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(71) Applicant: **TEIJIN ARAMID B.V.** [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL).

(72) Inventors: **ROLINK, Ben Gerhardus Antonius**; Brouwersmolenweg 407, NL-7339 EC Ugchelen (NL). **TJADEN, Hendrik Jacob**; Leonard Springerlaan 219, NL-7424 AA Deventer (NL). **BERNAERTS, Katrien Veerle**; Ringlaan 127, B-3900 Overpelt (BE). **TIECKEN, Jan David Cornelis**; Meeuwstraat 23, NL-6942 KK Didam (NL). **KWINT, Huibert Cornelis**; Margriet van Arkellaan 3, NL-3903 WP Veenendaal (NL).

(74) Agent: **HEIMANN, Anette**; CPW GmbH, Kasinostrasse 19-21, 42103 Wuppertal (DE).

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(54) Title: ANTISTATIC ARAMID MATERIAL

(57) Abstract: The invention pertains to a method for manufacturing an antistatic aramid material selected from pulp, shortcut, fibrid, and fibril, comprising the steps of providing an aqueous medium comprising said aramid material, polymerizable monomer of a conductive polymer, anionic surfactant in an amount of at least 0.1 mole of anionic surfactant per kg aramid material (dry weight), and dopant in an amount of at least 0.1 mole per mole of monomer, adding an oxidizing agent to the medium to polymerise the monomer to form a polymer, and separating the aramid material provided with a polymer coating from the medium. The invention also pertains to an antistatic aramid material selected from pulp, shortcut, fibril, and fibrid, wherein the pulp, fibrid or fibril has a coating comprising a mixture of a conductive polymer and a dopant, and optionally at least 0.01 wt.% of an anionic surfactant. The antistatic aramid material according to the invention is suitable for use in, e.g., the 1 manufacture of paper, brake pads, and gaskets.

ANTISTATIC ARAMID MATERIAL

The invention pertains to antistatic aramid material selected from aramid pulp, shortcut, fibrid, or fibrils, to compositions comprising the aramid material, to various uses thereof, and to the manufacture thereof. The invention also pertains to electroconductive aramid material selected from pulp, shortcut, fibrid, or fibrils, to compositions thereof, to various uses thereof, and to the manufacture thereof.

Dry aramid material such as pulp becomes negatively charged during processing. Such electrically charged material may lead to problems in the processing thereof, particularly with respect to its free flowing properties. To prevent these problems methods have been developed to obtain conductive and antistatic aramid material.

WO 02/070796 describes a pulp of sulphonated polyaniline blended with para-aramid, wherein the para-aramid is a continuous phase in the pulp and the sulphonated polyaniline is a discontinuous phase. The pulp is manufactured through spinning of a spin dope containing para-aramid and sulphonated polyaniline, and subjecting the fibers thus obtained to a pulping step. This pulp contains the electrically conductive polyaniline throughout the pulp. Such pulp has a number of disadvantages. In the first place, as compared to pure aramid pulp, its properties change. Moreover, only the polyaniline contained at the surface is effective as antistatic agent. Most of the polyaniline is contained in the core of the pulp rather than at the surfaces and has no antistatic effect.

It is an objective of the present invention to provide a method for manufacturing an aramid material selected from pulp, shortcut, fibril, and fibrid with antistatic properties which effect is maintained after washing and wherein the properties of the aramid material itself are affected to the lowest possible extent. A further object of the invention is the provision of a method for manufacturing conductive aramid material selected from pulp, shortcut, fibril, and fibrid, which is suitable for various uses where a material is required which combines electrical conductivity with the properties of the aramid material itself.

To solve this problem, the present invention provides a method for manufacturing an antistatic aramid material selected from pulp, shortcut, fibrid, and fibril, comprising the steps of providing an aqueous medium comprising said aramid material, polymerizable monomer of a conductive polymer, anionic surfactant in an amount of at least 0.1 mole of anionic surfactant per kg aramid material (dry weight), and dopant in an amount of at least 0.1 mole per mole of monomer, adding an oxidizing agent to the medium to polymerise the monomer to form a polymer, and separating the aramid material provided with a polymer coating from the medium.

The invention also pertains to an antistatic aramid material selected from pulp, shortcut, fibril, and fibrid, wherein the surface of the aramid material has a coating comprising a mixture of a conductive polymer and a dopant. In one embodiment the antistatic aramid material comprises at least 0.01 wt.% anionic surfactant, calculated on the dry weight of the final product.

It has been found that, among other aspects, the use of an anionic surfactant is essential to obtaining a product with good properties. If no surfactant is used, or if a cationic or nonionic surfactant is used instead of an anionic surfactant, the effect of the invention will not be obtained.

