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<b>(21) International Application Number:</b> PCT/KR95/00175 <b>(22) International Filing Date:</b> 27 December 1995 (27.12.95) <b>(30) Priority Data:</b> 1995/39631 3 November 1995 (03.11.95) KR <b>(71) Applicant (for all designated States except US):</b> KOLON INDUSTRIES, INC. [KR/KR]; 45, Mugyo-dong, Jung-gu, Seoul 100-170 (KR). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> CHOE, Won, Jun [KR/KR]; 201-607, Green Apartment, Bon-dong, Dalseo-gu, Daegu 704-350 (KR). RHIM, Moo, San [KR/KR]; 109-1101, Park-mansion, Doryang-dong, Gumi-si, Kyungsangbuk-do 730-030 (KR). CHUNG, Hoon, Ki [KR/KR]; 649-23, Susung 1 ga, Susung-gu, Daegu 706-031 (KR). <b>(74) Agent:</b> RO, Wan, Goo; Kyongwon Building, 3rd floor, 823-6, Yeocksam-dong, Gangnam-gu, Seoul 135-080 (KR).		<b>(81) Designated States:</b> BR, CN, JP, US, European patent (DE, ES, FR, GB, IT, NL).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> METHOD FOR PREPARING WHOLLY AROMATIC POLYAMIDE PULP  <b>(57) Abstract</b> <p>A method for preparing wholly aromatic polyamide pulp which comprises conferring an orientation to the polymer just before gelation of the polymer and ageing the gel, wherein the polymerization solvent is used as a heating medium for the ageing, can improve the physical properties of the pulp, such as molecular weight, crystallinity and development of fibril, as well as bring remarkable effects economically including exclusion of the processes for regenerating nitrogen and removing moisture, and low production cost. In addition, there is no danger of explosion of the liquid heating medium.</p>		

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## METHOD FOR PREPARING WHOLLY AROMATIC POLYAMIDE PULP

## BACKGROUND OF THE INVENTION

## Field of the invention

The present invention relates, in general, to a  
5 method for preparing wholly aromatic polyamide pulp and,  
more particularly, to reuse of polymerization solvent as  
a heating medium for ageing.

## Description of the Prior Art

Wholly aromatic polyamide pulp is typically prepared  
10 through polymerization, ageing, extraction and  
pulverization. Among them, ageing is recognized to be one  
of the most important process for determining the quality  
of wholly aromatic polyamide pulp.

In order to better understand the background of the  
15 present invention, a description will be given of  
conventional techniques in connection with ageing.

U.S. Pat. No. 4,511,623 discloses a method in which  
a polymer is produced by polymerizing in the presence of  
pyridine and then, aging by standing it for at least 5  
20 hours at ordinary temperatures.

According to a method proposed in U.S. Pat. No.  
5,028,372, wholly aromatic polyamide pulp is prepared by  
conferring an orientation on a prepolymer with a porous  
die, ageing the oriented prepolymer at 25-60 °C for 90  
25 minutes in air or a nitrogen atmosphere while cutting it  
at a time between 2 and 8 minutes after the start of  
ageing, placing the resulting prepolymer in a solidifying  
solution and pulverizing it.

Ageing in an oven for 60 minutes and, in extreme  
30 case, for 8 hours is executed as disclosed in U.S. Pat.  
No. 5,106,560.

International Patent Appln. No. PCT/KR95/0037 to the

present applicant discloses that ageing is performed at a temperature of 25 to 150 °C which comprises an obligate step of treating aromatic polyamide at 100 °C for 1 hour and at 80 °C for 2 hours in air or a nitrogen atmosphere.

5 As described above, it takes a long time to age the polymer by the conventional techniques, the main reason of which is that nitrogen or dry air, usually used for the ageing, is very low in thermal conductivity.

10 When oriented polymers are aged by standing or heating them in air or particular atmospheres, hydrogen chloride gas occurs which results from the reaction of with aromatic diamine with aromatic diacid chloride. In the ageing process using air or nitrogen, the hydrogen chloride gas and solvent gas which are generated during  
15 the solidification should be re-collected. This is not a preferable method in economic terms.

