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(54) Title: PROCESS FOR THE MANUFACTURE OF A FIBER COMPRISING META-ARAMID

(57) Abstract: Process for manufacturing a fiber comprising meta-aramid having a breaking tenacity of at least 300 mN/tex comprising the steps of preparing a spin dope comprising meta-aramid and sulfuric acid having a concentration of at least 80 wt% and passing the spin dope through a spinneret into a coagulation bath, wherein the spin dope has a meta-aramid concentration of at least 10 wt%. The invention also pertains to a meta-aramid fiber, a multifilament yarn, a textile sheet and protective clothing.

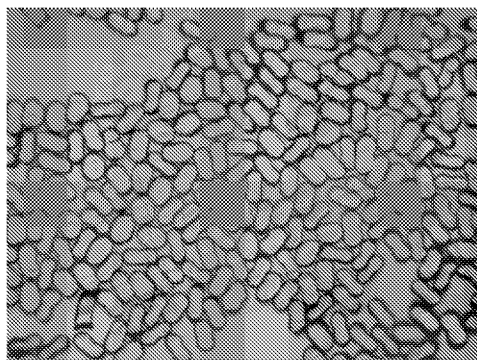


Fig. 1 a)



## Process for the manufacture of a fiber comprising meta-aramid

### Description:

The present invention relates to a process for manufacturing a meta-aramid fiber  
5 by preparing a spin dope comprising meta-aramid and sulfuric acid and passing  
said spin dope through a spinneret, and to the meta-aramid fiber obtained by said  
process. Furthermore, the invention also relates to a meta-aramid fiber having a  
sulfonic acid group content of at least 1 meq/kg, to multifilament yarn comprising  
said fiber and to a textile sheet and protective clothing.

10

Spinning processes for aramid fibers are known.

KR20100001782 describes aramid fibers and a manufacturing processes  
therefore. Various para-aramid polymers (e.g. paraphenylene terephthalamide,  
15 paraphenylene – 4,4'-biphenylene dicarboxylic acid amide or paraphenylene – 2,6-  
naphthalene dicarboxylic acid amide) may be used for the spinning process,  
wherein the para-aramid is dissolved in sulfuric acid, the spin dope is passed  
through a spinneret into a coagulation bath, the filaments are washed, dried and  
wound up. The time in the coagulation bath may be adjusted to improve the  
20 circularity of the filament cross section. KR20100001782 does not describe that  
meta-aramid is dissolved in sulfuric acid.

A spinning process for a meta-aramid fiber is disclosed in US3094511. This  
document discloses a dry spinning process wherein meta-aramid is dissolved in  
25 an organic solvent and passed through a spinneret into a heated air column. The  
latter step causes evaporation of the solvent.

Also known are meta-aramid wet spinning processes where the spin dope is directly passed from the spinneret into the coagulation bath, as e.g. described in EP0226137. Also for the wet spinning processes organic solvents are used.

- 5 The use of organic solvents has several disadvantages. Due to legislation, the use of organic solvents might be banned or only be allowed under more stringent conditions in the future for environmental reasons.
- Also, fibers spun with the use of organic solvents have to be extensively washed to remove the solvents, which is not economic.
- 10 Despite of extensive washing, meta-aramid fibers spun from organic solvents still contain organic solvents.

Therefore, there is the need for a spinning process for meta-aramid without the use of organic solvents.

15

- KR20140075197 pertains to a meta-aramid composition providing discoloration prevention by adding antioxidants into the spin dope. KR20140075197 describes that a meta-aramid fiber is produced from a meta-aramid composition, after dissolving the meta-aramid composition in sulfuric acid with a concentration of
- 20 99% to a meta-aramid concentration of 20%. After passing the spin dope through a spinneret, the spin dope is passed directly and without any air gap into a coagulation bath, the filament is washed, dried and wound up. KR20140075197 does not disclose a meta-aramid fiber having a breaking tenacity of at least 300 mN/tex.

25

- An object of present invention is to provide a meta-aramid fiber which is substantially free of organic solvents and has good mechanical properties, in particular a high breaking tenacity.
- It is also an object of present invention to provide an improved meta-aramid fiber,
- 30 in particular with improved fire retardancy and improved even cross section.

In order to achieve the above objects, the present invention provides a process for manufacturing a fiber comprising meta-aramid having a breaking tenacity of at least 300 mN/tex comprising the steps of preparing a spin dope comprising meta-aramid and sulfuric acid having a concentration of at least 80 wt% and passing the  
5 spin dope through a spinneret into a coagulation bath, wherein the spin dope has a meta-aramid concentration of at least 10 wt% (based on the weight of the spin dope).

Preferably, the fiber comprising meta-aramid has a breaking tenacity of at least  
10 350 mN/tex, more preferably at least 400 mN/tex and even more preferably at least 450 mN/tex. The instant process may also result in fibers comprising meta-aramid having a tenacity of at least 500 mN/tex.

The breaking tenacity of the fiber comprising meta-aramid is determined according  
15 to ASTM D7269-17 for multifilament yarns and according to ASTM D3822 for single filaments.

The fiber comprising meta-aramid may also be referred to as meta-aramid fiber.

20 For the purpose of this invention, the term meta-aramid refers to a class of wholly aromatic polyamide polymers and copolymers having at least 70%, preferably at least 80% and more preferably at least 90% of meta-oriented bonds between the aromatic moieties. In one embodiment, at least 95% or all (i.e. 100%) of the bonds are meta-oriented bonds. The amide bonds between the aromatic moieties are  
25 thus located substantially in the meta-oriented or nearly meta-oriented positions of the aromatic rings (as e.g. in a 1,3-phenylene group or 1,3-naphthalene group).

The meta-aramid of the present invention may be of recurring units of formula I and II:

30  $[-\text{NH-Ar1-NH-CO-Ar2-CO-}]$ - (formula I)  
 $[-\text{NH-Ar1-CO-}]$ - (formula II),

where Ar1 and Ar2 are aromatic, divalent, meta-oriented radicals which may be the same or different and at least one of Ar1 and Ar2 is a m-phenylene radical.

5 Meta-aramids may be produced by polymerization of meta-type aromatic amine and meta-dicarboxylic acid halide.

Suitable aromatic meta-diamines are meta-phenylenediamine, 3,4'-diaminodiphenylether, and 3,4'-diaminodiphenylsulfone; and derivatives thereof having substituents such as halogen atoms and/or alkyl groups having 1 to 3  
10 carbon atoms, attached to the aromatic cyclic structures thereof, for example, 2,4-toluylenediamine, 2,6-toluylenediamine, 2,4-diaminobenzene, and 2,6-diaminobenzene, may be employed. Preferably, meta-phenylene diamine or mixed diamines containing meta-phenylene diamine in a content of 85 molar % or more, more preferably 90 molar % or more, still more preferably 95 molar % or  
15 more are employed.

