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677053

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PATENT

NOTICE OF ENTITLEMENT

We, **E. I. DU PONT DE NEMOURS AND COMPANY**, of 1007 Market Street, Wilmington, Delaware 19898, United States of America, being the applicant and the person nominated for grant of patent in respect of the Application for an invention entitled

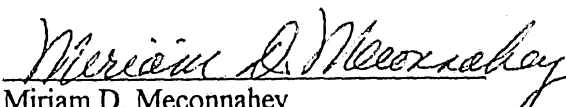
PREPARATION OF POLY(M-PHENYLENE ISOPHTHALAMIDE) FILAMENTS

state the following:

PCT-CONVENTION NATIONAL PHASE FILING

The person nominated for the grant of the patent has entitlement from the inventors and the applicants of the application listed in the declaration under Article 8 of the PCT by virtue of an assignment of the invention from the actual inventors.

The basic application listed on the request form and in the declaration made under Article 8 of the PCT is the first application made in a Convention country in respect of the invention.


Miriam D. Meonnahey
Asst. Secretary - Patent Board

September 20, 1995
Date



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(Modified Examination)

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PREPARATION OF POLY(M-PHENYLENE ISOPHTHALAMIDE) FILAMENTS
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039564 29.03.93 US UNITED STATES OF AMERICA
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- (71) Applicant(s)
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- (56) Prior Art Documents
US 3063966
US 3498955
- (57) Claim

1. A process for preparing poly(m-phenylene isophthalamide) filaments comprising:

a) reacting m-phenylene diamine with isophthaloyl chloride in an amide solvent to produce poly(m-phenylene isophthalamide) in an HCl-containing amide solution;

b) passing the polymer solution through a bed of ion exchange resin in base form to remove HCl and collecting an amide solution of the polymer as effluent;

c) removing amide solvent from the effluent as necessary to attain suitable viscosity and concentration of the solution for spinning; and

d) spinning the solution to form filaments.

4. A process for preparing poly(m-phenylene isophthalamide) filaments comprising:

a) reacting m-phenylene diamine with isophthaloyl chloride in an amide solvent to produce poly(m-phenylene isophthalamide) in an HCl-containing amide solution;

- b) passing a major portion of the polymer solution through a bed of ion exchange resin in base form to remove HCl and combining the HCl-free effluent of polymer in amide solvent with the remaining HCl-containing polymer solution;
- c) neutralizing the HCl of the combined solutions by addition of lime;
- d) removing solvent as necessary to attain suitable viscosity and concentration of the solution for spinning; and
- e) spinning the solution to form filaments.

5. A process for preparing poly(m-phenylene isophthalamide) filaments comprising;

- a) reacting in an amide solvent, isophthaloyl chloride with a stoichiometric excess of m-phenylene diamine to produce an HCl-containing solution of low molecular weight polymer having an excess of amine ends;
- b) passing the polymer solution through a bed of ion exchange resin in base form to remove HCl and recovering the HCl-free effluent of polymer in amide solvent;
- c) adding isophthaloyl chloride to the effluent to form high molecular polymer and byproduct HCl;
- d) neutralizing the HCl by addition of lime;
- e) removing solvent as necessary to attain suitable viscosity and concentration of the solution for spinning; and
- f) spinning the solution to form filaments.

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(21) International Application Number: PCT/US94/03145 (22) International Filing Date: 28 March 1994 (28.03.94) (30) Priority Data: 08/039,564 29 March 1993 (29.03.93) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors: PEASE, Richard, Arthur; 50 South Bridge Road, Bear, DE 19701 (US). RODINI, David, Joseph; 1401 Lady Ashley Court, Midlothian, VA 23113 (US). (74) Agents: SHAFER, Robert, J. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AU, BR, BY, CA, CN, JP, KZ, RU, UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.	
(54) Title: PREPARATION OF POLY(M-PHENYLENE ISOPHTHALAMIDE) FILAMENTS			
(57) Abstract In the preparation of poly(m-phenylene isophthalamide) filaments, hydrogen chloride is removed from as-produced amide solution of poly(m-phenylene isophthalamide) by contact with basic ion exchange resin.			

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TITLE

PREPARATION OF POLY(M-PHENYLENE
ISOPHTHALAMIDE) FILAMENTS

5 BACKGROUND OF THE INVENTION

In a standard procedure for preparing filaments of poly(m-phenylene isophthalamide) (MPD-I), isophthaloyl chloride (ICl) is condensed with m-phenylene diamine (MPD) in dimethylacetamide (DMAC) as solvent. Hydrogen chloride (HCl) is a by-product. The HCl is ordinarily neutralized with lime since it is highly corrosive. The salt which forms, calcium chloride, must ultimately be removed and disposed of. Presence of the salt in the solution limits the solubility of the MPD-I and hinders removal of the solvent during the spinning process. This all works against obtaining high solids MPD-I solutions which are desirable for spinning processes.

