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54 **Conductive composite filaments and fibrous articles containing the same.**

57 A conductive composite filament comprising a non-conductive sheath component of a fiber-forming thermoplastic polymer and a conductive component consisting of a thick conductive core and a thin conductive path, which is lapped in said sheath and composed of a mixture of a thermoplastic polymer with inorganic conductive particles. The conductive path extends laterally from the periphery of the core, transversely through the sheath, up to or close to the outer circumference of the sheath and longitudinally along the entire length of the core, exposing its tip lengthwise continuously or intermittently and not more than 1.5 μm in width on the surface of the filament.

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CONDUCTIVE COMPOSITE FILAMENTS AND FIBROUS ARTICLES CONTAINING THE SAME

The present invention relates to novel conductive composite filaments, more particularly, conductive composite filaments which are industrially easily manufacturable, having substantially no metal abrasive property, and further relates to antistatic fibrous articles containing the same.

It is well known that fibers, particularly, hydrophobic fibers consisting of polyester, polyamide, polyacrylonitrile, polyolefin or the like, generate a lot of static electricity due to friction, etc., often exceeding 10 kV, which causes various troubles. Therefore, many proposals relating to destaticization (imparting of antistatic properties) have been made.

One of them is a process to blend electrifiable fibers with metallic fibers. However, the metallic fibers have shortcomings, such as brittleness to induce breakages by bending during processing and using, which cause a decrease in antistatic property. Also the metallic fibers are difficult in blending, mixed weaving or mixed knitting with other fibers and, moreover, have an inherent metallic luster that impairs the quality of articles when the metallic fibers are incorporated therewith.

Alternatively, metal deposited fibers and conductive material coated fibers also have many drawbacks, such as an extremely high cost of production, a low durability owing to liability to detachment of the coating by bending or due to friction during processing and using, or the like.

Meanwhile, fibers composed of a thermoplastic polymer that contains conductive particles, for example, carbon black, metal particles, etc., dispersed therein, when the conductive particles are dispersed in an amount large enough to provide a conductivity, cannot avoid decreases in spinnability, tenacity and elongation. Consequently, it is extremely difficult to obtain practicable such fibers.

In order to obviate such drawbacks, composite filaments in which a conductive component composed of a thermoplastic polymer containing conductive particles, for example, carbon black, metal particles, etc., dispersed therein and a non-conductive component of a fiber-forming thermoplastic polymer are bonded together in a side by side or sheath-core relationship uniformly extending along the longitudinal axis of the filament have been proposed in the gazettes of Japanese Patent Application Publication Nos. 31,450/77, 44,579/78 and 25,647/82, Japanese Patent Application Laid-open No. 60-224,813, etc.

Among the above proposed sheath-core type composite filaments, those having a non-conductive component completely encapsulating a conductive particles containing conductive component, since dielectric breakdown in the sheath portion to induce corona discharge hardly occurs, have a shortcoming that is a poor antistatic property. In contrast, sheath-core type composite filaments, different therefrom, having a sheath composed of a conductive component as well as side by side type composite filaments wherein a conductive component and a non conductive component are bonded together in a side by side relationship, since the conductive component is exposed on the filament surface, are excellent in corona discharging property, i.e., antistatic property. However, these composite filaments exhibit noticeable black or dark grey color of carbon black or inorganic conductive particles, deteriorate the appearance of articles containing these filaments. Moreover, these composite filaments having a hard conductive particles containing conductive component exposed on the filament surface, when the filaments travel as rubbing upon a stationary body, abrade and eventually mar the body due to friction. Therefore, such composite filaments thus provided with an augmented metal abrasive property are involved in serious problems in the course of manufacturing and processing.

In order to solve such problems, some proposals have been made. For example, the gazette of Japanese Patent Application Laid-open No. 60-110,920 discloses a core and thin skin type composite filament that comprises a skin component having the thinnest portions of 3 μm or less on the cross section. This filament is very excellent for obviating the metal abrasive property as well as providing the antistatic property. However, if the non-conductive skin is made thin enough to provide a satisfactory antistatic property, the skin becomes liable to break, resulting in metal abrasion by the uncovered core. Accordingly, this type of filament still poses a problem such that stable manufacture is difficult to be performed. The gazette of Japanese Patent Application Laid-open No.60-224,812 discloses an improved core and thin skin type composite filament, where the skin is composed of a fiber-forming polymer having conductive particles of metal oxide or metal compound, and more preferably the particle size satisfies the formula; $0.5 \leq \text{size of conductive particle/minimum thickness of skin} \leq 4$. However, if the conductive particles in the skin are contained much enough to provide a satisfactory antistatic property, the color or metal abrasion is revealed again.

Further, in order to mitigate the metal abrasion during manufacturing and processing of composite filaments, for example, of side by side type or the like that expose a conductive component on surfaces of the filament, there is disclosed, for example, in Japanese Patent Application Laid-open No. 61-132,626 a

sheathcore type composite filament of which the sheath component is composed of a solvent soluble polymer. The sheath component of this filament can be removed by dissolving, after fabricated into articles, to expose the conductive core component. In the gazette of Japanese Patent Application Laid-open No. 61-152,823, there is also disclosed a conductive composite filament prepared by conjugating a mixture (A) consisting of a conductive polymer composition (P1') and a fiber-forming thermoplastic polymer (P2) which is incompatible with (P1') with non-conductive fiber-forming thermoplastic polymer. In this filament, the mixture (A) occupies part of the surface area of the filament and part of (P1') comes up to the surface in the lengthwise direction of the filament through an opening. However, such a conductive composite filament, in fact, is unstable in yarn-spinnability and, moreover, insufficient in electroconductivity for lack of a conductive core as in the Case of Comparative Example Y₁₇, that will be described hereinafter. Accordingly, fibrous articles containing such a filament are deficient in antistatic property and less practical. In the Japanese Patent Application Laid-open No. 57-161,126, there is also disclosed a composite filament whose exposed conductive component occupies 30% or less of the surface of the filament. Although both of these filaments have an excellent antistatic property and, in addition, careful consideration has been given to prevent the metal abrasion in manufacturing and processing steps, these filaments inconveniently necessitates use of special polymers or complicated apparatuses or imposition of extraordinarily delicate conditions for manufacture.

An object of the present invention is to provide improved conductive composite filaments which have high whiteness, excellent antistatic property, exhibiting no abrasive property, which can be commercially easily manufactured.

Another object of the present invention is to provide fibrous articles with excellent antistatic property and aesthetic appearance which contain the conductive composite filaments of the invention.