It is noted that EP352882 describes a method for making electrically conductive textile materials through a process wherein a conductive polymer is polymerized in the presence of fibers, fabrics, or filaments. There are a number of key differences between the process of this reference and that of the present invention. In the first place, fibers fabrics and filaments have a surface area well below 1 m2/g, and can be brought into a liquid in amounts of dozens of weightpercent. In contrast, shortcut, fibril, and fibrid have higher surface areas, while they can only be used at much lower concentrations. This means that in the process of EP352882 there is less surface to be coated, and there is less solution

to interfere with the coating process. Further, the reference indicates that the presence of a surfactant may interfere with or slow down the polymerization rate. The advantageous effects of the use of an anionic surfactant are not disclosed or suggested.

The aramid material according to the invention has antistatic properties, and, depending on the amount and properties of the polymer, may also be conductive. Within the context of the present specification, the word antistatic is used to describe a material with a conductivity of at least 1.10^{-7} S/cm. The word conductive is used to describe a material with a conductivity of at least 1 S/cm. In one embodiment, the coated aramid material has a conductivity of at least 1.10^{-6} S/cm, in particular at least 1.10^{-4} S/cm. In some embodiments the coated aramid material has a conductivity of at least 1.10^{-2} S/cm, or at least 1.10^{-1} S/cm, or at least 1 S/cm.

The conductivity of the aramid material is determined through measurement of the conductivity of a standard paper made therefrom. The standard paper is made from 1.6 g of the aramid material to be tested (based on dry weight), in accordance with ISO 5269-2, resulting in sheets of 50 g/m². The papers are made on a Rapid Koethe handsheet former. Drying is done using the RK-dryer under vacuum at 95°C. The thickness of the papers is measured according to TAPPI 411 om-05. The specific electrical conductivity of the aramid papers is determined in a sample-holder consisting of two copper bars separated by two polytetrafluorethylene rods. The mutual distance of the bars is 52 mm. The paper to be tested is cut to a rectangle and folded once around the two copper bars which are connected with a DC high voltage power source and a Keithley electrometer. With the Keithley electrometer the electrical current is determined after a voltage of 500 V or lower was applied over the copper bars at 20ºC and 65% relative humidity. The specific electrical conductivity of the paper is calculated using Ohm's law based on the paper length between the copper bars and the cross-section area of the paper.

The aramid material is coated with the conductive polymer. Coating is performed by polymerizing monomers in the presence of the aramid material, to form a coating on the surface of the aramid material. This coating composition also contains surfactant, dopant, and oxidizing agents, which are required for the process of making polymers and for ensuring an adequate coating process. In the invention, the aramid material has a coating of a conductive polymer. Conductive polymer is not present in the aramid material itself.

In the polymerisation process, when the polymer is formed from the monomers, it precipitates on the surfaces of the aramid material in the dispersion. The oxidizing agent is used to allow oxidative polymerization to take place.

It has been found that the use of an anionic surfactant is essential in the present invention. If no anionic surfactant is used, the coating of the aramid material will not be adequate. Not wishing to be bound by theory it is believed that the surfactant is required to increase the deposition of the polymer onto the dispersed aramid material.

Suitable anionic surfactants include sulphate-based surfactants, sulphonate-based surfactants, phosphate-based surfactants, and carboxylic acid based surfactants. Suitable surfactants include alkyl sulphate, in particular sodium alkyl sulphate, in particular sodium lauryl sulphate. Suitable surfactants also include alkyl ether sulphate, in particular sodium or ammonium alkyl ether sulphates, more in particular sodium or ammonium laureth sulphate. Suitable surfactants further include sulphonates, such as cumene sulphonates, in particular sodium cumene sulphonate, xylene sulphonates, in particular sodium xylene sulphonate, and alkane sulphonates, in particular sodium alkane sulphonate, wherein alkane stands for C14-C18 alkyl. Suitable carboxylic acid surfactants include fatty acids or salts thereof, in particular fatty acid (salts) with 8-18 carbon atoms in the fatty acid chain. Suitable phosphate-based surfactants include compounds wherein an

R-chain of e.g. 8-18 carbon atoms is connected to a phosphate group. The use of sulphate-based surfactants is considered preferred at this point in time.
The surfactant is used in an amount of at least 0.1 mole per kg of aramid material (dry weight). If the amount of surfactant is too low, the formation of the polymer on the aramid material will not be adequate. Preferably, at least 0.2 mole of surfactant per kg aramid material is used. If the amount of surfactant is very high, processing may be hampered by foam formation. Further, the provision of coating on the aramid material may not be further improved, and may sometimes be detrimentally affected. It is preferred for the amount of surfactant to be at most 4 mole per kg aramid material, more in particular at most 2 mole/kg aramid material. In one embodiment, the amount of surfactant is in the range of 0.3-1 mole/kg.
The coated aramid material obtained by the process of the present invention can be completely free from surfactant. However, in one embodiment surfactant is also present in the coated aramid material, e.g., in an amount of 0.01 wt.%, calculated on the dry weight of the product. In one embodiment, the amount of surfactant in the final product is in the range of 0.01-1 wt.%.