SUMMARY OF THE INVENTION

20 The present invention provides a process for preparing poly(m-phenylene isophthalamide) filaments comprising:

- a) reacting m-phenylene diamine with isophthaloyl chloride in an amide solvent to produce poly(m-phenylene isophthalamide) in an HCl-containing amide solution;
- b) passing the polymer solution through a bed of ion exchange resin in base form to remove HCl and collecting an amide solution of the polymer as effluent;
- 30 c) removing amide solvent from the effluent as necessary to attain suitable viscosity and concentration of the solution for spinning; and
- d) spinning the solution to form filaments.

Also provided is a substantially HCl-free, clear spinning solution consisting of at least 18% by weight of poly(m-phenylene isophthalamide) in dimethylacetamide.



DETAILED DESCRIPTION OF THE INVENTION

This invention offers a novel process for preparing MPD-I filaments.

As is known in the art, for example U.S. Patent No. 3,063,966 MPD-I is made by reacting MPD with ICl in an amide solvent such as DMAc. If desired, minor amounts, generally less than 10%, of p-phenylene diamine and/or terephthaloyl chloride may be included in the reaction mixture to form copolymers with slightly different solubility, melting point, etc. provided their presence does not adversely interfere with the normal preparation of polymer and manufacture of filaments. Other amide solvents such as dimethylformamide (DMF) and N-methylpyrrolidone (NMP) may also be useful.

Suitable conditions for reacting the diamine and diacyl chloride are well-known to those skilled in the art. The reaction produces a solution of MPD-I in the amide solvent. Also present is HCl formed as an undesirable byproduct. In the prior art processes, for example U.S. Patent No. 3,498,955, the HCl has been neutralized with lime to minimize corrosion. The high concentration of calcium chloride produced by the neutralization limits the solubility of the polymer and hinders removal of the solvent during the spinning process.

In accordance with the present invention, the HCl is removed by passing the as-produced solution of the polymerization through a bed of basic ion exchange resin. It may be desirable to first add more amide solvent to the solution to reduce viscosity before contact with the ion exchange resin, so that it can pass through the ion exchange column more efficiently. Useful ion exchange resins for this purpose are commercially available. They react with strong mineral acids to form amine salts of the acid. Preferably the resin is weakly basic. One such resin having tertiary amine functional groups is Amberlyst® A-21 available from Rohm and Haas Company of Philadelphia, Pennsylvania.



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The concentration and viscosity of the HCl-free effluent from the ion exchanger is normally adjusted as desired for preparing a spin dope. Ordinarily, a portion of the amide solvent is removed by evaporation
5 under reduced pressure to increase solids concentration in the dope or to adjust viscosity for spinning. This process permits the production of clear high concentration, i.e., 18% by wt. of polymer in amide solvent, and above. Efforts to prepare a similar
10 solution by other techniques have been found to result in cloudy mixtures that are not suitable for spinning.

Finally, the dope is dry spun or wet spun by techniques well-known in the art. Thus, in dry spinning, the dope is extruded through a spinneret into
15 a hot gaseous atmosphere that removes a portion of the solvent and then the solvent depleted filaments are quench coagulated in an aqueous medium that removes further amounts of solvent. This is commonly followed by extraction-drawing in which the filaments are drawn
20 and washed to remove residual solvent.

In a wet-spinning process, the extruded filaments pass directly into an aqueous quench coagulation bath and the solvent depleted filaments are extraction-drawn as before.

25 Variations of the above described process may be employed. For example, the solution resulting from the polymerization may be divided and a major portion thereof processed as described above to remove HCl and the remainder combined with the HCl-free solution. The
30 combined solution can be neutralized with lime and a spin dope prepared by adjusting solvent content to attain suitable viscosity and concentration for spinning. Since the combined solution contains a relatively small amount of HCl, most having been removed
35 upon passage through the ion exchange resin column, only a small amount of lime will be needed to effect neutralization. Similarly, the small amount of calcium chloride which is formed will interfere less with



solvent removal in the spinning process and will present less of a disposal problem.

Still another procedure that is useful employs the polymer-forming reactants in less than equivalent proportions. For example, a stoichiometric excess of diamine will produce low molecular weight polymer having an excess of amine ends. Because of the low molecular weight of the polymer, the solution viscosity will be low and it can be passed through the ion exchange column very efficiently. The effluent can then be combined with additional ICl to form high molecular weight polymer in a solution that contains less HCl than it would have, had equivalent quantities of MPD and ICl been used initially. The solution containing a reduced amount of HCl can then be processed as described above.

