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(54) Title: METHOD FOR PRODUCTION OF POLY-VINYL ALCOHOL -FILAMENT FIBRE OF HIGH STRENGTH AND ELASTICITY

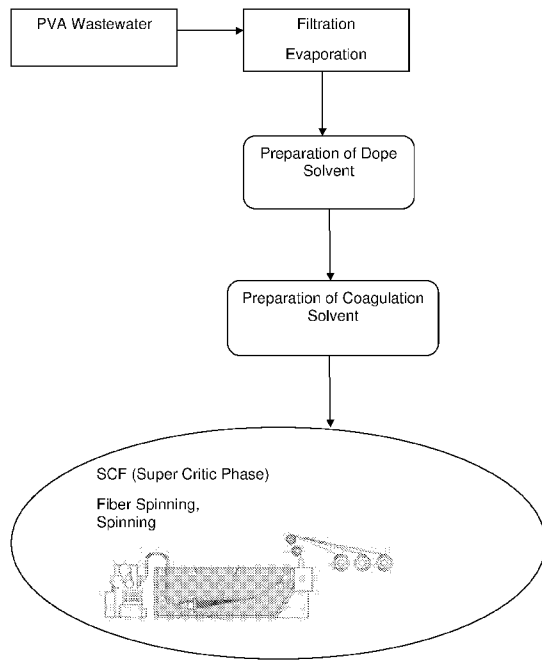


Figure 1

(57) Abstract: Invention relates to a filament fibre production method comprising process steps of: filtration of and/or applying evaporation process to wastewater containing Polyvinyl alcohol polymer from sizing process and/or painting process in a manner to contain Polyvinyl alcohol polymer at rate of 20 - 30% by mass, adding Carbonyl dimidazole and Ethylenediamine or 4-chloro -Propionyl chloride and Etylendiamine into wastewater comprising Polyvinyl alcohol polymer in 20 - 30% rate as a result of filtration and/or evaporation process and obtaining PVA-Etylendiamine hydrogel solvent, adding dimethyl sulfoxide, Boric Acid, Acetic Acid and surface active agent into solvent bath containing PVA-Etylendiamine hydrogel solvent at 20-30% rate, applying coagulation process to obtained PVA-Etylendiamine hydrogel solvent with acetone of critic fluid phase, stretching Polyvinyl alcohol polymer passing through coagulation bath at 200 C° - 250 C° temperature range when wet, and subjecting to fixing process.



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METHOD FOR PRODUCTION OF POLY-VINYL ALCOHOL -FILAMENT FIBRE OF HIGH STRENGTH AND ELASTICITY

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THE RELATED ART

Invention relates to wet drafting method of super critic fluidity phase to obtain polyvinyl alcohol filament fibre of high strength and elasticity from polyvinyl polymer gained from wastewater recycling for use in textile sector.

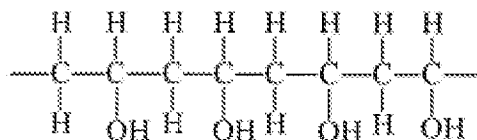
The invention particularly relates to filament fibre obtaining by use of preparing dope solvent, coagulation bath and super fluid phase drafting process by means of enhancing concentration of polyvinyl alcohol (PVA) polymer in wastewater arising from sizing process or painting process.

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BACKGROUND OF THE RELATED ART

Polyvinyl alcohol (PVA) is polymer dissoluble in water, non-toxic and commonly used in various industrial fields. Polyvinyl Alcohol (PVA) polymer being studied in various studies since 1960s because of its non-toxic structure has a production capacity over 1 million tons a year and 1 billion euro market size a year. In this context, developments to be achieved in production of Polyvinyl Alcohol (PVA) polymer are highly important. One of essential area of use of Polyvinyl alcohol (PVA) polymer is textile. Several companies such as Kuraray, Du Pont, Wanwei Group, Sinopec Sichuan Vinyon Works, Xiangwei, Mini Fiber, Unitika, Fuwei, NITIVY, Nycon Corporation, Sinopec-SV worldwide use Polyvinyl alcohol (PVA) polymer to produce yarn. Polyvinyl alcohol (PVA) polymers has an essential advantage in various fields such as composite applications concrete and external reinforcing because of their high strength. Polymer chain structure of said Polyvinyl alcohol (PVA) polymer is given below.