Conductive polymers are known in the art. Examples are polymers derived from one or more of the monomers selected from thiophene, aniline, pyrrole or derivatives thereof. Polymers of this kind contain a conjugate chain, so that charge carriers can readily shift. Particularly suitable conductive polymers are polyaniline, PEDOT, alkylenedioxythiophene derivatives, polymers formed from thiophene and substituted thiophene monomers such as poly(3,4-dialkoxythiophene) with polyanion, and the like. Such conductive polymers usually have electrical conductivity of more than 10^{-8} S/cm, determined on the polymer itself. Preferred conductive polymers have electrical conductivity of more than 10^{-5} S/cm.
Conductive polymers usually contain conjugated chains, so that charge can readily move. In the case of a doped electrically conductive polymer, the charge carriers are created via a doping process (by oxidation or reduction).

Preferred polymers according to the invention are polymers that are obtained by in-situ polymerization of monomers rendering poly(3,4-ethylenedioxythiophene) (PEDOT), poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) copolymer (PEDOT/PSS), polyaniline (PANI), and polypyrrole (PPy). These polymers are preferably doped with ions, such as metal ions, to increase their conductive properties. The amount of monomer added to the system is adjusted so as to obtain the desired amount of polymer on the aramid material. In general, the amount of polymer on the aramid material in the end product is in the range of 0.1-30 wt.%, calculated on the weight of the final product, wherein the amount of polymer is selected such that the desired degree of antistatic properties or conductive properties are obtained. In general, the addition of more polymer than is required to obtain the desired antistatic or conductive properties is not desired, because it brings on additional costs without additional benefits being obtained. The amount of polymer, calculated on the dry weight of the coated pulp, shortcut, fibrid, or fibril, preferably is at least 0.2 wt.%, in particular at least 0.5 wt.%, still more in particular at least 1 wt.%. The amount of polymer is in particular at most 20 wt.%, more in particular at most 10 wt.%, still more in particular at most 5 wt.%.

While the anionic surfactant may also have dopant properties, it has been found that the amount of anionic surfactant that is preferably used is insufficient to obtain a polymer with good conducting properties. Accordingly, in the process according to the invention a dopant is used in an amount of at least 0.1 mole/mole of monomer. Preferably the amount of dopant is at least 0.2 mole/mole of monomer. To ensure that the proper amount of dopant is built into the final polymer, the amount of dopant in the aqueous medium may be much higher. The maximum amount of dopant is not critical to the present invention. It is within the scope of the skilled person to select the suitable amount of dopant. The use of an amount of dopant which is such that the amount of dopant in the final polymer is between 0.1 and 4 moles/mole of polymer repeating unit, in particular 0.2-2 moles/mole of polymer repeating unit, more in particular 0.3 – 1 mole of dopant

per mole of polymer repeating unit is considered preferred for reasons of efficacy and efficiency.

Suitable dopants include anionic counter ions, such as iodine chloride and perchlorate, provided by, for example, I_2, HCl, $HClO_4$, and their salts and so on, can be used. Other suitable anionic counter ions include, for example, sulfate, bisulfate, sulfonate, sulfonic acid, fluoroborate, PF^{6-}, AsF^{6-}, and SbF^{6-} and can be derived from the free acids, or soluble salts of such acids, including inorganic and organic acids and salts thereof. Furthermore, as is well known, certain oxidants, such as ferric chloride, ferric perchlorate, cupric fluoroborate, and others, can provide the oxidant function and also supply the anionic counter ion. However, if the oxidizing agent, to be discussed later, is itself an anionic counter ion it may be desirable to use one or more other doping agents in conjunction with the oxidizing agent. In the present invention the dopant is not an anionic surfactant. The dopant does not show surfactant behaviour in the sense that in water it does not show a CMC (critical micelle forming concentration).