Suitable aromatic meta-dicarboxylic acid dihalides are isophthalic acid halides, for example, isophthalic acid chloride and isophthalic acid bromide; and derivatives thereof having substituents, for example halogen atoms and/or alkoxy groups  
20 having 1 to 3 carbon atoms, for example 3-chloroisophthalic acid chloride and 3-methoxyisophthalic acid chloride may be employed. Preferably, isophthalic acid chloride and mixed carboxylic acid halides containing isophthalic acid chloride in a content of 85 molar % or more, more preferably 90 molar % or more, still more preferably 95 molar % or more, are employed.

25

The meta-aramid of instant invention may comprise further monomers besides meta-type aromatic diamines and meta-type dicarboxylic acid halides. Suitable copolymerization components usable in combination with the diamines and the carboxylic acid halides include benzene derivatives such as para-phenylene  
30 diamine, 2,5-diaminobenzene, 2,5-diaminobromobenzene and aminoanisidines; and 1,5-naphthylenediamine, 4,4'-diaminodiphenylether, 4,4,-

- diaminodiphenylketone, 4,4'-diaminodiphenylamine and 4,4'-diaminodiphenylmethane. Suitable comonomeric aromatic dicarboxylic acid dihalides include terephthalic acid dichloride, 1,4-naphthalenedicarboxylic acid dichloride, 2,6-naphthalenedicarboxylic acid dichloride, 4,4'-biphenyldicarboxylic acid dichloride and 4,4'-biphenyletherdicarboxylic acid dichloride. In one embodiment the meta-aramid polymer of present invention may include such copolymerization components in a content of at most 15 molar%, preferably at most 10 molar%, more preferably at most 5 molar%.
- 5
- 10 In one embodiment, the meta-aramid used in present invention is co-poly(m-phenylene isophthalamide) comprising at most 5 molar% of aromatic moieties other than m-phenylene. In another embodiment, the meta-aramid is poly(m-phenylene isophthalamide).
- 15 In one embodiment the spin dope is free of para-aramid polymer, i.e. comprises less than 5 wt%, preferably less than 1 wt%, more preferably less than 0.5 wt%, and most preferably less than 0.1 wt% of para-aramid polymer (based on the weight of the spin dope).
- 20 In one embodiment, the spin dope comprises sulfuric acid having a concentration of at least 80 wt% and polymer, which polymer consists of meta-aramid as defined above. The spin dope may consist of polymer, preferably consisting of meta-aramid as defined above, and sulfuric acid. The spin dope (and the resulting fiber) may be free of additives, in particular antioxidants.
- 25
- The spin dope preferably has a meta-aramid concentration in the range of 10 – 30 wt%, more preferably 12 – 20 wt%, even more preferably 14-16 wt%, based on the weight of the spin dope.

The spin dope may be prepared by mixing meta-aramid and sulfuric acid. Mixing of the sulfuric acid and the polymer may be carried out using a (double screw) extruder or a (twin shaft) kneader, preferably including degassing.

5 Preferably, the spin dope is prepared at a temperature in the range of 30 to 90°C.

Preferably, the spinning process of present invention is a dry-jet wet spinning process. This means, that the spin dope is passed through a gaseous medium after exiting the spinneret and before entering the coagulation bath.

10 The spin dope comprising meta-aramid and sulfuric acid is processed into fibers by passing the spin dope through a spinneret into a coagulation bath.

The spinning mass is deaerated and heated to spinning temperature.

The spinning temperature, i.e. the temperature at which the spin dope is lead to and passes the spinneret, is preferably at most 110°C, more preferably in the  
15 range of 25 to 80°C, or 45 to 60°C.

In the dry-jet wet spinning process, the liquid spin dope first passes through a non-coagulating gaseous atmosphere, such as air, and immediately afterwards is led into a coagulation bath. In the gaseous zone (also referred to as air gap) through  
20 which the spinning mass passes, the meta-aramid is drawn.

After coagulation, the filaments formed are removed from the coagulation bath, washed, dried and taken up on a bobbin.

The spinnerets that are used in the process according to the invention may be of a type known in itself in the dry jet-wet spinning of fully para-aromatic polyamides.

25 The gaseous non-coagulating medium preferably consists of air.

The gaseous medium (or air gap) preferably has a length in the range of 2 to 20 mm, more preferably 3 to 15 mm and even more preferably of 5 to 10 mm.

30 In the process according to the invention the spinning mass leaving the spinneret orifices is drawn in the non-coagulating gaseous medium. The degree of drawing,

that is the ratio between the length of the filaments upon leaving the coagulation bath and the average length of the spinning mass upon leaving the spinning orifices of the spinneret may be in the range of 1.5 to 15, preferably 2 to 6.

- 5 The composition of the coagulation bath may vary. It may entirely or partly consist of water or other substances, such as bases, acids, salts and organic solvents. The coagulation bath preferably consists of dilute aqueous sulfuric acid having a concentration of 0-40% by weight, preferably 2-20% by weight. In the embodiment where the coagulation bath comprises dilute aqueous sulfuric acid, the pH of the
- 10 coagulation bath may have a pH of below 7, preferably below 2. According to another embodiment, the coagulation bath may consist of a diluted caustic aqueous solution e.g. an aqueous NaOH solution with a concentration in the range of 0-10 % by weight, preferably 0.05 to 5% by weight and in particular 0.1 to 1% by weight. The coagulation bath may consist of water, in particular
- 15 softened or demineralized water.

The temperature of the coagulation bath may have any value desired. Depending on the other spinning conditions the temperature of the coagulation bath is generally in the range of -10°C to 50°C, and preferably between 0°C and 25°C,

20 more preferably between 2 and 10°C.

As small amounts of residual acid may have a detrimental influence on the fiber properties, the sulfuric acid used should completely be removed from the spun fibers, in particular by washing or neutralization and washing. The neutralization

25 may be done by subjecting the fiber obtained by coagulation to a treatment at room temperature or at elevated temperature with solutions of alkaline substances, for instance caustic solutions of NaOH, NaHCO<sub>3</sub> or Na<sub>2</sub>CO<sub>3</sub>. In one embodiment, the fibers are treated after coagulation with solutions having a NaOH concentration in the range of 0.1 to 2 wt%, preferably 0.3 to 1 wt%. Preferably, the

30 neutralization solution has a pH of at least 9, more preferably at least 11.