The above objects of the present invention will be achieved by a unitary conductive composite filament which comprises:

(a) a non-conductive component composed of a fiber-forming thermoplastic polymer, forming a sheath extending along the entire length of the filament, and

(b) a conductive component consisting of a conductive core and a conductive path, being lapped in and extending lengthwise along said sheath, said conductive core being composed of a mixture of a thermoplastic polymer with inorganic particles, said conductive path having a composition the same as or different from the conductive core, comprising a thermoplastic polymer and inorganic conductive particles, which is characterized in that said conductive path extends laterally from a part of the periphery of said conductive core, transversely through the sheath, up to or close to the outer circumference of the sheath and that the conductive path is exposed at least partly lengthwise and not more than 1.5 μm in width on the outer peripheral surface of the sheath.

For better understanding of the invention, reference is made to the accompanying drawings, wherein:

FIGS. 1-6 show the cross-sectional views of the conductive composite filaments of the present invention;

FIGS. 7-11 show the cross-sectional views of the conventional conductive composite filaments, FIG. 7 of a sheath core type and FIGS. 8-11 of side by side type filaments;

FIGS. 12-14 are polymer flow diagrams in a spinneret assembly to be preferably employed for manufacturing the filaments according to the present invention;

FIG. 15 is a graph showing the relation between the blend ratio of the conductive composite filaments and the amount of the electrified charge in an example of the fibrous article, a nonwoven fabric composed of polyethylene terephthalate staple fibers, of the present invention;

FIG. 16 is a graph showing the relation between the pitch of the conductive composite filaments spacedly incorporated into a fibrous article, i.e., a circular knitted fabric, and the voltage of frictional electrification;

FIGS. 17 and 18 are SEM photomicrographs showing the cross-sectional view and side surface view, respectively, of the conductive composite filaments of the present invention (undrawn filaments); and,

FIG. 19 is a SEM photomicrograph showing the cross-sectional and peripheral views of an example, the conductive composite filament Y₁, of the invention (the PE composing a conductive component has been removed from the undrawn filament).

The cross-sectional figure of the composite filaments according to the present invention is not specifically limited. It may be either circular or non-circular, but the circular one is preferred.

In the composite filaments of the present invention, the cross-sectional figure of the conductive component is important. As is shown in FIGS. 1-6, the cross-sectional figure of the conductive component consists of a thick conductive core 1 and a thin conductive path 2, both lapped in a sheath 3 composed of a non-conductive component extending along the entire length of the filament. The conductive path 2 extends

laterally from a part of the periphery of the thick conductive core 1, transversely through the sheath 3, up to or close to the outer circumference of the sheath. Longitudinally, it extends along the entire length of said core in such a manner that the conductive path is exposed at least partly lengthwise and not more than 1.5 μm in width on the outer peripheral surface of the sheath.

5 For the conductive component, a tadpole-like figure is particularly preferred which is composed of the conductive core as its head and the conductive path as its tail. With respect to the position of the conductive component in the cross-section of the filament, it is preferred that the conductive core embedded in the sheath is positioned nearly in the center of the filament and only the tip of the conductive path barely reaches the circumference of the filament.

10 The cross-sectional figure of the conductive component may be either same or different throughout the entire length of the filament. In particular, the figure or width of the conductive path may vary gradually along the longitudinal axis of the filament. This means that the thick conductive core extends continuously along the length of the filament and the thin conductive path can be exposed either continuously or intermittently lengthwise on the surface of the filament.

15 The cross-sectional figure of the conductive core may be arbitrarily selected from circular, elliptical, triangular, rectangular or the like. The conductive core occupies a major portion, for example, at least 60% by volume, of the conductive component. Its thickness, for example, d_1 in FIG. 1, is preferably at least 5 μm . There may be either case where the core is clearly distinguishable (e.g., FIG. 1) or indistinguishable (e.g., FIGS. 2 and 5).

20 The conductive path means a thin portion conjoined with the conductive core. Its cross-sectional figure may be straight and, however, a bent or crooked one is more preferred for narrowing the exposed width of its tip. Additionally, from the joint with the conductive core to the tip, of the conductive path, the thicknesses may be substantially same (FIG. 1) and, however, those gradually attenuated (FIGS. 2, 4 and 5) or thin-and-thick (FIG. 6) are preferred for controlling the exposed width narrow as desired. In contrast, when the
25 conductive component consists solely of a thin band without having a core (thick portion) as shown in FIG. 10, the electric conductivity or antistatic property is apt to decrease or become unstable, while, if it is formed thick, the metal abrasive property will increase appreciably, so that this type of the conductive component is not suitable.

30 The width of the conductive path that is exposed on surfaces of the filament (e.g., d_2 in FIG. 1) is not more than 1.5 μm , preferably not more than 1.2 μm , most preferably not more than 1.0 μm . If the exposed width is too large, the metal abrasion becomes liable to occur.

In the composite filaments according to the present invention, the conductive path may be exposed lengthwise intermittently on the surface of the filament. The portion to be exposed is the tip or a part of its vicinity of the conductive path. The length along the longitudinal axis of the filament of the exposed portion
35 is not specifically defined. However, the proportion of the exposed length to the entire length of the filament is preferably not more than 90%, more preferably not more than 70%, most preferably not more than 50%. Too large the width or the length proportion of the exposed portion tends to cause metal abrasion.

As explained above, the composite filaments according to the present invention have a novel cross-sectional figure that is quite different from those of any conventional sheath-core or side by side type
40 conductive composite filaments.

The conjugate ratio, that is, the area ratio occupied by the conductive component in the cross-section of the composite filaments is preferably 3-40%, more preferably 4-20%, most preferably 5-15%. When the conjugate ratio is too small, the conductivity will decrease, lessening therefore the antistatic property. Alternatively, when it is too large, physical or mechanical properties of the filaments will be deteriorated and
45 the metal abrasive property will be augmented.

As the inorganic conductive particles to be used in the present invention, any kind of particles can be employed insofar as they have a specific resistance in powdery form of not more than about $10^4 \Omega \cdot \text{cm}$. Not only those particles coated with a metal oxide or metal hydroxide having high whiteness but also metallic powders (e.g., silver, nickel, copper, iron, alloys thereof, etc.) and metallic compounds such as copper
50 sulphide, copper iodide, zinc sulphide, cadmium sulphide and the like, can be employed.

As metal oxide particles, mention may be made of particles of tin oxide, zinc oxide, copper oxide, cuprous oxide, indium oxide, zirconium oxide, tungsten oxide, etc. Most metal oxides are insulators or semi-conductors and do not show enough conductivity to satisfy the object of the present invention. However, the conductivity is increased, for example, by adding a small amount (not more than 50%, particularly not more
55 than 25%) of a proper secondary component (impurity) to the metal oxide, whereby conductive metal oxide powders having sufficient conductivity to satisfy the object of the present invention can be obtained. As such a secondary component, i.e., a conductivity modifier, antimony oxide can be used for tin oxide, and also oxides of aluminum, gallium, indium, germanium, tin and the like for zinc oxide.