Particularly, nitrogen, even more expensive than air, is required to be reclaimed. To this end, the hydrogen chloride gas contained in the reclaimed nitrogen should  
20 be neutralized by use of acid-base reaction, followed by the removal of the moisture which is produced during neutralization. Indeed, the removal of moisture from the reclaimed nitrogen in an industrial scale, if possible, requires a considerable amount of energy. That is, when  
25 employing nitrogen, a large amount of nitrogen with high temperature is charged continuously and considerable energy cost is needed to reclaim it.

In the case of using air for the ageing, not only is the hydrogen chloride gas generated but an amide solvent  
30 which is first used for the solution polymerization of amide, vaporizes into the air. Such amide solvent includes dangerous compounds which explode at particular concentrations under heat. For example, N-methyl-2-pyrrolidone (hereinafter referred to as "NMP") is known  
35 to explode at 2.18 % vapor in air at 182 °C and at 12.24

% vapor in air at 188 °C. It is highly possible that, while the dry air along with hydrogen chloride gas and the solvent gas is circulated or exhausted, the concentration of the compound in air reaches said dangerous range and explodes by, for example, electrical spark, at last. In practice, if, after being polymerized, wholly aromatic polyamide is stands at ordinary temperatures, it is observed that about 30 % of solvent is extracted spontaneously. Therefore, while the ageing process is executed for several hours under air, the concentration of the vaporized amide solvent in the air is likely to reach the explosion-danger range. Additionally, there is needed a recovering process for the vaporized solvent.

Consequently, the use of dry air or nitrogen is uneconomic in industrial aspects and includes the danger of explosion.

The ageing process of polymerized and oriented wholly polyamide is very important because its molecular weight and crystallinity increase with the development of fibril during the process. In such ageing process, heating is critical. Dry air or nitrogen gas may be used as a heating medium in a laboratory scale but it is not preferable to use it on an industrial scale because of the above-mentioned problems.

Microwaving may be employed as a heating means for ageing but it has a higher possibility of explosion. Thus, the industrial application of microwaving is improper.

It is also disadvantageous to use hot water to provide heat necessary for the ageing, the reason of which is that water may stop polymerizing the reaction, to yield a polymerization degree short of expectation. As a result, the pulp exhibits poor physical properties.

In a non-solvent system for ageing the wholly aromatic polyamide, one free of water is used as an ageing

medium. It is difficult to select such medium. If solvents other than polymerization solvent are used for the ageing, one or more processes is needed to recover them. So, this is disadvantageous economically.

5           SUMMARY OF THE INVENTION

Therefore, it is an object of the present invention to overcome the problems encountered in prior arts and to provide a method for preparing wholly aromatic polyamide pulp on an industrial scale.

10           It is another object of the present invention to provide a method for safely preparing wholly aromatic polyamide pulp.

          It is a further object of the present invention to provide a method for economically preparing wholly  
15 aromatic polyamide pulp.

          To accomplish the above objects, the present inventors have researched and made various experiments on the preparing methods of wholly aromatic polyamide pulp comprising the step of conferring an orientation to the  
20 polymer just before gelation, ageing and pulverizing the gel, with an expectation that if the solvent used in the polymerization is employed as a heating medium for ageing oriented gel, it might not adversely affect the polymerization by swelling the polymerized and oriented  
25 gel, so that the polymerization solvent can simply and economically be reclaimed without additional facilities. The matter of grave concern to the present inventors is that the heating medium might have a considerable ill influence on the crystallinity of polymer and the  
30 development of fibril. As a result, the effect upon which the present inventors calculate, that is, reuse of the polymerization solvent without additional facilities, can be accomplished. In addition, surprisingly, when the

solvent used in the polymerization is reused as the heating medium for the ageing, the matter of concern, however, does not occur. On the contrary, not only the improvement in molecular weight of polymer, crystallinity, and development of fibril can be brought about, but also the danger of explosion can be excluded.