In one embodiment, the fibers are only treated with water (e.g. demineralized water or softened water) after coagulation, in particular once, twice, three or more than three times (only washing, without neutralization).

In a preferred embodiment, the fibers are washed, neutralized and again washed.

5 After they have been washed, the fibers are dried. This may be done in any convenient way, either on-line or off-line. It is preferred that the drying should be carried out immediately after (neutralization and) washing, e.g. by passing the fibers over heated rollers having a temperature in the range of 50 to 220°C, preferably in the range of 75 to 200°C, more preferably in the range of 100 to  
10 175°C or 125 to 150°C.

To increase the tenacity of the fibers, optionally, the fibers obtained in the process according to the invention may be subjected to a wet –drawing step. During the wet-drawing step, the coagulated, wet fibers are subjected to a tension resulting in  
15 a drawing ratio in the range of  $\geq 1$  to 2, preferably 1.1 to 1.5. At this stage of the process, the drawing ratio may be defined as [length of the fiber after wet-drawing step] / [length of the fiber before wet-drawing step]. For a continuous online process the drawing ratio may also be determined based on the speed of the godets guiding the yarn before and after the wet-drawing, thus [speed of godet  
20 after wet-drawing step] / [speed of godet before wet-drawing step].

Preferably, the wet-drawing step is carried out between the coagulation and the washing, during washing or after washing at a temperature above room temperature.

25 The fibers may be subjected to a heat treatment, in which the fibers are heated under tension in an inert or non-inert gas. The heat treatment may be carried out after the drying step (online) or otherwise after the winding of the fiber (offline). The heat treatment may comprise one or multiple steps of heating under tension. In one embodiment, the process according to the invention comprises heating the  
30 fiber in at least one heating step to a temperature in the range of 250 to 400°C, preferably in the range of 280 to 350°C, preferably in the range of 300 to 320°C.

The heating treatment of the fiber may comprise at least two steps. In one process according to the invention, the fiber obtained in the first heating step as described above is heated in a second heating step to a temperature in the range of 250 to 5 400°C, preferably in the range of 280 to 350°C, preferably in the range of 300 to 320°C.

In a preferred embodiment, during at least one of the heating steps a tension is applied which results in a drawing ratio in the range of 1.5 to 10, preferably 1.5 to 10 2.5 and during the other heating step no tension (relaxation) is applied or a tension with is sufficient to allow transport of the fiber over processing equipment (e.g. guiding rolls) or a tension which results in a drawing ratio of at most 1.5. Higher tension may be applied either in the first or the second heating step. Preferably, a higher drawing ratio is applied in the first heating step.

15 In another embodiment, during each of the heating steps a tension is applied, which results in a total drawing ratio in the range of 1.5 to 10, preferably 1.5 to 2.5. At this stage of the process, the drawing ratio may be defined as [length of the fiber after heating step] / [length of the fiber before heating step]. The drawing ratio refers to one heat treatment step, the total drawing ratio to the drawing achieved in 20 all applied heat treatment steps (accumulated). For a continuous online process the drawing ratio may also be determined based on the speed of the godets guiding the yarn before and after the heat treatment, thus [speed of godet after at least one heating step] / [speed of godet before at least one heating step].

25 The process may include a wet-drawing step and a heat treatment.

The process according to the invention is a solvent-based process.

As solvent for the meta-aramid polymer, concentrated sulfuric acid is used.

Preferably, the sulfuric acid has a concentration of at least 85 wt%, more 30 preferably at least 90 wt% and even more preferably at least 95 wt%. Sulfuric acid

having a concentration of at least 98 wt% or at least 99 wt% is particularly preferred.

The process results in a meta-aramid fiber, preferably being a multifilament yarn.

- 5 The present invention also pertains to a meta-aramid fiber obtainable by the process of the invention, as disclosed in any of the embodiments above.

Within the scope of the invention fibers are to be understood as flexible units of matter having a high ratio of length to width (the width is defined across the cross-  
10 sectional area, perpendicular to the length of the fiber). The term fiber includes all usual types of fiber, such as filaments of particularly unlimited length, filament yarns comprising one or more twisted, co-mingled or non-twisted filaments (monofilaments and multifilament yarns), tow made up of a collection of a large number of filaments which are bundled practically without any twist being imparted  
15 to them, and the like. Filaments of practically unlimited length formed during spinning may, if desired, be cut into staple fibers, which may in their turn be processed into spun yarns. Filament yarns may also be cut into even smaller lengths called floc.

Furthermore, filament yarns may also be processed into pulp.

- 20 These fiber variants are encompassed by the term "fiber".

Potentially, multifilament yarn may comprise fibers according to the invention and fibers of other materials. The cross section of the fiber or filament of the invention can be of any shape, but is typically circular (round).

- 25 The invention also pertains to a meta-aramid fiber having a breaking tenacity of at least 300 mN/tex and a sulfonic acid group content of at least 0.001 wt% (mass / mass fiber).

Generally, the sulfonic acid group content is at most 1 wt%, preferably at most 0.5 wt%, more preferably at most 0.3 wt%. Alternatively, this may also be expressed in  
30 parts per million resulting in a sulfonic acid group content of >1 ppm, preferably 5-300 ppm, more preferably 10-100 ppm.

The sulfonic acid groups are formed as a consequence of using sulfuric acid as solvent for the meta-aramid. To some extent, on the aromatic groups an aromatic substitution reaction takes place, such that hydrogen moieties on aromatic groups are replaced by sulfonic acid groups. Preferably, these groups are neutralized.

5

The sulfonic acid group content is determined by nuclear magnetic resonance analysis (NMR), in particular  $^1\text{H-NMR}$  on as-spun, not-heat-treated samples. The method for determination of the sulfonic acid group content is provided in the example section.

10

Alternatively, the sulfur content may be determined to determine the degree of sulfonation of the fiber. In one embodiment, the sulfur content of the fiber according to the invention is at least 0.025 wt%, preferably at least 0.05 wt% (based on the weight of the fiber). The sulfur content may be determined on the obtained meta-aramid fibers, including on heat-treated fiber.

15

The sulfur content may be determined by inductively coupled plasma optical emission spectrometry (ICP-OES) as detailed in the example section.

Sulfonation of the meta-aramid fibers seems to be advantageous for the flame retardancy and flame resistance of the meta-aramid fibers. In particular, the LOI (Limiting Oxygen Index) of fibers of the instant invention is higher than that of meta-aramid fibers spun from organic solvents. Preferably, the LOI of the meta-aramid fibers according to the invention is increased by at least 10% compared to fibers spun from organic solvent.