Further, particles wherein a conductive film of the above-described metal oxides or other metallic compounds is formed on surfaces of non-conductive inorganic particles, such as titanium oxide, zinc oxide, magnesium oxide, tin oxide, iron oxide, silicon oxide, aluminum oxide and the like, also can be used. In the case where particularly high whiteness is required, it is preferred to use conductive particles which is obtained by mixing tin-oxide-coated titanium oxide particles with antimony oxide and firing the resulting mixture.

The conductivity of the conductive metal oxide particles is preferred to be not more than about $10^4 \Omega \bullet \text{cm}$, particularly not more than about $10^2 \Omega \bullet \text{cm}$, most preferably not more than about $10^1 \Omega \bullet \text{cm}$ in specific resistance in the powdery state. In fact, the particles having about $10^2 \Omega \bullet \text{cm} \sim 10^{-2} \Omega \bullet \text{cm}$ are obtained and can be suitably applied to the object of the present invention. The particles more excellent in conductivity are more preferable. The specific resistance (volume resistivity) is measured by charging 5 g of a sample into an insulative cylinder having a diameter of 1 cm and applying a pressure of 200 kg to the cylinder from the top by means of a piston and applying a direct current voltage (for example, 0.001-1,000 V, current of 1 mA or less).

The conductive particles are preferred to be sufficiently small in the grain size. Particles having an average grain size of 1-2 μm can be used but, in general, those having an average grain size of not more than 1 μm , particularly not more than 0.5 μm , most preferably not more than 0.3 μm , are suitably used.

The term "grain size" used herein means the weight average diameter of single particles. A sample is observed by an electron microscope and is separated into single particles. Diameters (mean values of the long diameter and the short diameter) of about 1,000 particles are measured and classified by a unit of 0.01 μm to determine the grain size distribution and then the weight average grain size is determined from the following formulae (I) and (II).

$$\text{Grain average weight } \overline{W} = \frac{\sum_{i=1}^n NiWi^2}{\sum_{i=1}^n NiWi} \quad (I)$$

wherein

Ni: Number of particles classified in No. i, and

Wi: Weight of particles classified in No. i.

$$\text{Grain weight } W = \frac{\pi}{6} \rho D^3 \quad (II)$$

wherein

ρ : Density of particle, and

D : Diameter of particle.

The mixed ratio of the conductive particles in the conductive component depends upon the kind, conductivity, grain size, chain forming ability of particles, and the property, crystallinity, etc. of the polymer binder the particles are mixed with. However, it is generally within a range of about 10-85%, preferably about 20-80%, by weight. For example, the mixed ratio of titanium oxide particles coated with a conductive film is generally in the range of about 40-85%, more preferably 50-80%, most preferably 60-80%, by weight.

The thermoplastic polymer to be mixed with the inorganic conductive particles, which forms the conductive component, is not particularly limited and can be selected arbitrarily from a host of thermoplastic polymers such as polyamides, polyesters, polyolefins, polyvinyls, polyethers and the like. These polymers are preferred to have fiber-formability from the standpoint of spinning operation. However, even though those polymers deficient in fiber-formability are used, composite filaments can be provided with sufficiently good spinnability by using a fiber-forming thermoplastic polymer as the non-conductive component to be conjugated therewith. As the thermoplastic polymers used for the conductive component, particularly preferred are those having a crystallinity of at least 60%, which are poor in compatibility with the non-conductive fiber-forming thermoplastic polymers. Such polymers include polyethylene, polypropylene, polyoxymethylene, polyethylene oxide and its derivatives (for example, ethylene oxide/ethylene terephthalate block copolymers), polyvinyl alcohol, polypivalolactone, polycaprolactone, etc. Among these polymers, polyethylene, polypropylene polyoxymethylene, and copolymers thereof, are particularly suitable.

The conductive component is preferred to have a specific resistance (volume resistivity) of less than $10^7 \Omega \bullet \text{cm}$, more preferably not more than $10^4 \Omega \bullet \text{cm}$, and not more than $10^2 \Omega \bullet \text{cm}$ is particularly preferred.

To the conductive component may be further added dispersants (for example, waxes, polyalkylene oxides, various surfactants, organic electrolytes, etc.), coloring agents, pigments, stabilizers (antioxidants, ultraviolet ray absorbers, etc.) flow improvers and other additives.

As the fiber-forming thermoplastic polymers to form the non-conductive component in the composite
 5 filaments of the invention, any spinnable polymers can be used. Among the spinnable polymers, polyamides such as nylon-6, nylon-66, nylon-12, nylon-610 and the like, polyesters such as polyethylene terephthalate, polyethylene oxybenzoate, polybutylene terephthalate and the like, polyacrylonitrile and copolymers and modified polymers thereof, are particularly suitable. To the fiber-forming thermoplastic polymers may be added additives, such as delustrants, pigments, coloring agents, stabilizers, antistatic
 10 agents (such as polyalkylene oxides, various surfactants or the like). However, addition of inorganic particles in such a large amount as to possibly induce metal abrasion is not preferred. The non conductive component composed of a fiber-forming thermoplastic polymer as described above is preferred to have a specific resistance of at least $10^7 \Omega \bullet \text{cm}$.

Meanwhile, in the conductive component of the composite filaments according to the present invention,
 15 the conductive core and conductive path usually have substantially the same composition. However, in a preferred embodiment, the thermoplastic polymer composition in the conductive path consists of a mixture of the polymer for the non-conductive sheath component with the polymer composition for the conductive core component. the mixing ratio of the both components is not specifically limited. However, a mixing ratio such as to bring the content in the mixture of the conductive inorganic particles into the range of 3-50%,
 20 particularly 5-40%, by weight, is preferred. If the content is too large, the composite filaments too much increase in metal abrasive property, while, if too small, the antistatic property becomes insufficient. The mixture is preferred to occupy at least the exposed portion on filament surfaces of the conductive path.

The above-described polymer mixture can be produced according to any known processes. For example, use may be made of a process for mixing by means of a static mixer composed of relatively a
 25 few, preferably 1-3 mixing elements which is provided in a polymer flow path inside a spinneret assembly (FIG. 12), a mechanical mixer such as an impeller or rotor (FIG. 13), a hydrodynamic mixing utilizing collision of fluids caused by high pressure injection or a breaker such as glass beads or a filter layer provided in the flow path (FIG. 14), etc., and combinations thereof. In FIGS. 12-14, the numeral 101 denotes an entrance for a fiber-forming thermoplastic polymer; 102, an entrance for a conductive component
 30 polymer composition; 103, a static mixer; 104, a kneader; 105, a mixing zone; 106-108, meeting points; 109, a constriction device, and 110, a spinneret.