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In the said related art, Polyvinyl alcohol (PVA) polymer is used as sizing agent to increase strength of cotton yarns during weaving process. When polyvinyl alcohol (PVA) dissoluble easily in water is removed from centre yarn, it reaches hollow yarn structure and wastewater

comprising Polyvinyl alcohol (PVA) is released. On the other hand, yarn is made by means of twisting opposing regular twist of cotton when made with Polyvinyl alcohol (PVA). Thus, cotton yarn untwisted by help of PVA can be woven without breaking (can be done up to zero twisting) and final fabric can be manufactured by removal of PVA from woven fabrics during painting phase. Said obtained final fabric is considerably softer in comparison to its similar fabrics, has high water absorbing and feature of releasing water in period shorter in comparison to similar ones. Wastewater releasing during it comprises Polyvinyl alcohol (PVA). It is highly essential for sector to increase concentration of Polyvinyl Alcohol (PVA) polymer in wastewater containing polyvinyl alcohol polymer releasing in said sizing operation and painting process, and to regain said polymer. However, although filtration systems used for wastewater today are adequate to concentrate Polyvinyl alcohol (PVA) polymer, recycling process capable to gain Polyvinyl alcohol (PVA) polymer based filament fibre is not available. Another technical problem experienced in the related art is the failure to provide viscosity value of Polyvinyl alcohol (PVA) polymer concentrated from wastewater appropriate for wet drafting process. If it is not achieved to obtain waste Polyvinyl Alcohol (PVA) polymer molecules in desired concentration, breaking is experienced during wet drafting process and breaking strength, elasticity and efficiency of filament to be obtained will be low. Concentration of polyvinyl alcohol (PVA) polymer gained from wastewater in solvent is low and polymer chain size is low. For that reason, efficiency of Polyvinyl Alcohol (PVA) polymer is low during conventional wet fibre spinning process. The related art does not have an application solving said technical problems.

During patent search conducted for the current status of related art, an American patent application numbered US5455114 A is encountered. Said document discloses a method comprising process steps of preparation of dope solvent comprising dimethyl sulfoxide and dry-jet wet spinning bath for production of water soluble high tensile strength PVA filament. In aid method. process of fibre spinning in methanol medium is also applied. However, fibre obtained as a result of said processes is under high rate spinning values. In another patent application numbered US6743859 B2 for polyvinyl alcohol (PVA) polymer based filament production, water, acetone, benzene, toluene, dimethyl formamide, dimethylacetamide and dimethyl sulfoxide are used as solvents and alcohols such as methanol, ethanol are used as coagulants. For said coagulation bath, mixtures of a fixed rates of solvents and coagulants are preferred. However, in case of drying at temperatures under 200 °C, molecule chains do not have sufficient motion for higher spinning rates and crystallinity and mechanical strength decrease. Patent application numbered US5229057 aims to produce a high mechanical strength fibre by use of a coagulating bath at and under 20 °C. Polyvinyl alcohol (PVA) polymers having polymerization rate above 1500 enable achievement of high strength fibres because of having less molecule end sections causing micro structural faults.

In conclusion, several problems and negativities as described above are experienced in the related art and present systems are insufficient for settlement of the problems and negativities. This case makes it necessary to make a development and novelty in the related art.

5 BRIEF DESCRIPTION OF THE INVENTION

The present invention relates to a filament fibre production method meeting the needs mentioned above, eliminating all disadvantages and providing some additional advantages.

