfonic acid are used as the monomer(s).

13. A method according to claim 12, wherein pyrrole is used as the monomer.

14. A method according to any one of claims 10 to 13, wherein the short or long fibers are colored fibers.

15. A method according to any one of claims 10 to 14, wherein the chemical oxidative polymerization agent to be used as catalyst is a water-soluble ferric salt.

16. A method according to any one of claims 10 to 15, wherein, after the polymerization reaction, the coated fibers are washed with water together with a softening agent or smoothing agent.

17. Flock produced in accordance with a method according to any one of the claims 10 to 16.

18. Electrostatically pile-planted goods produced by electrostatically pile planting onto the surface of a substrate to be pile-planted in accordance with the up-type, down-type, up/down type or side-type electrostatic pile planting method or by means of a fluidizing tank-type electrostatic pile planting apparatus, using the flock for electrostatic pile planting according to any one of claims 1 to 9 and 17.

Amended claims

1. Flock for electrostatic pile planting, characterized in that the entire surfaces including the ends of short fibers are substantially or completely coated with an electrically conductive polymer layer.

2. Flock according to claim 1, characterized in that the ratio of the portion of the surface of the flock which is not coated with the electrically conductive polymer layer to the entire surface is 3 % or less.

3. Flock according to claims 1, characterized in that the electrically conductive polymer layer is a polymer layer or a copolymer layer formed by polymerizing one or more monomers selected from the group consisting of pyrrole, N-methylpyrrole, aniline, thiophene and thiophene-3-sulfonic acid.

4. Flock according to claims 2, characterized in that the electrically conductive polymer layer is a polymer layer or a copolymer layer formed by polymerizing one or more monomers selected from the group consisting of pyrrole, N-methylpyrrole, aniline, thiophene and thiophene-3-sulfonic acid.

5. Flock according to claim 4, characterized in that the electrically conductive polymer layer is a polymer layer obtainable by polymerizing pyrrole as a monomer.

6. Flock according to any one of claims 1 to 4, characterized in that the thickness of the electrically conductive polymer layer is within the range of from 0.01 μm to 0.1 μm on average.

7. Flock according to claim 5, characterized in that the thickness of the electrically conductive polymer layer is within the range of from 0.01 μm to 0.1 μm on average.

8. Flock according to any one of claims 1 to 5, characterized in that the thickness of the electrically conductive polymer layer is about 0.01 μm to 0.03 μm on average when the short fibers are permeable fibers, and about 0.02 μm to 0.05 μm on average when they are non-permeable fibers.

9. Flock according to any one of claims 1 to 5 and 7, characterized in that the short fibers comprise natural, semi-synthetic or synthetic fibers, and the aspect ratio of the fibers is within the range of 1:30 to 1:100.

10. Flock according to any one of claims 1 to 5 and 7, characterized in that the surface electric leakage resistance of the flock is within the range of 10^5 Ω/cm to 10^8 Ω/cm.

11. Flock according to claim 9, characterized in that the surface electric leakage resistance of the flock is within the range of 10^5 Ω/cm to 10^8 Ω/cm.

12. Flock according to any one of claims 1 to 5 and 7, characterized in that the short fibers are colored.

13. Flock according to claim 9, characterized in that the short fibers are colored.

14. Flock according to claim 11, characterized in that the short fibers are colored.

15. A method of producing the flock for electrostatic pile planting according to claim 1 or 2, comprising allowing polymerization reaction of monomer(s) to proceed in a treating liquid containing short fibers, using a chemical oxidative polymerization agent as catalyst, together with a dopant and/or a surface tension reducing agent which are optionally added, thereby coating the surfaces of the fibers in the treating liquid with resulting electrically conductive polymer layer.

16. A method according to claim 15, wherein one or more monomers selected from the group consisting of pyrrole, N-methylpyrrole, aniline, thiophene and thiophene-3-sulfonic acid are used as the monomer(s).

17. A method according to claim 16, wherein pyrrole is used as the monomer.

18. A method according to any one of claims 15 to 17, wherein the short fibers are colored fibers.

19. A method according to any one of claims 15 to 17, wherein the chemical oxidative polymerization agent to be used as catalyst is a water-soluble ferric salt.

20. A method according to any one of claims 15 to 17, wherein, after the polymerization reaction, the coated fibers are washed with water together with a softening agent or smoothing agent.

21. Flock produced in accordance with a method according to any one of the claims 15 to 20.

22. Electrostatically pile-planted goods produced by electrostatically pile planting onto the surface of a substrate to be pile-planted, using the flock for electrostatic pile planting according to any one of claims 1 to 14 and 21.