The fiber-forming thermoplastic polymer and conductive component polymer composition to be mixed with each other are preferred to be mutually incompatible. Such a combination provides a mixture in a mutually phase-separated state. Alternatively, in the case of mutually compatible combinations, an unevenly
 35 mixed state, for example, a fine archipelagic or multi-layeredly dispersed state is preferred from the viewpoint of corona discharging.

The reason why the excellent antistatic property and metal abrasion resistance that are the objects of the present invention are achieved by virtue of the specified figure of the conductive component comprising a thick conductive core and a conductive path of which only the tip reaches to the peripheral surface of the
 40 filament, is accounted as follows: the thick conductive core, for example, having a thickness of not less than $5 \mu\text{m}$ and a specific resistance of not more than about $10^7 \Omega \bullet \text{cm}$, extending continuously along the entire length of the filament, is considered to make movements in the longitudinal direction of the electric charge easy. This function, since the conductive core has a thickness larger than a certain degree, will not be deteriorated in processes such as drawing, false-twisting, rewinding, knitting, weaving and the like.
 45 Alternatively, since the conductive path conjoined with the thick conductive core reaches its tip up to or close to the surface of the filament and is exposed lengthwise continuously or intermittently, when the filaments are electrified, destaticization by corona discharge is considered to occur at a low potential.

Thus, by incorporating the composite filaments of the present invention in a very small amount, fibrous articles provided with an excellent antistatic property can be produced without impairing aesthetic appear-
 50 ance, such as apparels, lingerie, foundations, hosiery, particularly working clothes for clean rooms, sheetings, carpets, upholsteries, interior cloths, or the like. The composite filaments of the invention may be mixed with other natural fibers or artificial fibers and used as continuous filament yarns, staple fibers, in a non-crimped, crimped, undrawn or drawn form.

The present invention will be further explained by way of examples.

55 In the examples, the antistatic property was evaluated according to the following method. An ordinary nylon-6 drawn yarn (210 deniers/54 filaments) was knit on a circular knitting machine, incorporating a conductive composite filament yarn in every eleventh course, to prepare a tubular knitted fabric mixed with 0.85% based on the weight of the fabric of the conductive composite filaments. The resulting fabric in which

oils were removed by scouring was thoroughly washed with water, then dried at 80°C for 3 hours and further conditioned at 25°C in an atmosphere of 30% R.H. for 6 hours. Thereafter, the fabric was rubbed 15 times with a cotton cloth at the same temperature and humidity as the above, and the electrified charge after 10 seconds was measured.

5 The metal abrasive property was measured by the time required for breaking a stainless steel wire having a diameter of 35 μm , when the filament yarn traveled on the stainless steel wire at a speed of 100 m/min. (The yarn tension before contacting was 4-5 g and the contact angle was 45°).

The electric resistance was measured of a yarn consisting of 5 single filaments having a length of 10 cm. Both ends of the yarn were bonded to metal terminals with a conductive adhesive (Dodite D-550, 10 manufactured by Fujikura Kasei K.K.), 10 V of direct current was applied between both the terminals, and the electric resistance was determined. The specific resistance of the conductive component was calculated from the above obtained value of the filament yarn.

The following examples are given for the purpose of illustration of this invention and are not intended as limitations thereof.

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EXAMPLE 1

Conductive particles having an average grain size of 0.25 μm and a specific resistance of 6.3 $\Omega\cdot\text{cm}$ was obtained by firing a mixture of titanium oxide particles coated with a tin oxide film and 0.75% by weight of said particles of antimony oxide. Seventyfive parts by weight of the above obtained particles and 25 parts by weight of polyethylene having a molecular weight of 80,000 were kneaded together to prepare a conductive polymer composition A. This conductive polymer composition A, and nylon-6 having a relative viscosity in 95% conc. H_2SO_4 of 2.3 were simultaneously spun from orifices having a diameter of 0.25 mm 25 at a spinning temperature of 280°C into composite filament yarns having cross-sectional figures as shown in Table 1, with a conjugated ratio of 1/9 (areal ratio in cross section). The as-spun yarns were taken up on a bobbin at a rate of 800 m/min., while cooling and oiling. Then the taken-up filament yarns were drawn at a draw ratio of 2.6 times on a hot roll at 80°C, further contacting with a plate heater at 170°C, to produce drawn yarns $Y_1\sim Y_5$ of 20 deniers/3 filaments which were wound up on a pirn.

30 The conductivity (specific resistance), antistatic property and metal abrasive property of these filament yarns are given in Table 1.

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Table 1

5	Yarn No.	Y ₁	Y ₂	Y ₃	Y ₄	Y ₅
	Cross-sectional figure	FIG. 1	FIG. 3	FIG. 6	FIG. 7	FIG. 9
10	Thickness of core: d ₁ (μm)	8	8	8	9	7
	Width of conductive path: d ₂ (μm)	1.2	1.2	≤2.0	-	2.5
15	Width of exposed portion (μm)	1.2	≤1.2	≤0.9	-	2.5
20	Specific resistance (Ω·cm)	5×10 ²	1×10 ³	4×10 ²	7×10 ²	9×10 ³
	Antistatic property (kV)	1.6	1.7	1.7	3.4	1.6
	Metal abrasive property (min.)	24	30	31	35	8
25	Remarks	This invention	This invention	This invention	Prior art	Prior art

Any of the yarns Y₁~Y₅ had a specific resistance of not more than the order of 10³ Ω·cm and exhibited good conductivity. The yarns Y₁~Y₃ and Y₅ had good antistatic properties but the yarn Y₄ that had not exposed the conductive polymer component on the filament surface was poor in antistatic property. Additionally, the yarns Y₁~Y₄ had a little metal abrasive property but the yarn Y₅ exposing the conductive component largely in width on the surface of the filament had an extremely increased metal abrasive property. The yarn Y₅ could not be stably manufactured due to increased abrasion of thread guides.

Next, the yarns Y₁~Y₄ were respectively plied with a nylon-6 filament yarn of 2,600 deniers/140 filaments and the plied yarns were crimped by texturizing. Using the texturized yarn in every fourth course and only the nylon yarn in every three courses, a tufted carpet (looped, the mixed ratio of the conductive filaments: 0.17%) was produced. A charged voltage of a human body generated when a man putting on leather shoes walked on the resulting carpet in a room at 25°C with 20% R.H. was measured. The charged voltages of the carpets incorporated with the yarns Y₁~Y₃ of the present invention were -2.0 kV, -2.3 kV and -1.8 kV, respectively. In contrast, that of the carpet incorporated with the yarn Y₄, a sheath-core type composite filament yarn, was -4.3 kV and an electric shock was received from a grounded doorknob. For the purpose of comparison, the charged voltage of human body of a carpet composed only of nylon was measured -9.2 kV and the electric shock received from the grounded doorknob was so violent that a considerable fear was felt.