10 Primary purpose of the invention is to obtain polyvinyl alcohol filament fibre having high strength and elasticity.

Another purpose of the invention is to produce filament fibre by use of wet or dry spinning method comprising concentrating Polyvinyl alcohol (PVA) polymer in dissolved form in wastewater during sizing and painting processes. The method of the invention provides
15 achievement of a high efficient and sustainable recycling process and a convenient process in economic terms.

In order to achieve said purposes, the invention is a method for filament fibre production comprising process steps of;

- 20 A filament fibre production method comprising process steps of:
- Filtration of and/or applying evaporation process to wastewater containing Polyvinyl alcohol polymer from sizing process and/or painting process in a manner to contain Polyvinyl alcohol polymer at rate of 20 - 30% by mass,
 - 25 • into wastewater comprising Polyvinyl alcohol polymer in 20 - 30% rate as a result of filtration and/or evaporation process,
adding
 - Carbonyl di-imidazole and Ethylenediamine
or
 - 30 • 4-chloro -Propionyl chloride and Etylendiamineand obtaining PVA-Etylendiamine hydrogel solvent,
 - Adding dimethyl sulfoxide, Boric Acid, Acetic Acid and surface active agent into solvent bath containing PVA-Ethylenediamine hydrogel solvent at 20-20% rate,
 - Applying coagulation process to obtained PVA-Ethylenediamine hydrogel solvent with
35 acetone of critic fluid phase,
 - Stretching Polyvinyl alcohol polymer passing through coagulation bath at 200 C° - 250 C° temperature range when wet, and subjecting to fi xing process.

The structural and characteristics features and all advantages of the invention will be understood better with detailed descriptions given below. Therefore, the assessment should be made taking into account the detailed description.

5 FIGURES FOR BETTER UNDERSTANDING OF INVENTION

Figure 1 shows schematic view of filament fibre production method of the invention.

DETAILED DESCRIPTION OF THE INVENTION

10 In this detailed description, the preferred embodiments of the invention have been described in a manner not forming any restrictive effect and only for purpose of better understanding of the matter.

15 The invention relates to a method for filament fibre production for use in textile sector. In the method of the invention, said filament fibre is obtained by means of recycling of wastewater containing polyvinyl alcohol (PVA) polymer. Process steps of the method of invention are shown schematically in figure 1. According to the figure, wastewater containing Polyvinyl alcohol (PVA) polymer is obtained from two different sources. One of the is sizing process. Said sizing process

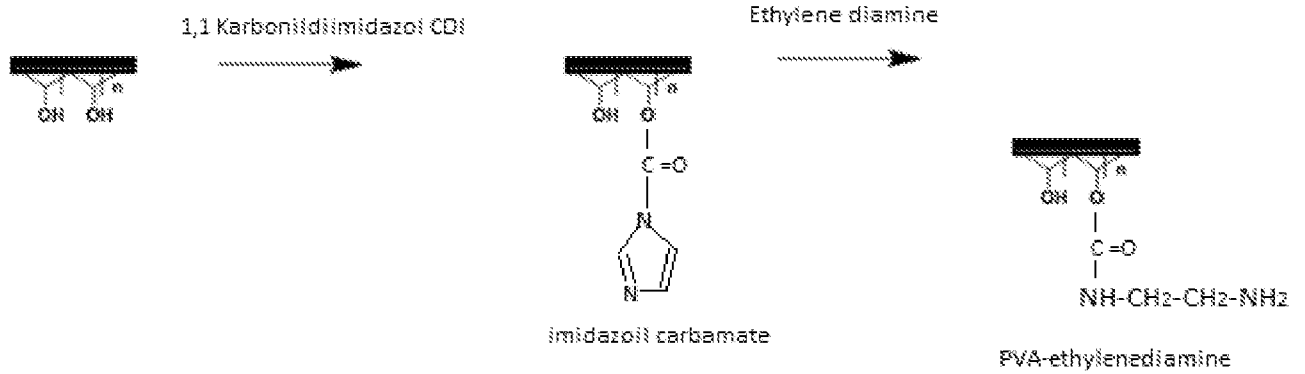
20 is realized by means of providing absorption of agents such as carboxy methyl cellulose, polyvinyl alcohol by yarns to be used in weaving in order to increase resistance of yarn. During that time while said sizing agents (carboxy methyl cellulose, polyvinyl alcohol) are fixed onto yarn surface by physical powers, the section not applied is discharged into wastewater. Rate of Polyvinyl alcohol (PVA) in said wastewater is 1-1,5% by mass. Another source of wastewater