The polymerization is started by the addition of an oxidizing agent. Suitable oxidizing agents are known in the art, and include, for example, compounds of polyvalent metal ions, such as, for example, $FeCl_3$, $Fe_2(SO_4)_3$, $K_3(Fe(CN)_6)$, $H_3PO_4.12MoO_3$, $H_3PO_4.12WO_3$, CrO_3,$(NH4)_2$ $Ce(NO_3)_6$, $CuCl_2$, $AgNO_3$, etc., especially $FeCl_3$, and compounds not containing polyvalent metal compounds, such as nitrites, quinones, peroxides, peracids, persulfates, perborates, permanganates, perchlorates, chromates, and the like. Examples of such non-metallic type of oxidants include, for example, HNO3, 1,4-benzoquinone, tetrachloro-1, 4-benzoquinone, hydrogen peroxide, peroxyacetic acid, peroxybenzoic acid, 3-chloroperoxybenzoic acid, ammonium persulfate, ammonium perborate, etc. The alkali metal salts, such as sodium, potassium or lithium salts of these compounds, can also be used. The use of cerium sulphate, cerium persulphate, and ammonium persulfate is considered preferred. The amount of oxidizing agent is generally in the range of 0.1-4 moles per mole of

monomer to be polymerized, preferably in an amount of 0.5-2 moles per mole of monomer.

The aramid material used in the present invention is selected from aramid pulp, shortcut, fibril, and fibrid. Aramid is short for poly(phenylenetherephthalamide), which exists in the meta-form or the para-form. Both types may be used in the present invention. The use of para-aramid is considered preferred.

In one embodiment of the present invention aramid pulp is used which is derived from aramid fibres which are cut to a length of, e.g., 0.5-6 mm, and then subjected to a fibrillation step, wherein the fibers are pulled apart to form the fibrils, whether or not attached to a thicker stem.

In another embodiment of the present invention pulp is used which is directly spun from solution, e.g., the pulp obtained in WO2004/099476. The pulp may have a structural irregularity expressed as a difference in CSF (Canadian Standard Freeness) of never dried pulp and dried pulp of at least 100, preferably of at least 150.

In one embodiment aramid shortcut is used, which in the present invention are aramid fibres cut to a length of, e.g., 0.5-15 mm.

In one embodiment aramid fibrils are used, i.e., in the context of the present specification, “pulp” which predominantly contains the fibrillated part and little or no fiber stems. In one embodiment fibrils are used having in the wet phase a Canadian Standard Freeness (CSF) value less than 300 ml and after drying a specific surface area (SSA) less than 7 m2/g, and preferably a weight weighted length for particles having a length > 250 micron (WL 0. 25) less than 1.2 mm, more preferably less than 1.0 mm. Suitable fibrils and their preparation method are described, e.g., in WO2005/059211.

In one embodiment, aramid fibrids are used. Fibrids are small, non-granular, non-rigid fibrous or film-like particles. The film-like fibrid particles have two of their three dimensions in the order of microns, and have one dimension less than 1 micron. Fibre-like fibrids have one of their dimensions in the order of microns and two dimensions below 1 micron. Their smallness and suppleness allows them to

be deposited in physically entwined configurations such as are commonly found in papers made from wood pulp. Meta-aramid fibrids may be prepared by shear precipitation of polymer solutions into coagulating liquids as is well known from U.S. Pat. No. 2,999,788. Fibrids of wholly aromatic polyamides (aramids) are also known from U.S. Pat. No. 3,756,908, which discloses a process for preparing poly(meta-phenylene isophthalamide) (MPD-I) fibrids in column 5 lines 37-54. Para-aramid fibrids are made via a much later developed jet spin process such as described in EP 1694914.
Obviously, combinations of various types of aramid materials may also be used.

In the process according to the invention first an aqueous medium is provided comprising aramid material, polymerizable monomer of a conductive polymer, anionic surfactant in an amount of at least 0.1 mole of anionic surfactant per kg of aramid material (calculated as dry weight), and dopant in an amount of at least 0.1 mole per mole of monomer. The aramid material is generally present in the aqueous medium in an amount of 0.1-10 wt.%, more in particular in an amount of 0.5-5 wt.%, still more in particular in an amount of 1-3 wt.%. The amount of aramid material in the medium is governed by processing considerations. If the amount of aramid material is too high, the medium may be too viscous for proper processing. On the other hand, if the amount of aramid is too low, the processing efficiency of the system will be affected.
The monomer concentration in the aqueous medium is generally in the range of 1 mmole/liter to 200 mmole/liter, in particular in the range of 5 mmole/liter to 100 mmole/liter, more specifically in the range of 15-60 mmole/liter.
The surfactant concentration in the aqueous medium generally is in the range of 0.1 mmole/liter to 40 mmole/liter, in particular in the range of 0.5 mmole/liter to 20 mmole/liter, more specifically in the range of 1 mmole/liter to 10 mmole/liter.
The molar ratio of surfactant to monomer in the aqueous medium generally is in the range of 1:0.025 to 1:2000, in particular in the range of 1:0.5 to 1:100, more in particular in the range of 1:2 to 1:40. A value in the range of 1:5 to 1:20 may give best results.