EXAMPLE 2

A polyethylene terephthalate polymer having a molecular weight of 15,000 blended with 0.65% based on the weight of the polymer of titanium oxide as a delustrant was used as a non-conductive polymer and the conductive polymer composition A, prepared in EXAMPLE 1 was used as a conductive polymer composition. These polymers were conjugated, in a spinneret, in side by side relation having a cross-sectional figure as shown in FIG. 3, and spun from orifices having a diameter of 0.3 mm at a spinning temperature of 285°C. After quenching and oiling, the as-spun filament yarn was wound up on a take-up roll at a rate of 1,000 m/min. Then the yarn was drawn 3.1 times its original length using a hot roll at 85°C, heat-set with a plate heater at 150°C and wound up on a pirn. Thus, conductive composite filament yarns Y6 Y9 were obtained. These filament yarns had properties shown in Table 2.

Table 2

Yarn No.		Y ₆	Y ₇	Y ₈	Y ₉
Structure	Filament composition (d/f)	20/3	20/4	20/5	20/6
	Thickness of core: d ₁ (μm)	8	7	6	5
	Width of conductive path: d ₂ (μm)	≤1.2	≤1.2	≤1.0	≤1.0
	Width of exposed portion (μm)	≤1.2	≤1.2	≤1.0	≤1.0
Properties	Specific resistance (Ω·cm)	3×10 ³	6×10 ²	2×10 ³	4×10 ⁴
	Antistatic property (kV)	1.7	1.5	1.7	1.8
	Metal abrasive property (min.)	30	28	31	30
Remarks		This invention	This invention	This invention	This invention

EXAMPLE 3

Titanium oxide particles coated with tin oxide (SnO₂) and 1.5% based on the weight of the particles of antimony oxide were mixed together and fired to produce conductive particles having an average grain size of 0.25 μm, a content of tin oxide of 15% by weight, a specific resistance of 7 Ω·cm and a whiteness, i.e., light reflection, of 83%. Seventy five parts by weight of the produced conductive particles and 25 parts by weight of a low density polyethylene having a molecular weight of about 50,000 and a melting point of 103°C were mixed and kneaded uniformly together with 0.5 parts by weight of magnesium stearate (a flow improver) to prepare a conductive polymer composition that was denoted as A₂. Nylon-6 having a molecular weight of about 16,000 and a melting point of 215°C admixed with 0.8% based on the weight of the nylon of titanium oxide to prepare a polymer B₁.

The conductive polymer A₂ and the polymer B₁ were conjugate-spun with a conjugate ratio of 9/1 at a spinning temperature of 280°C from orifices having a diameter of 0.25 mm into composite filaments having cross-sectional figures as shown in Table 3. The as-spun filament yarns were wound up on a take-up roll at a rate of 800 m/min., while quenching and oiling. Then the yarns were drawn 2.6 times their original lengths with a hot roll at 80°C, further brought into contact with a plate heater at 170°C, and wound up on a pirn. Thus, drawn yarns Y₁₀ ~Y₁₃ of 18 deniers/1 filament were obtained.

The properties of these drawn yarns, such as conductivity (specific resistance), antistatic property, metal abrasive property or the like, as well as the illustrations of side surface views of the filaments observed by SEM are shown in Table 3.

Table 3

Yarn No.		Y ₁₀	Y ₁₁	Y ₁₂	Y ₁₃
Structure	Cross-sectional figure	FIG. 3	FIG. 7	FIG. 8	FIG. 9
	Exposure of conductive path on filament surfaces	Intermittently, yes	no	continuously, yes	continuously, yes
	Width of conductive path: d ₂ (μm)	0.5~1.0	(0)	4	2
	Percent Exposure	40	(0)	100	100
Properties	Tensile strength (g/d)	3.1	2.9	2.8	2.5
	Elongation at break (%)	71	64	67	78
	Specific resistance (Ω·cm)	7×10 ³	7×10 ³	7×10 ³	7×10 ³
	Antistatic property (kV)	1.8	3.2	1.5	1.6
	Metal abrasive property (min.)	35	35	4	8
Remarks		This invention	Comparative	Comparative	Comparative

Any Of the yarns Y₁₀~Y₁₃, had a specific resistance of the order of 10³ Ω·Cm and exhibited good conductivity. The yarns Y₁₀~Y₁₂ had a good antistatic property of not more than 2.0 kV, but the yarn Y₁₁, whose conductive polymer component was not exposed on the surface of the filaments had a poor antistatic property. Further, the yarns Y₁₀ and Y₁₁ had a decreased metal abrasive property, while the yarns Y₁₂ and Y₁₃ showed a considerably increased metal abrasive property. The yarns Y₁₂ and Y₁₃ abraded travellers so remarkably during draw-twisting operation that the stable manufacture of the yarns could not be performed. The yarn Y₁₀ was the only yarn that had a good antistatic property as well as a decreased metal abrasive property.

EXAMPLE 4

A non-conductive polymer of polyethylene terephthalate having a molecular weight of 15,000, blended with 0.65 weight % of titanium oxide as a delustrant and the conductive polymer composition A₂ used in EXAMPLE 3, were conjugated, in a spinneret, in side by side relation such as cross sectional figures shown in Table 4, as covering the conjugated polymers with a thin sheath of the non-conductive polymer, and spun from orifices having a diameter of 0.3 mm at a spinning temperature of 282°C. After quenching and oiling, the as-spun filament yarn was wound up on a take-up roll at a rate of 1,000 m/min. Then the yarn was drawn 3.1 times its original length using a hot roll at 85°C, heat-set with a plate heater at 150°C and wound up on a pirn. Thus, composite filament yarns Y₁₄~Y₁₇ were obtained. Those filament yarns had cross-sectional figures and properties shown in Table 4.

Table 4

Yarn No.		Y14	Y15	Y16	Y17
Struc- ture	Cross-sectional figure	FIG. 1	FIG. 5	FIG. 6	FIG. 11
	Exposure of conduc- tive path on filament surfaces	Inter- mittent	Inter- mittent	Inter- mittent	Inter- mittent
	Width of conductive path: d_2 (μm)	0.5~1.0	0.5~1.0	0.5~1.0	0.5~1.5
	Percent exposure (%)	30	50	40	50
Proper- ties	Specific resistance (g/d)	5×10^3	5×10^3	5×10^3	3×10^7
	Antistatic property (kV)	1.8	1.6	1.5	3.8
	Metal abrasive property (min.)	35	33	30	28
Remarks		This inven- tion	This inven- tion	This inven- tion	Compar- ative

On the peripheral surfaces of the yarns Y₁₄~ Y₁₇, intermittent unevennesses caused by the conductive polymer were observed by SEM. All of these yarns exhibited substantially no metal abrasive property so that no troubles occurred in spinning, drawing, knitting and weaving processes. The yarns Y₁₄~Y₁₆ had a good antistatic property. The yarn Y₁₇ that lacked the thick conductive core was high in specific resistance and poor in antistatic property.