20

The LOI is determined in accordance with ASTM D2863 as detailed in the example section.

25

Preferably, the meta-aramid fiber has a breaking tenacity of at least 350 mN/tex, more preferably at least 400 mN/tex and even more preferably at least 450 mN/tex. The meta-aramid fiber may have a tenacity of at least 500 mN/tex.

30

The breaking tenacity of the meta-aramid fiber is determined according to ASTM D7269-17 for multifilament yarns and according to ASTM D3822 for single filaments.

- 5 One of the advantages of the meta-aramid fiber of current invention is the low content of organic solvents.

In one embodiment, the meta-aramid fibers have an organic solvent content below 250 ppm, preferably below 100 ppm, more preferably below 50 ppm, corresponding to an organic solvent content of below 0.025 wt% (based on the weight of the yarn), preferably below 0.01 wt%, more preferably below 0.005 wt%. This means that the combined content of organic solvents, in particular NMP (N-methyl pyrrolidone), THF (tetrahydrofuran) and DMAc (dimethyl acetamide) is below 250 ppm, preferably below 100 ppm and more preferably below 50 ppm. Meta-aramid fibers having an organic solvent content below 100 ppm may be referred to as "substantially free of organic solvents". A very low residual organic solvent content may be the result of the solvents used during polymerization of the meta-aramid.

The organic solvent content may be determined by different methods, depending on the specific organic solvent. Generally, gas chromatography (GC), NMR (nuclear magnetic resonance) and MS (mass spectrometry) are suitable to determine the organic solvent content, e.g. the NMP or DMAc content, of the fibers. In the context of the current invention, the organic solvent content is determined by gas chromatography, as detailed in the example section.

25

The invention also pertains to a meta-aramid multifilament yarn comprising the meta-aramid fiber. The meta-aramid multifilament yarn may consist of meta-aramid fibers.

Preferably, the meta-aramid multifilament yarn has a breaking tenacity of at least 350 mN/tex, more preferably of at least 400 mN/tex and even more preferably of at least 450 mN/tex.

5 Preferably, the meta-aramid multifilament yarn has an elongation at break of at least 15%, preferably at least 20%, more preferably at least 25%.

In one embodiment, the meta-aramid multifilament yarn has a breaking tenacity of at least 350 mN/tex and an elongation at break of at least 25%.

The mechanical properties of the meta-aramid yarn are determined in accordance with ASTM D7269-17.

10

In one embodiment, the invention pertains to a multifilament yarn wherein at least 50% of individual filaments have a round cross section such that the average ratio of [diameter of the minimum circumscribed circle] to [diameter of the maximum inscribed circle] is at most 1.3, preferably at most 1.1.

15

The term "minimum circumscribed circle" means the smallest or minimum circle which circumscribes the contour of the cross-section of one filament of the multifilament yarn at, at least, two points and contains the entire area of the cross-section of the one filament. The term "maximum inscribed circle" means the largest or maximum circle which inscribes the contour of said cross section at, at least, two points and is contained within said contour of the cross-section.

20

The average ratio of [diameter of the minimum circumscribed circle] to [diameter of the maximum inscribed circle] is determined by preparing a cross section of a multifilament yarn and determining the diameter of the minimum circumscribed circle, the diameter of the maximum inscribed circle and the corresponding ratio for 50 separate filaments and calculating the average of the ratio.

25

For a fully round circle, the minimum circumscribed circle and the maximum inscribed circle will overlap and therefore have the same diameter, resulting in a ratio of 1.0.

30

The round cross section is another advantage of the meta-aramid fibers of present invention over the prior art meta-aramid fibers.

5 The meta-aramid fibers of present invention have a lower porosity than prior art meta-aramid fibers. Due to the lower porosity, the fibers of instant invention may have better mechanical properties.

Especially advantageous is the combination of properties of the instant meta-aramid fibers. The fibers have an even, round cross section, improved flame retardancy and a lower porosity.

10

Instant application also pertains to a textile sheet comprising the meta-aramid fibers and/or the meta-aramid multifilament yarn of present invention. The textile sheet may have the form of a woven, knitted or plaited textile sheet or fabric or a nonwoven textile sheet.

15

The meta-aramid fibers of present invention may be used for textile applications, e.g. in textile sheets, including knitted and woven fabrics, or cords used as reinforcement of hoses, in protective apparel, especially for fire-resistant application.

20

The meta-aramid fibers of present invention are especially suited for textile applications where the meta-aramid fibers or fabrics comprising the fibers are in direct skin contact.

25 Current invention also pertains to protective clothing comprising the textile sheet of instant invention. Protective clothing may e.g. be a glove, jacket, trouser or shirt.

The present invention is described in more detail with reference to the following examples, which should not be construed to limit the scope of present invention.

30

ExamplesMethods

## 1. Mechanical properties

The breaking tenacity, elongation at break and toughness at rupture of the meta-  
 5 aramid multifilament yarns are determined according to ASTM D 7269-17.

## 2. Sulfonic acid group content

The sulfonic acid group content is determined by <sup>1</sup>H-NMR. 20 mg of as-spun non-  
 heat-treated sample are dissolved in 1 mL DMSO-d6 and 550 μL thereof is  
 10 transferred to a 5 mm NMR sample tube. <sup>1</sup>H NMR spectra are recorded at 300 K  
 on a Bruker Avance III 400 MHz NMR spectrometer equipped with a BBFO-plus  
 5mm broadband probe. Spectra are recorded by co-adding 64 scans with a 30°  
 excitation pulse using a pre-scan delay of 6 s and an acquisition time of 4 s. The  
 1H NMR spectra obtained were referenced by setting the DMSO-d6 residual  
 15 solvent signal to 2.5 ppm.

The sulfonic acid group content is calculated by the formula below and expressed  
 in meq/kg (mmol/kg):

$$A_{\text{SMPD}} = \text{integral (singlet @ 8.97 ppm)} [\text{mol}]$$

$$20 \quad A_{\text{meta aramid}} = (\text{integral 8.86} - 7.08 \text{ ppm} - (6 * A_{\text{SMPD}})) / 8 [\text{mol}]$$

$$\text{sMPD} = (A_{\text{SMPD}} * 186.1844) [\text{mg}]$$

$$\text{meta aramid} = (A_{\text{meta aramid}} * 238.2414) [\text{mg}]$$

$$25 \quad S = (\text{sMPD} / (\text{sMPD} + \text{meta aramid})) * (32.065 / 186.1844) * 100\%$$

$$\text{Sulfonic acid group content} = 106 * (S / 100) / 32.065 [\text{meq/kg}]$$

## 3. Sulfur content

30 The sulfur content may be determined by inductively coupled plasma optical  
 emission spectrometry (ICP-OES). To 100 mg of fiber, 9 ml of concentrated nitric



acid (70 wt%) is added. This mixture is exposed to microwave digestion in an Ultrawave (Milestone) until a clear liquid is obtained. The volume is adjusted to 25 ml by addition of MilliQ water. Precipitates are removed from this solution by filtration. The clear filtrate is analyzed by ICP-OES in a Perkin Elmer Optima 8300 DV apparatus. For the determination of the sulfur content emission lines at 181,972 nm and 180,669 nm wavelength are used.