25 containing Polyvinyl alcohol (PVA) polymer is obtained from painting process. In normal process, in order to achieve high water absorption and soft touching features, cotton yarn is spun in reverse spinning with polyvinyl alcohol (PVA) polymer and after said spinning, weaving is started and fabric of various constructions are obtained. When the obtained fabrics is treated with acidic water at high or low temperatures during painting process, wastewater containing

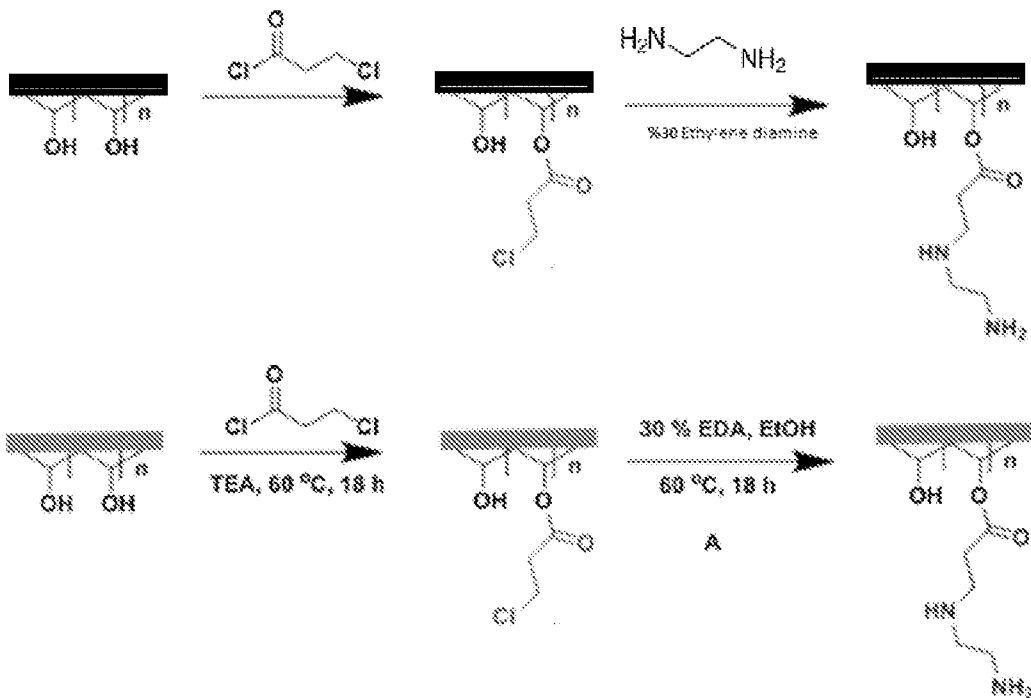
30 polyvinyl alcohol (PVA) polymer at 1-1,5% rate by mass is obtained. Rate of Polyvinyl alcohol (PVA) polymer rate in the wastewater obtained in said processes by mass is brought to 20 - 30% range by mass in filtration and / or evaporation process steps and thus regained concentrate Polyvinyl Alcohol (PVA) polymer is obtained. Polymerization date of said obtained

35 polymer is in the range of 500 - 3500. In the method of the invention, chemical reactions are performed to prepare dope solvent in the first process step. There are two alternative reactions for preparation of said dope solvent. In the first alternative reaction is initiated by adding

Carbonyldiimidazole (CDI) and Etylendiamine in rate of 10-20% rate by mass into medium having Polyvinyl alcohol (PVA) polymer. Said reaction is shown in figure below.