The dopant concentration in the aqueous medium generally is in the range of 2 mmole/liter to 500 mmole/liter, in particular in the range of 10 mmole/liter to 200 mmole/liter.

The pH in the reaction medium generally is in the range of 0 to 4, more in particular in the range of 0.5 to 2. A pH in the stipulated range leads to an efficient and high-yield coating process.

The manner and sequence in which aramid material, monomer, surfactant, and dopant are combined are not critical to the invention. The only important requirement is that these compounds should all be present in the system when the oxidizing agent is added.

Once the oxidizing agent is added, the mixture is brought to polymerization conditions so that a polymer is formed which precipitates on the aramid material. Polymerisation conditions generally include atmospheric pressure and a temperature between 0ºC and 100ºC, in particular between 5ºC and 80ºC, more in particular between 10 and 60ºC. Suitable temperatures will depend on the nature of the polymer, and it is within the skilled person to select a suitable temperature in a particular case.

The polymerization reaction is allowed to continue for the necessary period, which will depend on the nature of the polymer, the nature of the oxidizing agent, and the reaction conditions, and which can be determined by the skilled person on the basis of common general knowledge. In general, the polymerization time will vary between 10 seconds and 4 hours. It has been found that in the process of the invention, short polymerization times may be achieved. In some embodiments, the polymerization time may be less than 2 hours, or even less than 1 hours.

When short polymerization times are aimed for, it may be preferred to use oxidizing agents with a standard electrode potential of above 0.75 V, in particular at least 1 V. It has been found that oxidizing agents meeting this requirement a

shorter polymerisation time can be achieved. In one embodiment the medium is agitated during the polymerisation reaction.
Once the desired degree of polymerization has been obtained, the coated aramid material is isolated from the reaction medium. The coated material may be washed, if so desired, and/or dried, if so desired.

The coated aramid material obtained in accordance with the present invention may be used in numerous applications.
In one embodiment, the coated aramid material, in particular coated aramid pulp, is used in friction materials such as brake pads. In another embodiment, the coated aramid material is used in gaskets. In a further embodiment the coated aramid material, is used in the manufacture of paper, in particular paper with antistatic or conductive properties. If so desired, the coated aramid material may be combined with particle selected from pulp, fiber, fibrid, floc, and fibril, which is not coated with a conductive polymer. The uncoated material may be aramid material or other material. In one embodiment, where the coated aramid material is used in the manufacture of paper it may be combined with other materials, e.g., uncoated aramid materials, or non-aramid materials such as cellulose. The papers containing aramid material according to the invention may in one embodiment have antistatic and conductive properties as described above for the aramid material itself.

The invention is further illustrated by the following non-restrictive examples.

Example 1 – Influence of surfactant

Dry Twaron® 1099 pulp obtainable from Teijin Aramid was suspended in water to form a 1 wt.% pulp suspension. The water/pulp mixture was opened for 600 counts in an Lorentzen&Wettre desintegrator.
Pulp suspension (1 wt% in water) were dispersed in a 3 L beaker glass using mechanical stirring with a stirring speed of 500 rpm. A solution of 1 wt.% sodium

dodecylsulphate surfactant in water was added to a concentration as indicated in table 1. 25 mL of demineralized water and EDOT monomer solution (2.003 g of ethylene-dioxythiophene monomer per liter demineralized water) were added to obtain a mixture with pH 7-8. Oxidator solution (0.1 M cerium(IV)sulfate solution in 0.5 M hydrochloric acid) was added to this suspension over a period of 30 seconds under continuous stirring at 500 rpm, resulting in pH 1. This oxidizing solution is used to allow oxidative polymerization to take place and at the same time dope the resulting polymer. The suspension was stirred for one minute to allow the formation of a polymer coating on the aramid material. Then, the pulp was filtered off, and immediately washed with tap water to render a pulp dispersion with a pH of 7. The pulp suspension was filtered from the dispersion to form a wet cake. The experimental data of the polymerisations are given in Table 1.