In preparing wholly aromatic polyamide pulp, it was ascertained that gel was formed upon subjecting polymer to orientation and hydrogen chloride and the polymerization solvent exude out the oriented gel. Therefore, even though the polymerization solvent is used for the ageing, it does not swell the polymer so that fibril can be developed well without degradation of inherent viscosity. In addition, the generation into the air of hydrogen chloride can be somewhat prevented because it adsorbs into the polymerization solvent used as the heating medium. Consequently, it is possible to use the polymerization solvent as a heating medium for the ageing.

Therefore, in accordance with the present invention, there is provided a method for preparing wholly aromatic polyamide pulp which comprises conferring an orientation to the polymer just before gelation of the polymer and ageing the gel, wherein the polymerization solvent is used as a heating medium for the ageing.

## DETAILED DESCRIPTION OF THE INVENTION

In the present invention, a heating medium for ageing is a typical polymerization solution used to prepare aromatic polyamide pulp, with preferred examples including N-methyl-2-pyrrolidone (NMP), N,N'-dimethylacetamide (DMAc), N,N'-dimethylformamide (DMF), hexamethylenephosphoamide (HMPA) and the combinations thereof.

According to the present invention, the danger of

explosion in the ageing process can be excluded. For example, although NMP, which may explode at a particular concentration in air, is used, there is no danger of explosion because it does not evaporate in the air owing  
5 to its high boiling point, 203 °C.

A single amide solvent or the mixture of amide solvents may be used as a heating medium for the ageing, alone or in combination with inorganic salts, Lewis acids or the mixtures thereof. Useful inorganic salts include  
10 alkali metal salts and alkaline earth metal salts. Preferred alkali metal salts include alkali metal halides, such as LiCl, NaCl, KCl, LiBr, and KBr, and preferred alkaline earth metal salts include alkaline earth metal halides, such as CaCl<sub>2</sub>.

15 A significant advantage of the present invention is that because the same solvent used for the polymerization is employed as the heating medium for the ageing, the solvent coming out the oriented polymer replenishes the heating medium, allowing additional heating medium not to  
20 be supplemented continuously.

Another important advantage of the present invention resides in liquid heating medium. Thermal conduction of liquid is far more efficient than that of gas so that the ageing time in liquid can be remarkably reduced. Where  
25 the solvent used for the polymerization of polyamide is reused as the heating medium for the ageing, the ageing time, if affected by the thickness and temperature of the gel to be treated, generally ranges from 2 to 30 minutes. For example, when aromatic polyamide pulp is prepared on  
30 an industrial scale, the ageing of a gel about up to 3 cm thick can be finished in 30 minutes with the polymerization solvent while a gel with a thickness of not more than 1 cm can be treated in 20 minutes or less. In addition, if aromatic polyamide pulp is spun in the same  
35 manner as orientation, the gel with a thickness of 2 mm



or less can age in a short time ranging from 1 sec to 10 min.

When ageing an oriented gel, the factor critical in determining the ageing time is not the length to the oriented direction but the thickness or width perpendicular to the oriented direction. Preferred is less than 3 cm in the thickness or width perpendicular to the oriented direction. Gels with a large thickness or width can be aged without any problems other than a long ageing time.

It is advantageous that an oriented gel is cut to the oriented direction to make it relatively long. Particularly preferred is to cut gel in a length of 1 cm or longer to the oriented direction.

In the present invention, the heating medium for the ageing ranges from 30 to 100 °C and preferably from 35 to 70 °C. It is important to maintain the heating medium at a temperature as high as or higher than that of gel.

Moisture content in the heating medium for the ageing plays an important role. A moisture content higher than 10 % causes the resulting pulp to have a somewhat lowered polymerization degree, the reason of which is that its polymerization ceases as soon as the surface portion of the oriented gel comes into contact with moisture. In the present invention, the gel is restricted to have a moisture content of up to 5 % and preferably up to 3 %.