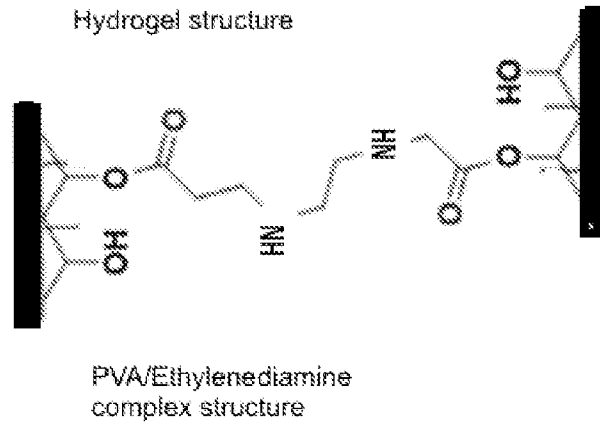
In other alternative, reaction is executed by adding 4-Chloro Propionyl chloride and Ethylenediamine in range of 10-20% onto Polyvinyl alcohol (PVA) polymer. Said reaction is shown in figure below.



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Thus PVA-Ethylenediamine hydrogel solvent is prepared by use of either of said two alternatives. This provides increase in disassociation arising as a result of getting closure between PVA polymers, cross bonding between non-concentrated PVA molecules. Thus, formation of aggregation increases, physical structure of colloidal suspension in homogeneity form occurs. The obtained hydrogel structure is shown below.

15



Colloidal suspension physical structure in homogenous form obtained in this stage is formed to increase polymerization rate, strength, elasticity and efficiency of Polyvinyl alcohol (PVA) in wastewater. In the second process step, dimethyl Sulfoxide in rate of 30-40% by mass, Boric Acid in rate of 0,1 - 1,0% by mass, Acetic Acid with pH value in range of 4 to 5 are added to waste water mixture containing Polyvinyl Alcohol (PVA) Etylendiamine hydrogel solvent in rate of 20 - 30% by mass. In addition to said added chemicals, surface active agent is also added in this stage. As surface active agent, Polyethylene Glycol in rate of 1/ 20% by mass or non-ionic Polyhydric alcohol in rate of 1 - 20% by mass can be used. However, coagulation process is needed to improve strength, elasticity features of Polyvinyl alcohol (PVA) polymer based filament aimed to be obtained and to provide surface homogeneity. Said coagulation process provides convey of acetone is diffused form between Polyvinyl alcohol (PVA) polymer and thus penetration of acetone into Polyvinyl alcohol (PVA) polymer is provided in critic phase. In said Coagulation Bath, nozzle diameter may vary from 0,11 mm to 0,08 mm and 10-100 g/lit NaOH, 100 - 300 g/lit Sodium Sulphate, acetone in rate of 2 - 20% by mass, 2-propanol in rate of 2-20% by mass are used. In the last process step, during super critic phase spinning process is applied. Transition of acetone into critical fluid phase is executed preferably at 235 °C temperature and pressure of 46,9 bars. Density rate of acetone under such circumstances varies from 0,2 g/cm³ - 0,9 g/cm³, viscosity 0,2 – 1,0 poise, and diffusion rate 0,1-3,3 cm²/sec. Polyvinyl alcohol (PVA) polymer solvent from nozzles gets solidified in coagulation bath and transformed into filament fibre structure. Polyvinyl alcohol (PVA) polymer from coagulation bath is wound onto roller in fibre form by pressure from nozzles. At this stage it is shrunk at saturated evaporation medium at temperature range of 200 °C - 250 °C and fixing between winding rollers is made. Said fixing process fixes spinning forces between Polyvinyl alcohol (PVA) polymer. For that purpose, wet spinning or wet jet dry spinning can be applied. In wet jet dry spinning process, differently from wet spinning, after coagulation bath, shrinking between winding rollers in saturated evaporation medium at temperature range of 200 °C - 250 °C is performed and then fixing process is performed.