#### 4. Organic solvent content

The organic solvent content is determined by gas chromatography. About 1.0mg of fibers was collected and heated over 500°C in an electric furnace. Gas chromatography (Shimadzu Corporation, Ltd., Model: GC-2010) was used to measure the amide solvent amount vaporized from the fiber. Subsequently, residual solvent concentration in the fiber was calculated by using the calibration curve prepared by using an amide-based solvent as a standard sample.

#### 5. Relative viscosity

A polymer sample is dried at 50°C in a vacuum oven for two hours for removal of water. The dried sample is then dissolved in sulfuric acid at room temperature overnight. The flow time of the 0.25 %(w/V) sample solution in 96 %(w/w) sulfuric acid was then measured at 25°C in an Ubbelohde viscometer (e.g. Schott AVS370). Under identical conditions the flow time of the solvent was measured as well. The relative viscosity was then calculated as the ratio between the two observed flow times.

#### 6. Microscopy

The yarn is embedded in melted paraffin, which is left for about five minutes and solidified. Thereafter, the embedded sample is cut, vertical to the fiber axis, by a microtome to obtain a cut piece of 5 to 7  $\mu\text{m}$  thick. Then, the cut piece is placed on a slide glass which is heated to melt the paraffin. Thereafter, the melt paraffin was removed by xylene and ethanol. Next, a cross-section of the fiber is observed and

photographed by using an optical microscope (manufactured by NIKON CORPORATION; trade name "ECLIPSE" LV100N) to obtain a cross-sectional photograph. The magnification is selected within a range from 100 to 1000 as necessary.

5

## 7. LOI

The limiting oxygen index (LOI) is determined in accordance with ASTM D2863. A yarn specimen of 168000 dtex is prepared from each sample by combining the required number of yarns. The yarns are wound on a precision reel, with a yarn  
10 tension during winding of  $5 \pm 3$  mN/tex based on the nominal linear density of the yarn. This specimen is encircled with thin copper wire. Each specimen has a length of approximately 150 mm, a width of approximately  $10 \pm 0.5$  mm and a thickness of approximately  $3 \pm 0.25$  mm. The specimen is marked at approx. 50 mm from the end which is to be ignited. Immediately before testing, the specimen  
15 is conditioned for at least 88 hours at  $23 \pm 2^\circ\text{C}$  and  $50 \pm 5\%$  relative humidity. The specimen were tested according to option A of ASTM D2863 (top surface ignition).

### Example 1

Fibers were spun from a spin dope comprising a m-aramid polymer (poly(m-phenyl isophthalamide) having a relative viscosity of 1.55.  
20

The m-aramid polymer was mixed in a Theysohn 20 mm twin screw extruder at a temperature of  $85^\circ\text{C}$  and a speed of 300 rpm with 99.8 wt% sulfuric acid to a polymer concentration of 18 w/w% to obtain a spin dope.

The spin dope was processed into filaments by passing it at  $55^\circ\text{C}$  through filters  
25 and at  $85^\circ\text{C}$  through a spinneret, through an air gap and into a static coagulation bath (under the conditions indicated in Table 1). The coagulation bath had a temperature of  $3^\circ\text{C}$ .

Table 1: Settings in spinning process

Sample	Spinneret openings (number/diameter in $\mu\text{m}$ )	Winding speed (m/min)	Air gap (mm)	Drawing ratio in air gap

1-1	50/80	60	5	3.6
1-2	50/80	60	5	3.6

The multifilament yarns obtained after coagulation were washed and neutralized by subsequently passing them through baths of water, 0.4% NaOH and again water. The yarns were dried at 150°C and wound on the bobbin.

5

The properties of the yarns obtained after drying (also indicated as “as-spun”) were determined.

Table 2: Mechanical properties of the as-spun yarns

Sample	Linear density (dtex)	Breaking tenacity (mN/tex)	Elongation at break (%)	Toughness at rupture (J/g)
1-1	232	195	56.3	81
1-2	237	197	56.9	83

- 10 For sample 1-1 the sulfonic acid group content was determined to be 116 meq/kg. Sample 1-1 was heat treated in a two-step process. Yarns were reeled off from the bobbin and lead through a first oven in which a draw ratio of 1.6 was applied, and through a second oven that was kept at a temperature of 333 °C and in which the draw ratio was kept at 1, the draw ratio being defined as the speed after the
- 15 oven divided by the speed before the oven. The residence time in both ovens (based on the speed between the ovens) was 18.8 s.

Table 3: Mechanical properties of heat treated yarns

Sample	Temperature oven 1 (°C)	Linear density (dtex)	Breaking tenacity (mN/tex)	Elongation at break (%)	Toughness at rupture (J/g)
1-1-1	305	140	325	49.0	91.8
1-1-2	315	141	304	44.1	83.4
1-1-3	325	142	317	39.5	79.0
1-1-4	335	146	273	26.9	56.1
1-1-5	345	145	276	27.8	59.7

## 20 Example 2

Fibers were spun from a spin dope comprising a m-aramid polymer having a relative viscosity of 1.55. The m-aramid polymer was mixed in a Theysohn 20 mm

twin screw extruder at a temperature of 55°C (2-1 and 2-3) or 60°C (2-2 and 2-4) and a speed of 450 rpm with 99.8 wt% sulfuric acid to a polymer concentration of 16 wt/wt% or 17.5 wt/wt% to obtain a spin dope.

The spin dope was processed into filaments by passing it through filters and  
 5 through a spinneret, through a 5 mm air gap, in which a draw ratio of 3.41 was applied, and into a static coagulation bath (under the conditions indicated in Table 4). The coagulation bath had a temperature of 5°C.