Table 1. Experimental details of the polymerizations

	pulp dispersion (1 wt%) (mL)	EDOT solution (mL)	SDS** g/L pulp suspension 1 wt%)	EDOT (g/L)	oxidizing solution (mL)	PEDOT per 1 g of pulp (g)
Comp. 1.1	500	325	-	2.003	125	0.13
Inv. 1.1	1000	650	1.150	2.004	250	0.13
Inv 1.2	500	325	5.750	2.004	125	0.13

To determine the antistatic properties of the coated pulp, handsheets were prepared as described above and the conductivity thereof was determined. The results are given in Table 2.

Table 2. Handsheet results antistatic behavior

	mol surfactant/kg dry pulp	specific electrical conductivity (S/cm)

Comp 1.1	0	$1.31*10^{-12}$
Inv 1.1	0.399	$1.79*10^{-02}$
Inv 1.2	1.994	$1.93*10^{-04}$

Example 2

Comp. 2.1 – aramid pulp

A 3 wt% Twaron ® 1099 pulp suspension was prepared from 60 g dry Twaron ® 1099 pulp and 2 liter water. The water/pulp mixture was opened for 1200 counts in a Lorentzen&Wettre desintegrator. The aramid suspension was dewatered over a filter and then dried in an oven at 105ºC.

Invention 2.1 – PEDOT coating

4L of pulp suspension (3wt% in water) as described above was dispersed in a 10L beaker glass using mechanical stirring with a stirring speed of 1200 rpm. To this, 4.605 gram sodium dodecyl sulphate was added and the mixture was stirred for 45 minutes at 1200 rpm. Then, 2.600L of a solution containing 6.003 gram ethylenedioxythiophene (EDOT) per litre of demineralized water was added and ~25 mL of demineralized water (used for rinsing of all glassware). This mixture had a pH of 7-8. The stirring speed was increased to 1500 rpm. 1L of an 0.1 molar cerium(IV)sulphate solution in 0.5 molar hydrochloric acid was added to this suspension over a period of 30 seconds while continuous stirring at 1500 rpm, resulting in a pH of 1. This oxidizing solution is used to allow oxidative polymerization to take place and at the same time dope the resulting polymer. The suspension was stirred for one minute to allow the formation of a polymer coating on the aramid material. The pulp was filtered off, immediately washed with tap water (eight times washing with ~5 L of tap water, resulting in a pH of 7 of the pulp dispersion). After washing, the pulp suspension was filtered off, resulting in a wet cake.

Invention 2.2 - polyaniline coating

4L of pulp suspension (3wt% in water) as described above was dispersed in a 10L beaker glass using mechanical stirring with a stirring speed of 1200 rpm. To this, 20.009 gram sodium dodecyl sulphate was added and the mixture was stirred for 45 minutes at 1200 rpm. Then, 2.600L of a solution containing 6.004 gram aniline per litre of demineralized water was added and ~25 mL of demineralized water (used for rinsing of all glassware). This mixture has a pH of 7-8. The stirring speed was increased to 1500 rpm. 1L of an 0.1 molar cerium(IV)sulphate solution in 0.5 molar hydrochloric acid was added to this suspension over a period of 30 seconds while continuous stirring at 1500 rpm, resulting in a pH of 1. This oxidizing solution is used to allow oxidative polymerization to take place and at the same time dope the resulting polymer. The suspension was stirred for one minute after which the pulp was filtered off, immediately washed with tap water (eight times washing with ~5 L of tap water, resulting in a pH of 7 of the pulp dispersion). After washing, the pulp suspension was filtered off, resulting in a wet cake.

Invention 2.3 - polypyrrole coating

4L of Pulp suspension (3wt% in water), was dispersed in a 10L beaker glass using mechanical stirring with a stirring speed of 500 rpm. To this, 20.008 gram sodium dodecyl sulphate was added and the mixture was stirred for 45 minutes at 1200 rpm. Then, 2.600L of a solution containing 6.003 gram pyrrole (Py) per litre of demineralized water was added and ~25 mL of demineralized water (used for rinsing of all glassware). This mixture has a pH of 7-8. The stirring speed was increased to 1500 rpm. 1L of an 0.1 molar cerium(IV)sulphate solution in 0.5 molar hydrochloric acid was added to this suspension over a period of 30 seconds while continuous stirring at 1500 rpm, resulting in a pH of 1. This oxidizing solution is used to allow oxidative polymerization to take place and at the same time dope the resulting polymer. The suspension was stirred for one minute after which the pulp was filtered off, immediately washed with tap water (eight times washing with ~5 L of tap water, resulting in a pH of 7 of the pulp

dispersion). After washing, the pulp suspension was filtered off, resulting in a wet cake.