It is actually impossible to completely remove moisture from the heating medium. In fact, most of the heating media have a moisture content of at least 10 ppm. In light of the fact that a heating medium with a moisture content of up to 10 % can be permitted for the ageing, it is believed that the thermal conduction rate is faster than the diffusion rate of water into the oriented gel.

The use of the polymerization solvent as a heating medium for the ageing can be applied to all processes that

comprise the orienting of wholly aromatic polyamide pulp during its polymerization and the ageing thereof. For example, not only a process in which a prepolymer is prepared with a continuous kneader, oriented in batch and subjected to ageing but also a process in which a prepolymer is prepared with a continuous kneader, oriented on a belt and subjected to ageing can adopt the method according to the present invention. In addition, the polymerization solvent can be used as a heating medium for the ageing in a process in which a continuous kneader is cleaned out by itself and equipped with a nozzle at its end and an orientation is conferred to polymer by extrusion spinning it from the nozzle.

As described above, a heating medium for ageing, exclusive of explosion, can be reclaimed simply and economically without installing additional facilities, according to the present invention. Besides, the method according to the present invention may not adopt processes of the regeneration of nitrogen and the removal of moisture. Further, the increase of inherent viscosity and crystallinity and the development of fibril are achieved together in the present invention, so that wholly aromatic polyamide pulp with excellent physical properties can be prepared at a low cost.

A better understanding of the present invention may be obtained in light of the following example which is set forth to illustrate, but is not to be construed to limit, the present invention.

In the following examples, physical properties were measured as follows.

Development of Microfibril : Observation can be done with an electron scanning microscope or optical microscope. An X-ray analyzer is used for the observation of orientation degree in molecular level. However, the

degree of orientation in pulp, the final article, is difficult to measure. Thus, the orientation degree of the pulp was observed with an X-ray analyzer after it was aged and dried.

- 5 Inherent Viscosity : As a reference to molecular weight, it was obtained according to the following formula.

$$IV = \frac{\eta_{rel}}{C}$$

- 10 wherein,  $\eta_{rel}$  is a relative viscosity obtained by measuring the relative retention time at 30 °C of a solution in which 0.5 g of a sample is dissolved in 100 ml of sulfuric acid, and C represents the concentration of the sample solution.

- 15 Specific Surface Area : It was measured according to TAPPI standard T227 om-85.

- Crystallinity, Crystal Size, Orientation Angle of Crystal : They were measured with an X-ray diffractometer by reference to BLADES disclosed in U.S. Pat. No. 3,869,430.  
20 Orientation angle and Crystal size were determined on the (110) face.

Canadian Standard Freeness (CSF) : It was measured according to ASTM-699-79.

#### EXAMPLE I

- 25 Into 2L, four neck-flask 500 ml of NMP was placed and then, 35 g of  $\text{CaCl}_2$  was dissolved at 80 °C. The flask was warmed at 60 °C, in which 24.5 g of 1,4-phenylenediamine

was added and dissolved. After being cooled into 6 °C, the solution was added with 45.95 g of terephthaloyl chloride and vigorously stirred. The stirring continued until just before gelation, to complete the orientation. Gel of poly(p-phenylene terephthalamide) thus oriented was cut into a size about 1 cm thick, which was then immersed in NMP bath warmed into 60 °C for ageing. The NMP had a moisture content of about 1 %. After ageing for about 10 minutes, the aged polymer was placed in water to extract the polymerization solvent. Thereafter, the polymer was pulverized to give pulp with an IV of 5.1 and a crystallinity of 49 %.

#### EXAMPLE II

Polymerization and orientation were achieved in the same manner as that of Example I, except that 30 g of CaCl<sub>2</sub> was dissolved in 500 ml of NMP. At the time of ageing the solution was 300 g in weight and after the ageing it was 290 in weight. It was certificated that NMP was extracted. The final pulp had an IV of 4.9 and a crystallinity of 51 %.