Table 4: Spinning settings example 2

Sample	Polymer concentration (wt/wt%)	Spinneret openings (number/diameter in $\mu\text{m}$ )	Draw ratio in air gap	Winding speed (m/min)	Temperature of spinneret ( $^{\circ}\text{C}$ )
2-1	16	106/75	3.41	60	65
2-2	16	106/75	3.41	60	70
2-3	16	106/75	3.41	60	110
2-4	17.5	106/75	3.67	40	90

10

The multifilament yarns obtained after coagulation were washed and neutralized by subsequently passing them through baths of water, 0.25% NaOH and again water. The yarns were dried at 150°C and wound on the bobbin.

The properties of the yarns obtained after drying (also indicated as “as-spun”)  
 15 were determined.

Table 5: Mechanical properties of the as-spun yarns

Sample	Linear density (dtex)	Breaking tenacity (mN/tex)	Elongation at break (%)	Toughness at rupture (J/g)
2-1	360	235	23	40
2-2	360	244	24	44
2-3	380	211	47	73
2-4	413	200	73	103

20

Table 6: Relative viscosity and sulfonic acid group content of the fiber

Sample	Relative viscosity	Sulfonic acid group content (meq/kg)
2-1	1.52	17.6
2-2	1.52	23.5
2-3	1.48	55.6

Sample 2-3 was heat treated in a two-step process. Yarns were reeled off from the bobbin and lead through a first oven in which at a temperature of 305°C various draw ratios were applied, and through a second oven that was kept at a temperature of 333°C and in which the draw ratio was kept at 1, the draw ratio being defined as the speed after the oven divided by the speed before the oven. The residence time in both ovens was calculated based on the speed between both ovens. The sulfur content of sample 2-3 was determined to be 0.18 wt%.

10 Table 7: Heat treatment and mechanical properties of meta-aramid yarns treated in a two-step heating process

Sample	Draw ratio in oven 1	Residence time ovens (s)	Linear density (dtex)	Breaking tenacity (mN/tex)	Elongation at break (%)	Toughness at rupture (J/g)
2-3-1	1.6	18.8	234	312	49.6	108.1
2-3-2	1.8	16.7	209	332	40.8	96.3
2-3-3	2.0	15.0	190	334	32.3	80.6
2-3-4	2.2	13.7	174	345	24.8	65.8
2-4-1	1.6	6.5	254	327	30.0	76.0

### Example 3

Fibers were spun from a spin dope comprising a m-aramid polymer having a relative viscosity of 1.58.

The m-aramid polymer was mixed in a Clextral 53 mm twin screw extruder at a temperature of 45°C and a speed of 250 rpm with 99.8 wt% sulfuric acid to a polymer concentration of 12 wt/wt% to obtain a spin dope.

The spin dope was processed into filaments by passing it at 50°C through filters and at 50°C through a spinneret containing 1000 capillaries of 65 µm diameter, through an air gap, in which the filaments were drawn by a factor of 2.9, and into a falling jet coagulation bath (under the conditions indicated in Table 1). The coagulation bath had a temperature of 5°C.

The multifilament yarns obtained after coagulation were washed and neutralized by subsequently passing them through baths of water, 0.35% NaOH and again water. The yarns were dried on a godet at 160°C. Optionally the yarns were hot drawn on heated godets and wound on the bobbin.

Table 8: Settings in spinning process

Sample	Drying godet speed (m/min)	Air gap (mm)	Hot drawing 1: speed (m/min)/temperature (°C)/ residence time (s)	Hot drawing 2: speed (m/min)/temperature (°C)/ residence time (s)
3-1	100	13	-	-
3-2	100	11	-	-
3-3	100	9	-	-
3-4	100	13	160/270/0.66	160/285/0.66
3-5	100	11	160/270/0.66	160/285/0.66
3-6	100	9	100/270/0.26	160/305/1.32
3-7	100	13	155/180/0.17	155/285/1.35

The properties of the yarns obtained were determined and are shown in table 9.

Table 9: Mechanical properties yarns

Sample	Linear density (dtex)	Breaking tenacity (mN/tex)	Elongation at break (%)	Toughness at rupture (J/g)
3-1	2625	155	65.0	79.6
3-2	2598	167	51.4	71.4
3-3	2598	173	49.8	68.7
3-4	1593	276	26.9	56.2
3-5	1586	294	26.3	57.3
3-6	1597	273	27.4	59.6
3-7	1650	282	23.7	53.9

Example 4

Fibers were spun from a spin dope comprising a meta-aramid polymer having a relative viscosity of 1.55. The m-aramid polymer was mixed in a Theysohn 20 mm twin screw extruder at a temperature of 60°C and a speed of 450 rpm with 99.8 wt% sulfuric acid to a polymer concentration of 16 wt/wt% to obtain a spin dope. The spin dope was processed into filaments by passing it through filters and through a spinneret, through a 5 mm air gap, in which a draw ratio of 2.08 was applied, and into a dynamic coagulation bath (under the conditions indicated in Table 10). The coagulation bath had a temperature of 5°C. After the coagulation bath the yarns were wet drawn between 2 roller sets.

Table 10: Settings in spinning process

Sample	Spinneret openings (number/diameter in $\mu\text{m}$ )	Temperature of spinneret ( $^{\circ}\text{C}$ )	Air gap (mm)	Drawing ratio in air gap	Speed after coagulation (m/min)	Wet drawing ratio (-)
4-1	106/65	110	5	2.08	40	1
4-2	106/65	110	5	2.08	40	1.2
4-3	106/65	110	5	2.08	40	1.3
4-4	106/65	110	5	2.08	40	1.4
4-5	106/65	105	5		40	1.2
4-6	106/65	105	5		40	1.2

The multifilament yarns obtained after coagulation and wet drawing were washed and neutralized by subsequently passing them through baths of water, 0.25% NaOH and again water. The yarns were dried at 150°C and wound on the bobbin.

The properties of the yarns obtained after drying (also indicated as “as-spun”) were determined.

Table 11: Mechanical properties of the as-spun yarns

Sample	Linear density (dtex)	Breaking tenacity (mN/tex)	Elongation at break (%)	Toughness at rupture (J/g)
4-1	480	157	105	122

4-2	430	176	98	124
4-3	390	196	84	120
4-4	363	202	67	100

Sample 4-2 was heat treated in a two-step process. Yarns were reeled off from the bobbin and lead through a first oven in which at a temperature of 315°C a draw ratio of 1 was applied, and through a second oven that was kept at a temperature of 315 °C and in which the draw ratio was varied, the draw ratio being defined as the speed after the oven divided by the speed before the oven.