EXAMPLE 5

Titanium oxide particles coated with tin oxide and 0.75% based on the weight of the particles of antimony oxide were mixed together and fired to produce conductive particles having an average grain size of 0.25 μm and a specific resistance of 6.3 $\Omega \cdot \text{cm}$. Seventyfive parts by weight of the produced conductive particles and 25 parts by weight of a polyethylene having a molecular weight of 80,000 were mixed and kneaded together to prepare a conductive polymer composition A₃.

Using a spinning machine provided with a static mixer comprising a couple of mixing elements in a spinneret assembly such as shown in FIG. 12, 10 parts by volume of the above conductive polymer A₃ and 90 parts by volume of a nylon-6 (N₁) having a relative viscosity in 95% conc. H₂SO₄ of 2.3 were spun from orifices having a diameter of 0.25 mm at a spinning temperature of 280°C to form filaments with cross-sectional figures and mixing ratios as shown in Table 5. In the spinning, the polymers N₁ and A₃ were introduced from the entrances 101 and 102, respectively, and the constriction devices 109 were adjusted to control the mixing ratio. The as-spun filament yarns were wound up on a take-up roll at a rate of 800 m/min., while quenching and oiling. Then the yarns were drawn 2.6 times their original lengths with a hot roll at 80°C, further brought into contact with a plate heated at 170°C, and wound up on a pirn. Thus, drawn yarns Y₁₈ ~Y₂₀ of deniers/3 filaments were obtained.

The properties of these conductive composite filament yarns, such as conductivity (specific resistance), antistatic property and metal abrasive property, are shown in Table 5.

Table 5

Yarn No.			Y ₁₈	Y ₁₉	Y ₂₀
Cross-sectional figure			FIG. 1	FIG. 7	FIG. 8
Area ratio	Exposure of conductive on filament surfaces	%	89	90	90
	Conductive component	%	9	10	10
	Mixture component	%	2(1+1)	-	-
Properties	Specific resistance	$\Omega \cdot \text{cm}$	4×10^2	2×10^2	5×10^2
	Antistatic property	kV	1.6	3.6	1.5
	Metal abrasive property	min.	31	35	4
Remarks			This invention	Comparative	

Any of the yarns Y₁₈~Y₂₀ had a specific resistance of the order of $10^2 \Omega \cdot \text{cm}$ and exhibited good conductivity. The yarns Y₁₈ and Y₂₀ had a good antistatic property but the yarn Y₁₉, whose conductive polymer component was not exposed on the surface of the filaments had a poor antistatic property.

Further, the yarns Y₁₈ and Y₁₉ had a decreased metal abrasive property, while the yarn Y₂₀ showed a considerably increased metal abrasive property and could not manufactured stably due to abrasion of thread guides.

Next, the yarns Y₁₈ and Y₁₉ were respectively plied with a nylon-6 yarn of 2,600 deniers/140 filaments and the plied yarns were crimped by texturizing. Using the texturized yarn in every fourth course and only the nylon yarn in every three courses, a tufted carpet (looped, the mixed ratio of the conductive filaments: 0.17%) was produced. A charged voltage of a human body generated when a man putting on leather shoes walked on resulting carpet in a room at 25°C with 20% R.H. was measured. The charged voltage of the carpet incorporated with the yarn Y₁₈ of the present invention was -2.1 kV. In contrast, that of the carpet incorporated with the yarn Y₁₉, a sheath-core type composite filament yarn, was -4.3 kV and an electric shock was received from a grounded doorknob. For the purpose of comparison, the charged voltage of human body of a carpet composed only of nylon was measured -9.2 kV and the electric shock received from the grounded doorknob was so violent that a considerable fear was felt.

Claims

1. A unitary conductive composite filament comprising:

- a non-conductive component composed of a fiber-forming thermoplastic polymer, forming a sheath extending along the entire length of the filament, and
- a conductive component consisting of a conductive core and a conductive path, being lapped in and extending lengthwise along said sheath, said conductive core being composed of a mixture of a thermoplastic polymer with inorganic conductive particles, said conductive path having a composition the same as or different from the conductive core, comprising a thermoplastic polymer and inorganic conductive particles, which is characterized in that said conductive path extends laterally from a part of the periphery of said conductive core, transversely through the sheath, up to or close to the outer circumference of the sheath and that the conductive path is exposed at least partly lengthwise and not more than $1.5 \mu\text{m}$ in width on the outer peripheral surface of the sheath.

2. A filament as claimed in claim 1, wherein in cross-section said conductive component has a tadpole-like shape consisting of a head of the conductive core having a thickness of not less than 5 μm and a tail of the conductive path.

5 3. A filament as claimed in claim 2, wherein said head occupies at least 60% in area of the conductive component.

4. A filament as claimed in claim 1, wherein said conductive path is exposed continuously along the longitudinal axis of the filament.

5. A filament as claimed in claim 4, wherein said conductive path is exposed not more than 1.2 μm in width.

10 6. A filament as claimed in claim 1, wherein said conductive path is exposed intermittently along the longitudinal axis of the filament.

7. A filament as claimed in claim 6, wherein said conductive path is exposed not more than 1 μm in width and not more than 50% of the entire length of the filament.

15 8. A filament as claimed in claim 1, wherein in cross-section said conductive component occupies 3-40% in area of the filament.

9. A filament as claimed in claim 1, wherein said conductive path has the same composition as the conductive core.

20 10. A filament as claimed in claim 1, wherein said conductive path comprises a mixture of the fiber forming thermoplastic polymer composing the non-conductive component with the mixture composing the conducting core.

11. A filament as claimed in claim 1, wherein said conductive component has a specific resistance of not more than $10^4 \Omega \bullet \text{cm}$.

12. A filament as claimed in claim 11, wherein the specific resistance is not more than $10^2 \Omega \bullet \text{cm}$.

25 13. A filament as claimed in claim 1, wherein said fiber-forming thermoplastic polymer is an organic synthetic linear polymer selected from the group consisting of nylon-6, nylon-66, nylon-12, nylon-610, polyethylene terephthalate, polyethylene oxybenzoate, polybutylene terephthalate, and copolymers and modified polymers thereof.

30 14. A filament as claimed in claim 1, wherein said thermoplastic polymers contained in the conductive component are organic synthetic linear polymers selected from the group consisting of polyethylene, polypropylene, polyoxymethylene, and copolymers thereof.