CLAIMS

1.

A filament fibre production method comprising process steps of:

- 5
- Filtration of and/or applying evaporation process to wastewater containing Polyvinyl alcohol polymer from sizing process and/or painting process in a manner to contain Polyvinyl alcohol polymer at rate of 20 - 30% by mass,
 - into wastewater comprising Polyvinyl alcohol polymer in 20 - 30% rate as a result of filtration and/or evaporation process,
- 10
- adding
- Carbonyl di-imidazole and Ethylenediamine
or
 - 4-chloro -Propionyl chloride and Etylendiamine
- and obtaining PVA-Ethylenediamine hydrogel solvent,
- 15
- Adding dimethyl sulfoxide, Boric Acid, Acetic Acid and surface active agent into solvent bath containing PVA-Ethylenediamine hydrogel solvent at 20-30% rate characterized comprising process steps of;
 - Applying coagulation process to obtained PVA-Ethylenediamine hydrogel solvent with acetone of critic fluid phase,
- 20
- Stretching Polyvinyl alcohol polymer passing through coagulation bath at 200 C° - 250 C° temperature range when wet, and subjecting to fixing process.
2. The filament fibre production method according to claim 1 characterized in comprising process steps of adding dimethyl Sulfoxide in rate of 30-70% by mass, Boric Acid in
- 25
- rate of 0,1 - 1,0% by mass, Acetic Acid with pH value adjusted in range of 4 to 5 and surface active agent in rate of 1-20% by mass into wastewater mixture containing Polyvinyl Alcohol polymer in rate of 20 - 30% by mass onto wastewater comprising Polyvinyl alcohol polymer in 20 - 30% rate as a result of filtration and/or evaporation process.
- 30
3. The filament fibre production method according to claim 1 or claim 2 characterized by comprising process step of adding non-ionic Polyethylene Glycol I as surface active agent.
- 35
4. The filament fibre production method according to claim 1 or claim 2 characterized by comprising process step of adding non-ionic Polyhydric alcohol as surface active agent.

5. The filament fibre production method according to any of above claims characterized by comprising process step of adding non-ionic Polyethylene Glycol in rate of 1 - 20% by mass as surface active agent.
- 5 6. The filament fibre production method according to any of above claims characterized by comprising process step of adding non-ionic Polyhydric alcohol in rate of 1 - 20% by mass as surface active agent.
- 10 7. The filament fibre production method according to any of above claims characterized by comprising coagulation process of nozzle diameter varying between 0,11 mm and 0,08 mm.
- 15 8. The filament fibre production method according to any of above claims characterized by comprising coagulation process containing 10-100 g/lit NaOH, 100 - 300 g/lit Sodium Sulphate, acetone in rate of 2 - 20% by mass, 2-propanol in rate of 2- 20% by mass.
- 20 9. The filament fibre production method according to any of above claims characterized by comprising process of transition of acetone into critical fluid phase is at 235 °C temperature and pressure of 46,9 bars.