#### EXAMPLE III

A polymerization solvent was prepared by completely dissolving 80 kg of CaCl<sub>2</sub> in 1000 kg of NMP at 80 °C. In the polymerization solvent, 48.67 kg of para-phenylene diamine was added and dissolved, to give a solvent premix, also known as an amine solution. This amine solution the temperature of which was adjusted into 5 °C was added into a mixer at a speed of 1128.67 g/min with a quantitative pump. Simultaneously, molten terephthaloyl chloride was added into the mixer at a speed of 27.41 g/min and mixed, to prepare primary polymer. Then, the primary polymer was

cooled into 5 °C and charged into a continuous reaction kneader at a speed of 1156.08 g/min, during which molten terephthaloyl chloride was also charged at a speed of 63.95 g/min.

5           The first kneader was 2 inches (about 5.08 cm) in diameter and showed a retention time of 5 seconds with a jacket warmed to 35 °C whereas the second continuous reactor was 6 inches (about 15.24 cm) in diameter and showed a retention time of about 2 min. with a temperature  
10 of 35 °C. Using a vacuum pump, vapor was drained at the middle upper cover of the 6 inch kneader. While polymerization proceeded, the viscosity increased with polymerization, yielding so-called prepolymer.

          The prepolymer was continuously output from the 6  
15 inch kneader at the end of which a nozzle was not amounted. The prepolymer had a temperature of 42 °C and an IV of 2.2.

          Using an air cylinder, 500 ml of the output prepolymer was extruded through a hole 1 mm in diameter.  
20 The extruded gel went through an air layer into an ageing bath 1 m in length which contained NMP heated into 80 °C. After 5 minutes in the ageing bath, a thread of gel was removed therefrom and measured for orientation angle. It was 22 °, an excellent orientation degree.

25           After extracting the solvent, the gel was pre-chopped and then, pulverized with a disc mill. The pre-chopping was performed by use of a 12 inch (about 30.48 cm) disc mill, such as that sold by Andritz Sprout Bauer Co. Ltd., and a plate of spike type. For the pulverization, a 12  
30 inch disc mill, commercially available from Andritz Sprout Bauer Co. Ltd., and a plate, such as that sold by the same company, identified as D2A507, were used.

          The concentration of the slurry on the disc mill was about 1 %. The first interval was 5 mils (about 0.127 mm)  
35 while the second was about 2 mils (about 0.05 mm). The

pulp thus obtained was  $10.2 \text{ m}^2/\text{g}$  in specific surface area when measured by nitrogen absorption. It had an IV of 4.5 and a crystallinity of 49 %.

#### EXAMPLE IV

5 A prepolymer was prepared in the same manner as that of Example III.

At the end of 6 inch kneader was mounted a nozzle with sixty holes, each 0.5 mm in diameter.

The temperature was  $32 \text{ }^\circ\text{C}$  for the 6 inch kneader and 10  $38 \text{ }^\circ\text{C}$  for the prepolymer passed through the nozzle. And, the prepolymer had an IV of 2.0.

Below the nozzle, a bath 5 m long was provided which contained a  $\text{CaCl}_2$  solution in NMP, the polymerization solvent. This solvent was maintained at  $70 \text{ }^\circ\text{C}$  and had a 15 moisture content of 7 %. The retention time in the bath was 2 min.

After being aged, the samples were extracted in water. At that time, a sample was taken and subjected to X-ray diffraction, to measure orientation angle, which was 20 identified as 19 degrees.

After the extraction of solvent, the same pulverization processes as those of Example III were carried out.

The final pulp had an IV of 4.6, a crystallinity of 25 55 % and was 53 Angstrom in crystal size of (110) face.

#### COMPARATIVE EXAMPLE I

A procedure was carried out in a manner similar to that of Example IV, except that the solution temperature in the bath was  $120 \text{ }^\circ\text{C}$  and the retention time was 5 30 minutes. The sample in the course of solvent extraction was dried and measured for orientation angle, which was

identified as 20 degrees. The final pulp had an IV of 4.3 and a crystallinity of 41 %.