FIG. 1

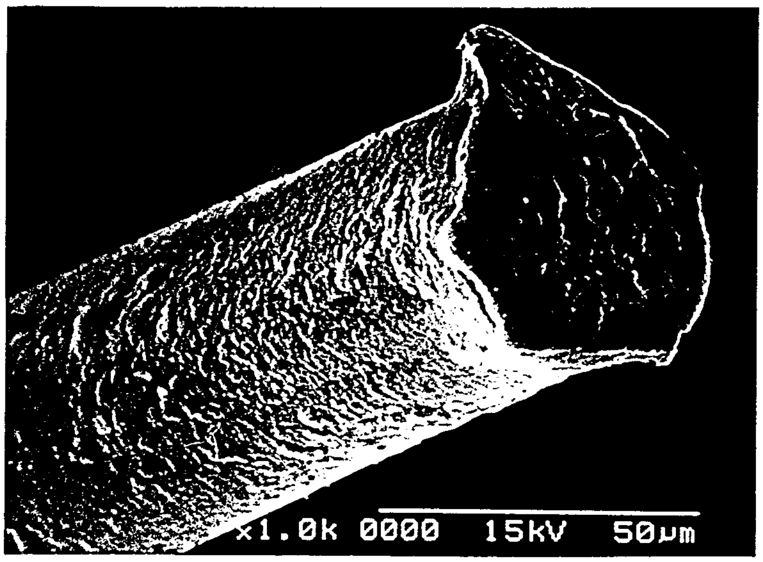


FIG. 2

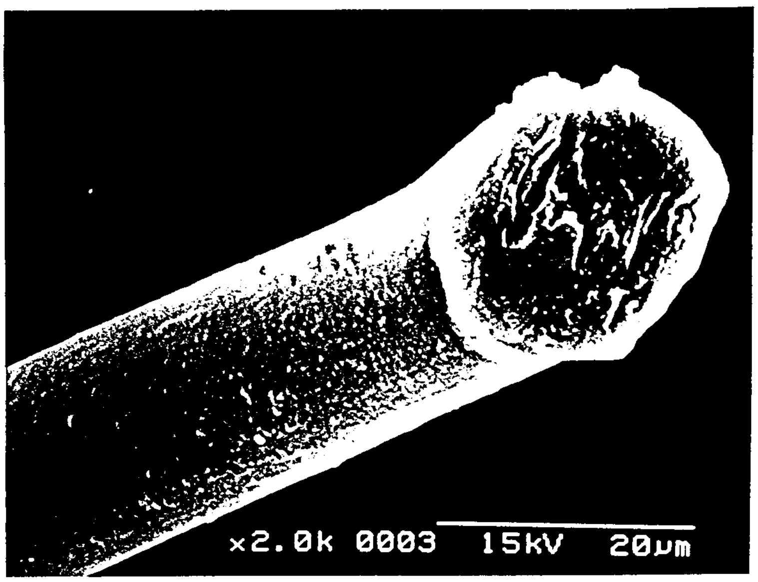
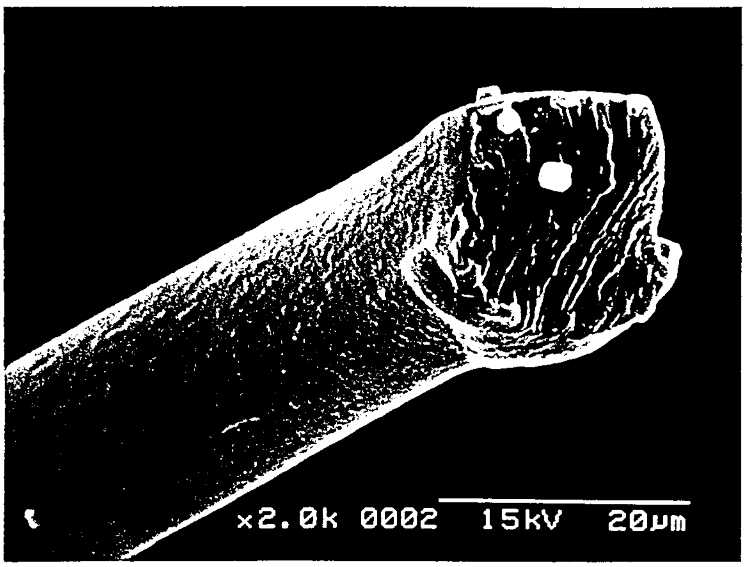


FIG. 3



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP93/01481

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl^5 D06M15/356

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl^5 D06M15/356

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, A, 2-33381 (Miriken Research Corp.), February 2, 1990 (02. 02. 90) & US, A, 4975317	1-18
Y	JP, A, 3-294580 (Achilles Corp.), December 25, 1991 (25. 12. 91), (Family: none)	1-18
Y	JP, A, 3-163709 (Achilles Corp.), July 15, 1991 (15. 07. 91), (Family: none)	1-18
Y	JP, A, 54-97647 (Unitika Ltd.), August 1, 1979 (01. 08. 79), (Family: none)	18
Y	"Newest Dyeing & Finishing Technique" edited by "The Textile Machinery Soc. of Japan" September 25,1973 (25. 09. 73), The Textile Machinery Soc. of Japan pages 333 to 341, particularly page 336	1-18

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
January 11, 1994 (11. 01. 94)	January 25, 1994 (25. 01. 94)
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Facsimile No.	Telephone No.