Washing and drying

The resulting cakes from Invention 2.1, 2.2, and 2.3were opened for 600 counts in a Lorentzen&Wettre desintegrator. After this they were washed again 5 times to get rid of the excess of sodium dodecyl sulphate surfactant. All pulps were dried in oven for 12 hours at 105°C. After this the pulps were completely dry.

Specific electrical conductivity

To determine the specific electrical conductivity of the pulps, papers were made according to the general procedure described above. The results are presented in table 3. The papers were designated antistatic when they have a specific electrical conductivity above $1*10^{-7}$ S/cm.

Filler retention

A mixture of 97% kaolin (Laude SP 20) and 3% of the pulp to be tested was prepared on a high-speed vertical mixer. 20 g of the mixture were sieved on a riddle sifter device using a 250 mesh sieve. The remaining material on the sieve given as percentage of the initial amount was determined. The filler retention is an indication of the suitability of a material for use in brake pads.

Green Strength

A mixture of 97% Kaolin (Laude SP 20) and 3% of the pulp to be tested was prepared on a high-speed vertical mixer. 10 g of the mixture were molded at 70 bar to a rod with a thickness between 7.5 and 11.0 mm and a width of 15 mm. The rod was fractured on a pendulum ram impact testing device perpendicular to its main axis. The green strength is given as mJ/mm². The green strength of the kaolin-aramid composite is an indication of the suitability of the aramid material for use in brake pads.

Table 3. Results different polymers

	monomer	antistatic	Filler retention (%)	Green strength (mJ/mm²)
Comp 2.1	None	No	89	2.01
Inv 2.1	EDOT	Yes	87	2.23
Inv. 2.2	Aniline	Yes	88	2.17
Inv. 2.3	Pyrrole	Yes	87	2.23

As can be seen from table 3, the coated aramid material according to the invention shows antistatic behaviour, while the comparative uncoated material does not. Within the measurement error the aramid pulp according to the invention shows the same filler retention properties as the comparative aramid pulp. The green strength of a kaolin-pulp composition containing the pulp according to the invention is the same as or slightly improved over the green strength of a kaolin-pulp composition containing the comparative pulp.

Example 3

Example 1 was repeated, except that other types of aramid material were used. The experimental details are presented in Table 4.

Table 4. Experimental details of the polymerizations

	Aramid product*	Aramid product dispersion (1 wt%) (mL)	EDOT solution (mL)	mol SDS/kg dry pulp	EDOT (g/L)	oxidizing solution (mL	PEDOT per 1 g of pulp (g)
Inv 3.1	1099	500	325	1.994	2.004	125	0.13
Inv 3.2	JSF	500	325	3.47	2.003	125	0.13
Inv 3.3	SC	1000	650	0.399	2.000	250	0.13
Inv. 3.4	MF	500	325	0.285	2.000	125	0.13

* 1099 is p-aramid pulp, commercially available from Teijin Aramid as Aramid Twaron ® 1099; JSF is p-aramid fibrid, commercially available from Teijin Aramid as Twaron ® D8016; SC is p-aramid short-cut fiber, commercially available from Teijin Aramid as Twaron ® 1080; MF are meta-aramid fibrids made from poly(meta-phenylene isophthalamide) as described in U.S. Pat. No. 3,756,908.

To determine the conductivity of the materials, handsheets were prepared as described above, except that for the shortcut material (inv 3.3) 5 wt.% of uncoated JSF is p-aramid fibrid, commercially available from Teijin Aramid as Twaron ® D8016 was added, to allow the manufacture of a stable paper. The conductivity data are presented in table 5.

Table 5. Handsheet results antistatic behavior

	Aramid material	specific electrical conductivity (S/cm)
Inv 3.1	1099	$1.93*10^{-04}$
Inv. 3.2	JSF	$4.00*10^{-03}$
Inv. 3.3	SC	$4.57*10^{-05}$
Inv. 3.4	MF	$1.10*10^{-03}$

Example 4

Analogous to Example 2, embodiment Inv. 2.2., polyanaline was polymerized on the surface of a Twaron 1099 ® pulp, and a wet cake was formed. The coated aramid from the wet cake was combined with cellulose, resulting in a mixture of cellulose and antistatic aramid material. The composition of the mixture is given in Table 6. Handsheets were made in accordance with the general procedure. The conductivity was measured with the Keithley electrometer. Results are presented in Table 6.