15. An antistatic fibrous article which is incorporated with 0.01 5% by weight of a filament as claimed in claim 1.

16. A fibrous article as claimed in claim 15, which is a carpet.

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FIG.1

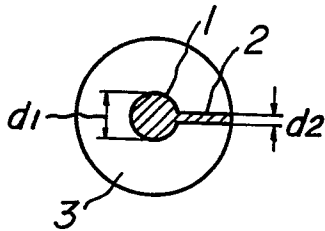


FIG.2

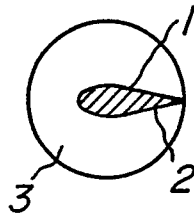


FIG.3

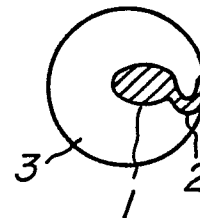


FIG.4

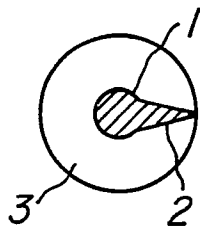


FIG.5

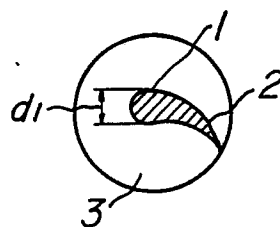


FIG.6

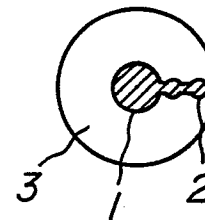


FIG.7

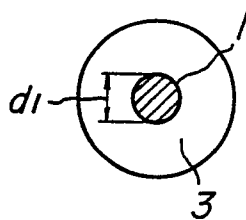


FIG.8

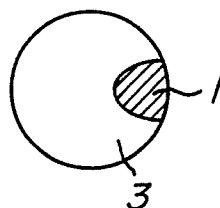


FIG.9

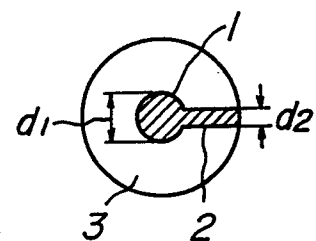


FIG.10

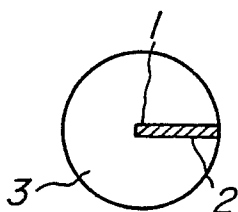


FIG.11

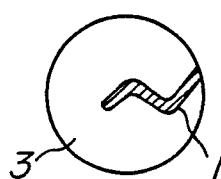


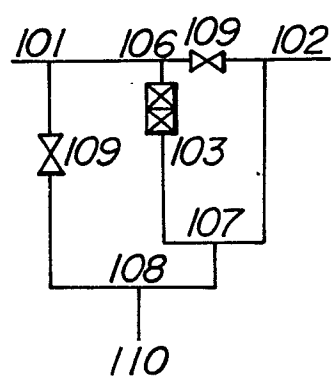
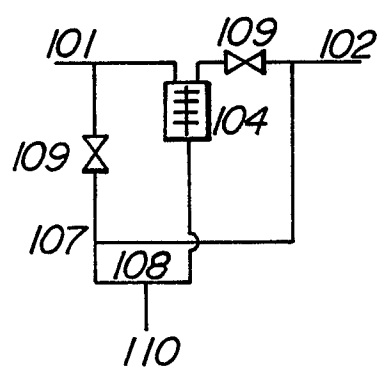
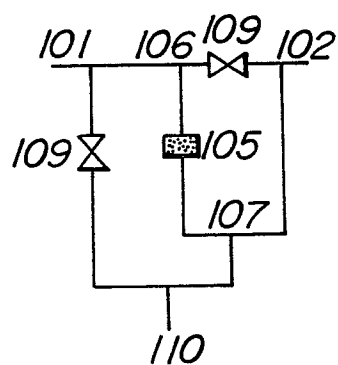
FIG. 12**FIG. 13****FIG. 14**