Table 12: Heat treatment and mechanical properties of meta-aramid yarns treated in a two step heating process

Sample	Draw ratio in oven 2	Linear density (dtex)	Breaking tenacity (mN/tex)	Elongation at break (%)	Toughness at rupture (J/g)
4-2-1	2.06	189	353	30	80
4-2-2	2.2	168	395	26	78
4-2-3	2.3	158	409	22	66
4-5-1	2.08	201	343	28	71
4-6-1	2.08	199	310	31	72

10

### Example 5

Fibers were spun from a spin dope comprising a meta-aramid polymer having a relative viscosity of 1.55. The m-aramid polymer was mixed in a Theysohn 20 mm twin screw extruder at a temperature of 50°C and a speed of 300 rpm with 99.8 wt% sulfuric acid to a polymer concentration of 16 wt/wt% to obtain a spin dope.

The spin dope was processed into filaments by passing it through filters and through a spinneret containing 106 capillaries with a diameter of 65 µm, maintained at temperature of around 75°C, through a 10 mm air gap, in which a draw ratio of 1.95 was applied, and into a dynamic coagulation bath. The speed after the coagulation bath was 40 m/min. After the coagulation bath the yarns were wet drawn 1.4 times between 2 roller sets. The yarns obtained after coagulation and wet drawing were washed and neutralized by subsequently

20



passing them through baths of water, 0.25% NaOH and again water. The yarns were dried on a roller set at 220°C. The yarns moved to 2 successive roller sets, of which the settings are indicated in table 13.

5 Table 13: Settings in spinning and hot drawing process

Sample	Coagulation bath temperature (°C)	Drying temperature (°C)	First roller set temperature(°C)/ drawing ratio (-)	Second roller set temperature(°C)/ drawing ratio (-)
5-1	2	220	295/1.7	295/1.3
5-2	3	220	290/1.6	290/1.35

The yarns were wound on a bobbin. The mechanical properties of the yarn are shown in table 14.

10 Table 14: Mechanical properties of the yarns

Sample	Linear density (dtex)	Breaking tenacity (mN/tex)	Elongation at break (%)
5-1	199	488	18.6
5-2	197	501	15.6

#### Example 6 – Organic solvent content

The NMP and DMAc content of commercially available TeijinConex® B, Nomex® and Yantai Tayho Advanced Materials' meta-aramid yarn was determined by gas chromatography. The results are shown in table 13. Yarn according to the invention does not comprise organic solvent.

Table 15 - organic solvent content

Sample	Sample type	NMP (wt%/wt)	DMAc (wt%/wt)
Comparative 1 (Nomex®)	Multifilament yarn	n.d.	1.2
Comparative 2 (TeijinConex® B)	Staple fiber	1.9	n.d.
Comparative 3 (Yantai)	Staple fiber	n.d.	0.28

n.d.= not determined

Example 7 – Cross section of filaments

Micrographs of embedded bundles of comparative samples 1 to 3 (as used in  
 5 example 6) and a meta-aramid yarn according to the invention were prepared. The  
 micrographs depicting the cross section of the filaments are shown in Fig. 1. Panel  
 a) shows a cross section of filaments of comparative sample 1, panel b) of  
 comparative sample 2, panel c) of comparative sample 3 and panel d) of the meta-  
 aramid yarn according to the invention.

10 As can be seen from the comparison, the filaments of the current invention have  
 an even, round cross section, while the comparative filaments have an oblong  
 cross section or a cross sections of varying diameter.

Example 8 – Limiting Oxygen Index

The LOI of meta-aramid yarns according to the invention and commercially  
 15 available meta-aramid yarn was determined. The results are shown in table 14.

Table 16: LOI of meta-aramid yarns according to the invention and commercially  
 available meta-aramid yarns.

Sample	LOI (% O <sub>2</sub> )
2-1	35
2-3	38
Comparative 2 (TeijinConex® B)	32
4-5-1	33
4-6-1	35

The data show that the samples according to the invention have a higher LOI  
 value than the comparative sample according to the prior art.

**Claims:**

1. Process for manufacturing a fiber comprising meta-aramid having a breaking tenacity of at least 300 mN/tex comprising the steps of preparing a spin dope comprising meta-aramid and sulfuric acid having a concentration of at least 80 wt% and passing the spin dope through a spinneret into a coagulation bath, wherein the spin dope has a meta-aramid concentration of at least 10 wt%.  
5
2. Process according to claim 1, wherein the fiber comprising meta-aramid has a breaking tenacity of at least 350 mN/tex, preferably at least 400 mN/tex, even more preferably of at least 450 mN/tex.  
10
3. Process according to claim 1 or 2, wherein the spin dope has a meta-aramid concentration in the range of 10 – 30 wt%, preferably 12 – 20 wt%, more preferably 14-16 wt%.  
15
4. Process according to any of the preceding claims, wherein the meta-aramid is co-poly(m-phenylene isophthalamide) comprising at most 5 molar% of aromatic moieties other than m-phenylene.
5. Process according to any of the preceding claims, wherein the spin dope is prepared by mixing meta-aramid and sulfuric acid.  
20
6. Process according to any of the preceding claims, wherein the spin dope is prepared at a temperature in the range of 30 to 90°C.  
25
7. Process according to any of the preceding claims, wherein the spin dope is passed through a gaseous medium after exiting the spinneret and before entering the coagulation bath.

8. Process according to claim 7, wherein the spin dope passes through a gaseous medium of a length in the range of 2 to 20 mm, preferably 3 to 15 mm, more preferably 5 to 10 mm.

5 9. Process according to any of the preceding claims, wherein the sulfuric acid has a concentration of at least 85 wt%, preferably at least 90 wt%, more preferably at least 95 wt%.

10 10. Process according to any of the preceding claims, wherein the fibers are heated in at least one heating step to a temperature in the range of 250 to 400°C, preferably in the range of 280 to 350°C, more preferably in the range of 300 to 320°C, optionally followed by a further heating step at a temperature in the range of 250 to 400°C, preferably in the range of 280 to 350°C, more preferably in the range of 300 to 320°C.

15 11. Meta-aramid fiber having a breaking tenacity of at least 300 mN/tex, obtainable by the process according to any one of claims 1 to 10.

20 12. Meta-aramid fiber having breaking tenacity of at least 300 mN/tex and a sulfonic acid group content of at least 0.001 wt%.

13. The meta-aramid fiber according to claim 11 or 12 having a breaking tenacity of at least 350 mN/tex, preferably at least 400 mN/tex, even more preferably at least 450 mN/tex.

25 14. The meta-aramid fiber according to any one of claims 11 to 13 having an organic solvent content below 250 ppm, preferably below 100 ppm, more preferably below 50 ppm.