Table 6. Handsheet results antistatic behaviour antistatic aramid material cellulose mixtures

	Antistatic aramid	Cellulose	Specific electrical

	material (wt%)	(wt%)	conductivity (S/cm)
Inv 4.1		100	$4.06*10^{-10}$
Inv 4.2	50	50	$1.21*10^{-6}$
Inv 4.3	24	76	$3.27*10^{-7}$
Inv 4.4	12	88	$1.84*10^{-8}$

Example 5

A polymerisation was done on Twaron 1099 ® pulp according to the procedure as described in example 1 but with the following adaptations. The reaction time was 30 minutes. The concentration of the pulp suspension was 3 wt %. The amount of pulp dispersion was 1 liter. The monomer concentration was 0.02973 M aniline. The aniline was added as pure liquid in an amount of 10.5 wt % (rel to dry pulp). The amount of surfactant was 351 mmol surfactant / kg dry pulp. The concentration HCl in the final mixture was 448 mol % relative to the monomer concentration. The HCl was added 15 min before the addition of oxidator, and after 30 min stirring of the mixture of pulp/surfactant/aniline. The type of surfactant was varied according to table 7. Handsheets were made and the conductivity determined as described above.

Table 7. Handsheet results antistatic behaviour with different surfactants

	Surfactant	Surfactant nature	Specific electrical conductivity (S/cm)
Comp. 5.1	None	None	$4.95*10^{-9}$
Inv. 5.1	sodium lauryl sulphate	Sulphate, anionic	$1.70*10^{-4}$
Inv 5.2	sodium dodecylbenzenesulfonate	Sulphate, anionic	$9.72*10^{-5}$
Inv. 5.3	potassium lauryl phosphate	Phosphate, anionic	$3.81*10^{-5}$

Comp 5.2	cetyltrimethyl ammonium bromide	Cationic	$1.87*10^{-7}$
Comp 5.3	tert-butyl alcohol	Non-ionic	$7.79*10^{-9}$

As can be seen from Table 7, the use of non-ionic or cationic surfactants does not result in a coated aramid material with appropriate conductivity.

Claims:

1. Method for manufacturing an antistatic aramid material selected from pulp, shortcut, fibrid, and fibril, comprising the steps of providing an aqueous medium comprising said aramid material, polymerizable monomer of a conductive polymer, anionic surfactant in an amount of at least 0.1 mole of anionic surfactant per kg aramid material (dry weight), and dopant in an amount of at least 0.1 mole per mole of monomer, adding an oxidizing agent to the medium to polymerise the monomer to form a polymer, and separating the aramid material provided with a polymer coating from the medium.

2. Method for manufacturing an antistatic aramid material wherein the aramid material is present in the aqueous medium in an amount of 0.1-10 wt.%.

3. Antistatic aramid material selected from pulp, shortcut, fibril, and fibrid, wherein the pulp, fibrid or fibril has a coating comprising a mixture of a conductive polymer and a dopant.

4. Antistatic aramid material according to claim 3 which comprises at least 0.01 wt.% of an anionic surfactant.

5. Antistatic aramid material according to claim 3 or 4 wherein the conductive polymer is 0.1 to 30 wt% of the total weight of the aramid material.

6. Antistatic aramid material according to claim 5 wherein the conductive polymer is 1 to 10 wt% of the total weight of the aramid material.

7. Antistatic aramid material according to any one of claims 3-6 wherein the conductive polymer is PEDOT.

8. Antistatic aramid material according to any one of claims 3-7 wherein the aramid is para-aramid, preferably PPTA.

9. Composition comprising the antistatic aramid material according to any one of claims 3-8 and a particle selected from pulp, fiber, fibrid, floc, and fibril, which is not coated with a conductive polymer.

10. Composition according to claim 9 wherein the particle not coated with conductive polymer is cellulose.

11. Use of the aramid material according to any one of claims 3-8 or a composition of claim 9 or 10 in the manufacture of paper.

12. Paper comprising the aramid material of any one of claims 3-8 or the composition of claim 9 or 1-.

13. Use of the aramid material according to any one of 3-8 in brake pads or gaskets.

14. Brake pad or gasket comprising the aramid material according to any one of claims 3-8.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/068665

A. CLASSIFICATION OF SUBJECT MATTER
INV. D06M15/00 D06M15/61 D06M15/63 D06M101/36 C09K3/10
C09K3/14 D21H13/26 F16D69/02
ADD.
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)
D06M C09K D21H F16D

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)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	column 4, line 19 - line 38 column 10, line 38 - line 40	1,2

Y	WO 2006/041188 A1 (SHOWA DENKO KK [JP]; TOKYO INST TECH [JP]; OOHATA HIDEKI [JP]; LEI YON) 20 April 2006 (2006-04-20) page 5, line 6 - line 25 page 17, line 9 - line 18 examples	1,2

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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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
7 January 2013	17/01/2013

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Fiocco, Marco

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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