#### COMPARATIVE EXAMPLE II

A procedure was carried out in a manner similar to  
5 that of Example IV, except that the solution temperature  
in the bath was 100 °C, the moisture content in the bath  
was 20 % and the retention time was 3 minutes. The  
sample in the course of solvent extraction was dried and  
measured for orientation angle, which was identified as  
10 25 degrees. The final pulp had an IV of 3.5 and a  
crystallinity of 40 %.

#### COMPARATIVE EXAMPLE III

Example III was repeated using a batch-type orienting  
machine for orientation which was equipped with a screw-  
15 type interior impeller. A gel was separated from the  
batch-type orienting machine and cut into a size of 5cm  
x 5cm x 5cm, followed by the immersion in NMP which had  
a temperature maintained at 70 °C and a moisture content  
of 300 ppm. The retention time was 10 minutes. The gel  
20 was washed by being immersed in water, to extract the  
polymerization solvent. Thereafter, the gel was subjected  
to pulverization in the same manner as that of Example  
III, to give pulp. Its IV and CSF were measured and  
identified to be 3.6 and 740 ml, respectively, which were  
25 known to be insufficient. Consequently, retention time  
of 10 minutes cannot provide a desirable ageing degree.

Meanwhile, the gel obtained in the batch-type  
orienting machine was whole immersed in NMP for ageing.  
Two hours were needed to confer good physical properties  
30 to the final pulp. After being aged for two hours, the  
gel was pulverized in the same manner as that of Example

III, to obtain pulp, which had an IV of 4.6, a crystallinity of 49 % and a CSF of 420 ml.

5 Other features, advantages and embodiments of the present invention disclosed herein will be readily apparent to those exercising ordinary skill after reading the foregoing disclosures. In this regard, while specific  
10 embodiments of the invention have been described in considerable detail, variations and modifications of these embodiments can be effected without departing from the spirit and scope of the invention as described and claimed.



## WHAT IS CLAIMED IS:

1. A method for preparing wholly aromatic polyamide pulp which comprises conferring an orientation to the polymer just before gelation of the polymer and ageing the gel, wherein the polymerization solvent is used as a heating medium for the ageing.  
5
2. A method in accordance with claim 1, wherein said heating medium is of amide solvent.
3. A method in accordance with claim 2, wherein said  
10 amide solvent is selected from the group consisting of N-methyl-2-pyrrolidone, N,N'-dimethylacetamide, N,N'-dimethylformamide, hexamethylenephosphoamide and the combinations thereof.
4. A method in accordance with one of claims 1 to 3,  
15 wherein said heating medium comprises inorganic salt, Lewis acid or the mixtures thereof.
5. A method in accordance with claim 4, wherein said inorganic acid is at least one selected from the group consisting of  $\text{CaCl}_2$ , LiCl, NaCl, KCl, LiBr and KBr.
- 20 6. A method in accordance with claim 1, wherein said polymerization solvent used as a heating medium for the ageing contains moisture at an amount of 10 ppm to 10 %.
7. A method in accordance with claim 1, wherein said heating medium has a temperature of 30 to 100 °C.
- 25 8. A method in accordance with claim 7, wherein said heating medium has a temperature of 35 to 75 °C.

9. A method in accordance with claim 1, wherein the temperature of said heating medium is higher than that of the gel.

10. A method in accordance with claim 1, wherein said  
5 ageing is carried out for a period of 1 second to 30 minutes.

11. A method in accordance with claim 1, wherein said gel ready for the ageing is 3 cm or less in the thickness or width perpendicular to the orientation direction.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR 95/00175

A. CLASSIFICATION OF SUBJECT MATTER

IPC<sup>6</sup>: D 21 H 13/26

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)

IPC<sup>6</sup>: D 21 H 13/26

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

AT

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

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 332 919 A2 (TEIJIN LIMITED) 20 September 1989 (20.09.89), claims 1-3,6,11.	1-11
A	EP 0 550 355 A1 (RHONE-POULENC FIBRES) 07 July 1993 (07.07.93), claims 1,16.	1-11
A	EP 0 232 757 A1 (TEIJIN LIMITED) 19 August 1987 (19.08.87), claims 1-3,6-8.	1-11
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Further documents are listed in the continuation of Box C.