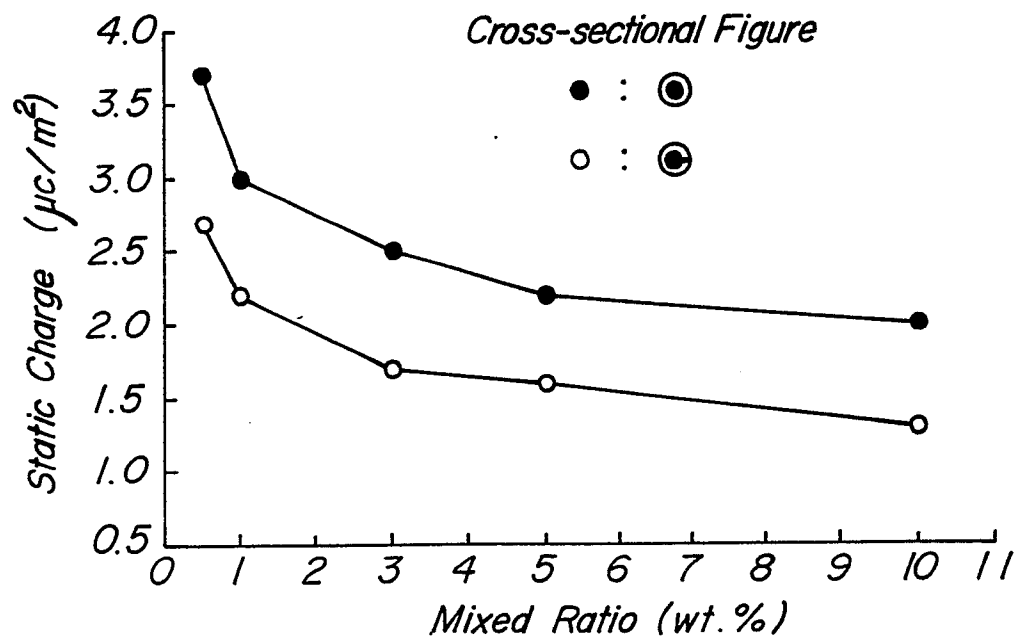
FIG. 15

FIG. 16*Cross-sectional Figure*

● : ⊙
△ : ⊖
○ : ⊕

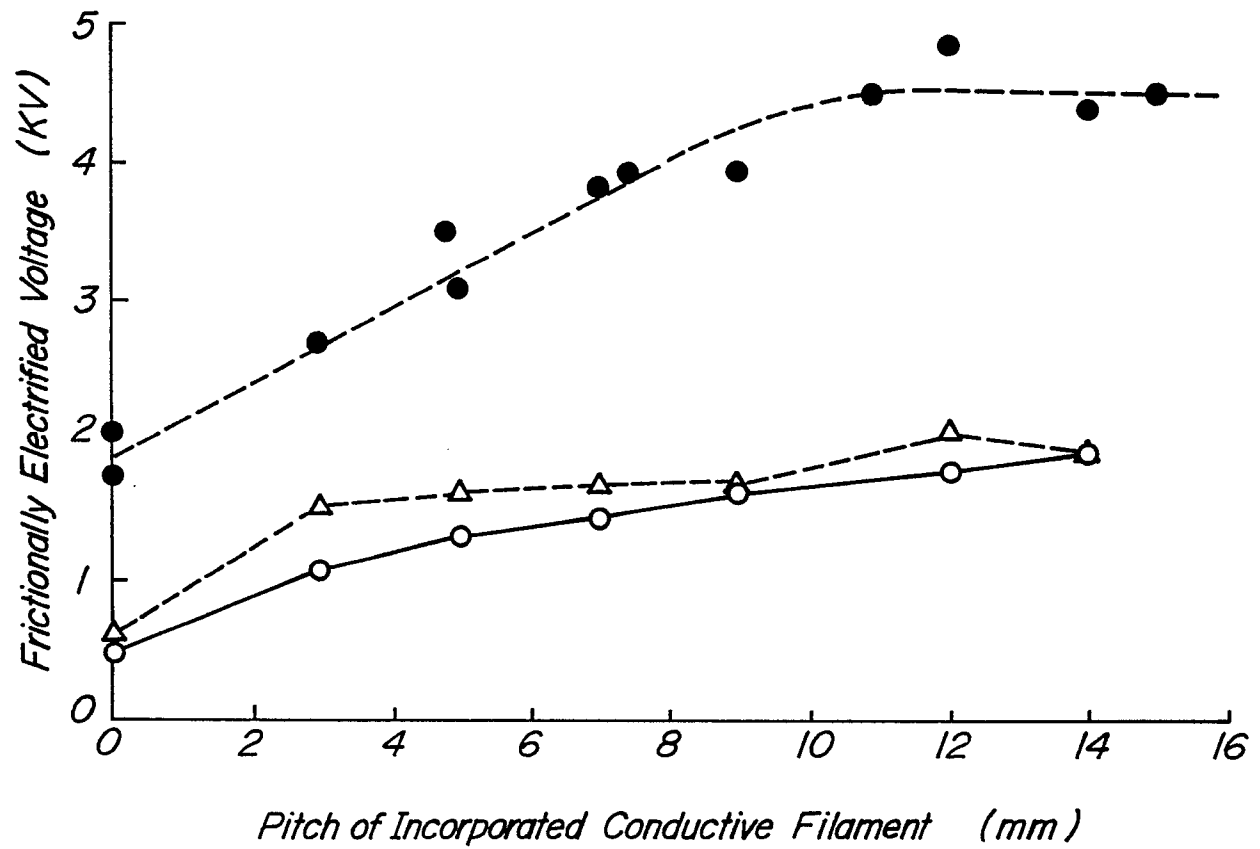


FIG. 17

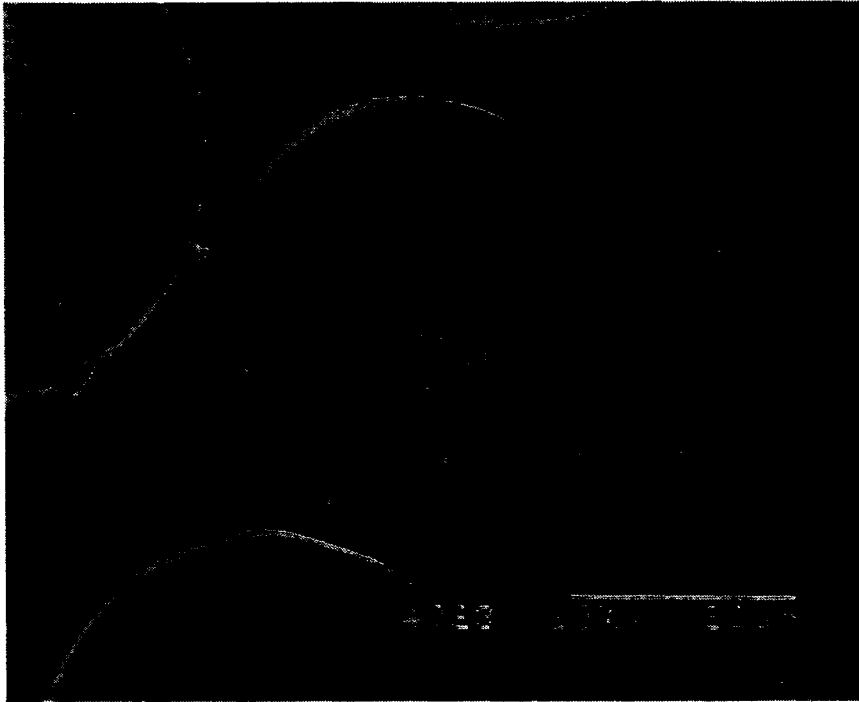


FIG. 18

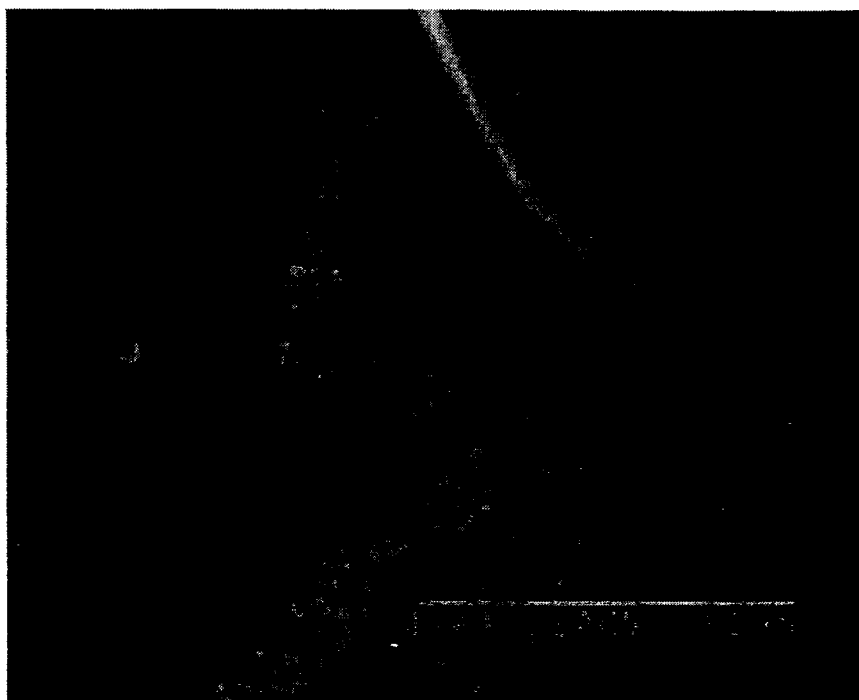


FIG. 19