30 15. Meta-aramid multifilament yarn comprising the meta-aramid fiber of any one of claims 11 to 14.

16. The meta-aramid multifilament yarn according to claim 15 wherein at least 50% of individual filaments have a round cross section such that the average ratio of [diameter of the minimum circumscribed circle] to [diameter of the maximum inscribed circle] is at most 1.3, preferably at most 1.1.

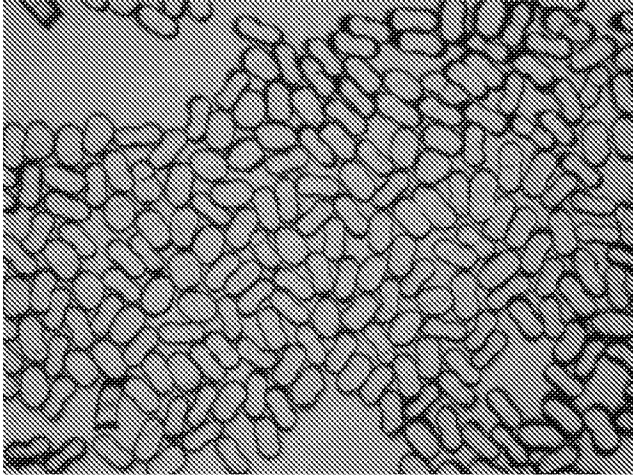
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17. Textile sheet comprising the meta-aramid fiber of any one of claims 11 to 14 and/or the meta-aramid multifilament yarn of claim 15 or 16, preferably a knitted, woven or nonwoven textile sheet.

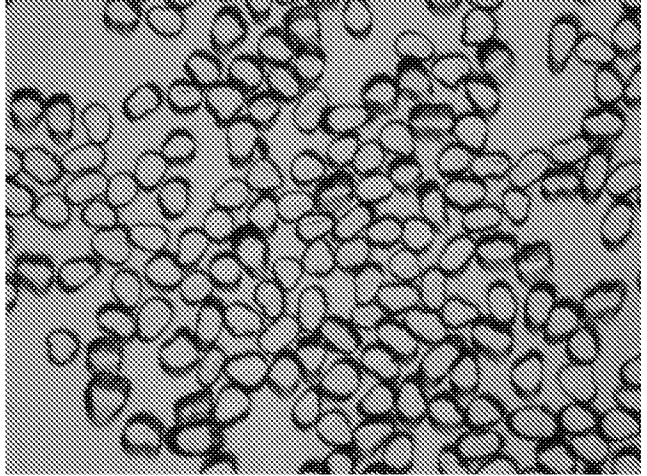
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18. Protective clothing comprising the textile sheet of claim 17.

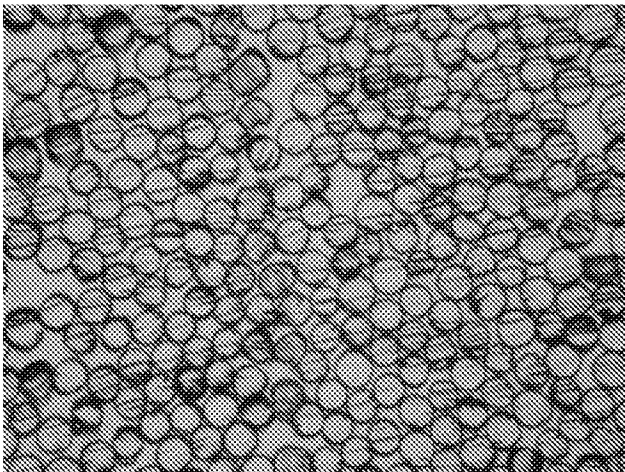
Fig. 1



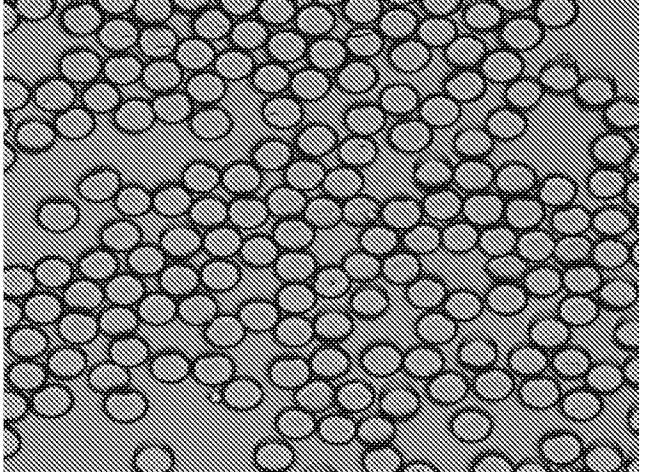
a)



b)



c)



d)

# INTERNATIONAL SEARCH REPORT

International application No PCT/IB2020/059360
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<b>A. CLASSIFICATION OF SUBJECT MATTER</b> INV. D01D5/06      D01F6/60      D02G3/44      D03D15/12      D04H1/4342 ADD.				
According to International Patent Classification (IPC) or to both national classification and IPC				
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) D01D D01F D02G D03D D04H				
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				
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	JP 2010 095831 A (TEIJIN TECHNO PRODUCTS LTD) 30 April 2010 (2010-04-30)	1-18		
Y	paragraphs [0002], [0010], [0017], [0018], [0021], [0029], [0031], [0024], [0053] -----	1-18		
Y	US 5 432 255 A (JUNG HOLGER [DE] ET AL) 11 July 1995 (1995-07-11) column 1, lines 10-19; example 1 column 4, lines 43-48; example 1 column 5, lines 1-18 -----	1-18		
Y	KR 2014 0075197 A (WOONGJIN CHEMICAL CO LTD [KR]) 19 June 2014 (2014-06-19) paragraphs [0001], [0007], [0036], [0038], [0040], [0087], [0088], [0098] ----- -/--	1-18		
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;"><input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.</td> <td style="width: 50%; border: none;"><input checked="" type="checkbox"/> See patent family annex.</td> </tr> </table>			<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.	<input checked="" type="checkbox"/> See patent family annex.
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.	<input checked="" type="checkbox"/> 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	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention			
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4 November 2020	16/11/2020			
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# INTERNATIONAL SEARCH REPORT

International application No PCT/IB2020/059360
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KR 2010 0001782 A (KOLON CO LTD [KR]) 6 January 2010 (2010-01-06) paragraphs [0001], [0002], [0009], [0016], [0021], [0033], [0034], [0037], [0040], [0049], [0051], [0052]; figure 1; example 1 -----	1-18



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2020/059360

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