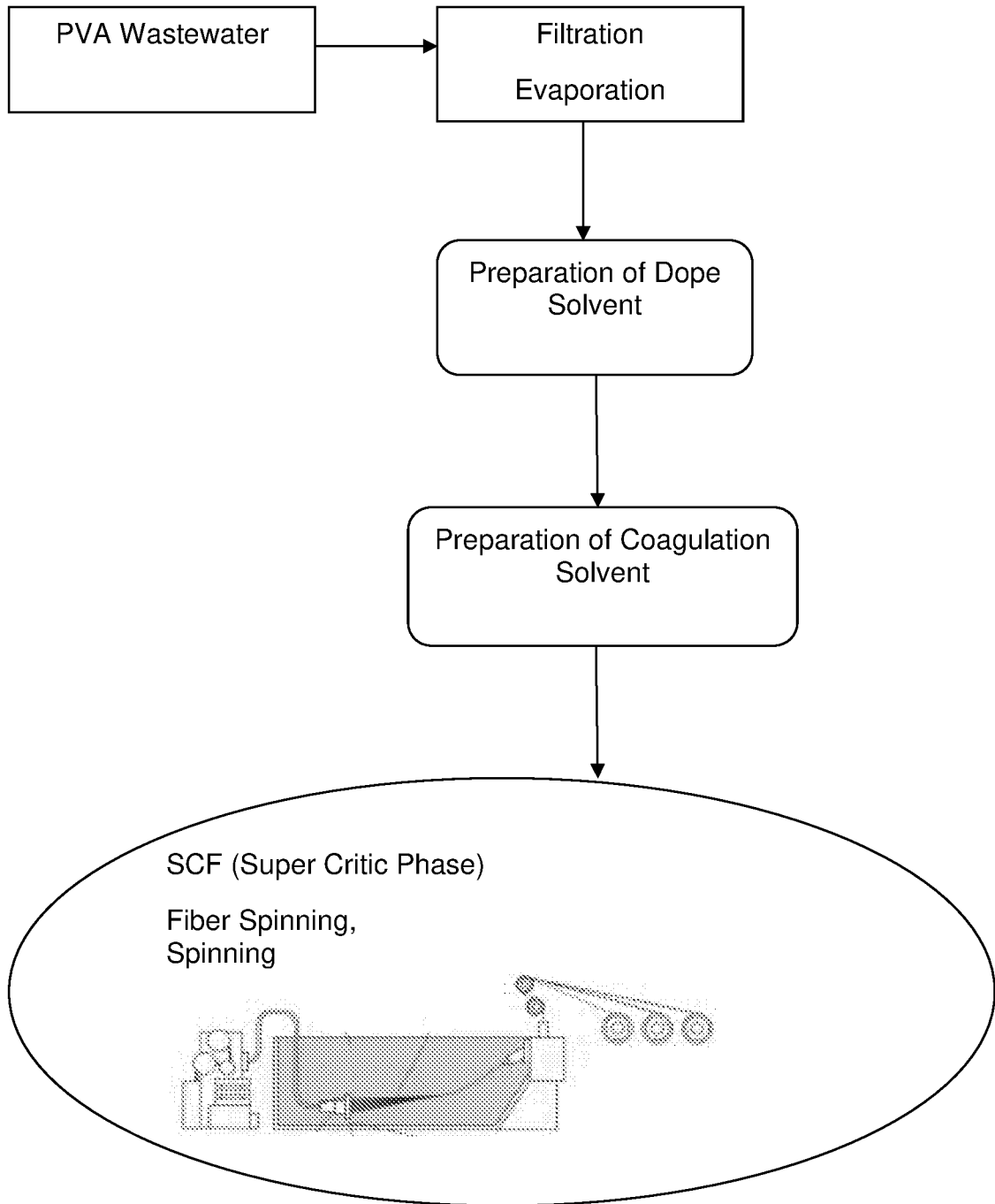


Figure 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/TR2020/050565

A. CLASSIFICATION OF SUBJECT MATTER		
D01F 6/14 (2006.01)i; C02F 103/30 (2006.01)i		
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) D01F; C02F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	CN 108975457 A (ZHOU WUHONG) 11 December 2018 (2018-12-11) Abstract	1-9
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A	CN 109912834 A (UNIV ZHONGYUAN TECHNOLOGY) 21 June 2019 (2019-06-21) Abstract	1-9
<input 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 "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "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 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 13 October 2020		Date of mailing of the international search report 13 October 2020
Name and mailing address of the ISA/TR Turkish Patent and Trademark Office (Turkpatent) Hipodrom Caddesi No. 13 06560 Yenimahalle Ankara Turkey Telephone No. (90-312) 303 11 82 Facsimile No. +903123031220		Authorized officer Ertan Bicer Telephone No.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No. PCT/TR2020/050565

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