See patent family annex.

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Date of the actual completion of the international search

20 June 1996 (20.06.96)

Date of mailing of the international search report

26 June 1996 (26.06.96)

Name and mailing address of the ISA/ AT  
AUSTRIAN PATENT OFFICE  
Kohlmarkt 8-10  
A-1014 Vienna  
Facsimile No. 1/53424/535

Authorized officer

Brus

Telephone No. 1/5337058/32

EP-550355

Activated paper prods. consists of linker-linked fibres linked by fibrous and chemical binders. The fibres are mineral or synthetic with a thermal stability of 180 deg. C and over, and the fibrous binder is a polyamide or polyester pulp (totally aromatic) with thermal stability of 180 deg. C plus. The chemical binder is either a polyether imide, a polyester, or a resin obtd. from a N,N' bis-imide of a carboxylic acid. In (I) D =divalent radical contg. a C=C bond A = 2-30C divalent organic radical and a polyamine R(NH<sub>2</sub>)<sub>x</sub> (II) R = organic radical of valence x. The amt. of bis-imide is 0.55-25 moles per NH<sub>2</sub> gp. in the amine (R being 1-50). The resin having a particle size less than 100 microns and still in the pre-polymer condition having:- (a) a softening pt. of 50-200 deg. C, (b) practically no free NH<sub>2</sub> gps. (c) a deg. of crosslinking 0.025-0.25 (expressed as unreacted bis-maleimide per 100g of prepolymer. Also claimed is a method for obtaining the synthetic papers and composite articles made from the prods.

The synthetic prods. have numerous applications:their activity depends on the degree of polymerisation of the polymer binder. For example, a paper contg. the necessary amt. of resin to fill the porosity of the films can be used as an electrical spacer. The prods. are resistant to high temps. and are easily obtd. by traditional paper manufacturing techniques. They have good homogeneity and are obtainable as unwoven leaf, film or felt laminae.

EP-332919

A surface-modified wholly aromatic polyamide fibre is claimed comprising: fibre matrix of wholly aromatic polyamide material; fine inorg. particles comprising cation-exchanging inorg. material(s) distributed on and insurface portion of (I); and (III) additive attached is (II) comprising member(s) selected from cationic org. cpds. and org. silicone cpds. having 2/more diff. types of reactive radicals. Also claimed is its prodn. by: converting wholly aromatic polyamide material to fibre through spinning step, drawing step(s) and heat-treating step(s); then applying (II) to fibre surface; and treating adhered (II) with (III), attaching (III) to (II). Fibre having high mechanical strength and elastic modulus and improved solvent-resistance, exhibits enhanced bonding to other resinous materials, providing useful reinforcing materials for resinous/rubber articles.

EP-232757

Method for treating synthetic pulp particles comprises treating a slurry of synthetic pulp particles having a Schopper-Riegler freeness of over 30 deg. SR by a concentrator having a rotary filter bed to lower the freeness to max. 30 deg. SR. The particles are water washed in a state where the freeness is max. 30deg. SR then dispersed in water to restore the freeness to over 30deg. SR. Also claimed are pulp particles (I) of a synthetic polymer obtd. by introducing a soln. of the polymer into a coagulation bath under highshear to effect coagulation and fibrillation, where (a) the S-R freeness of the pulp particles is 20-30 deg. SR, and (b) the freeness is restored to 40-85 deg. SR only by dispersing the pulp particles in water. Pref. (I) are of wholly aromatic polyamide, esp. poly(m-phenylene isophthalamide).

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.

PCT/KR 95/00175

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