The following examples are illustrative of the present invention.

EXAMPLES

20 Example 1

A jacketed flask, with an inlet port on the top and an outlet port on the bottom, which is approximately 10.2 cm in diameter and 30 cm in height is filled to a height of 21 cm with weakly basic A-21 ion exchange resin. The resin is conditioned by pumping the following solutions through ion exchange resin: two bed volumes of 1.5 N aqueous sodium hydroxide followed by a water wash until the effluent is neutral, and then two bed volumes of 2 N HCl, followed by water rinsing until the effluent is neutral. Next the resin in the column is treated with two bed volumes of 1.5 N aqueous sodium hydroxide and rinsed with water until the column effluent is neutral. Water is removed from the column by rinsing the resin with 5 bed volumes of anhydrous DMAC.

To a jacketed 3 L three-necked flask is added approximately 1000 grams of a 13% polymer solids solution of poly(m-phenylene isophthalamide) in DMAC containing 4% HCl. The solution is obtained by reacting



ICl with MPD in DMAc. This flask serves as the reservoir for the acid polymer. The jacketed flask containing polymer and the jacketed flask containing the resin are heated using a circulation water bath of 70°C.

5 The polymer solution is stirred and pumped into the top port of the resin containing flask at a rate of approximately 14 g/min. The eluent of the flask containing resin is collected at the outlet port of the flask and tested periodically for polymer (by sampling and testing for polymer via precipitation). Once

10 polymer is detected, the effluent is collected in a separate container. Polymer is collected until very little polymer is detected in the effluent. The collected material is a solution of poly(m-phenylene isophthalamide) in DMAc. Some dilution of the polymer

15 with DMAc occurs so that the final solids content of the acid free polymer solution is approximately 5% MPD-I in DMAc.

20 Example 2

To a jacketed 3 liter three-necked flask is added approximately 800 grams of MPD-I pre-polymer (80% of stoichiometric ICl added) consisting of approximately 17% polymer solids in DMAc containing 5% HCl. The

25 jacketed flask containing polymer and the jacketed flask containing the resin prepared as in Example 1, are heated using a circulating water bath of 70°C. The pre-polymer solution is stirred and pumped into the inlet port of the resin containing flask at a rate of

30 approximately 14 g/min. The eluent of the flask from the outlet port of the flask is tested periodically for polymer (by sampling and testing for polymer via precipitation). Once polymer is detected, the effluent is collected in a separate container. Polymer is

35 collected until very little polymer is detected in the effluent. The collected material is a solution of low molecular weight MPD-I in DMAc. The solids of the solution are determined by evaporation to be 13.21%.



Example 3

To a dry 500 ml resin kettle fitted with a mechanical stirrer, and a nitrogen purge are added 192.7 g of pre-polymer solution as prepared in Example 2. The solution is stirred and cooled using an ice bath and 4.8 g of molten isophthaloyl chloride (ICl) are added. The ice bath is removed and the solution is stirred at room temperature for 30 minutes. Next, 2 grams of calcium hydroxide are added and the solution is stirred for an additional 30 minutes. The polymer solution is then added to a blender containing a mixture of water and ice. The polymer is precipitated, filtered and washed with water until the water washes are neutral. The polymer is thoroughly dried. The inherent viscosity at 25°C is 0.57.

Example 4

Concentration of Polymer Solution

Polymer effluent from Example 1 is concentrated via vacuum distillation of DMAc as follows: 1000 ml of 5% solids salt free MPD-I polymer in DMAc is added to a 2000 ml single neck pear shaped flask. This flask is connected to a rotary evaporator apparatus. A vacuum of approximately 64 cm (28 inches) water is pulled on the apparatus and the flask is rotated at the rate of approximately 200 rpm. The rotating flask is then heated via a water bath of 70°C. DMAc is removed until the total weight of the polymer and DMAc in the flask is 208 grams. This corresponds to a 24% MPD-I polymer solids in DMAc.

Example 5

Wet Spinning

A salt-free solution consisting of 24% MPD-I in DMAc was extruded through a 50 hole, 0.127 cm (5 mil) per hole, spinneret submerged in a coagulation medium. The coagulating medium consisted of DMAc/CaCl₂/Water in a 10/36/54 by weight ratio. The coagulation medium was contained in an 2.44m (8 feet) long bath. The jet velocity of the spinning solution through the spinneret



✓ was 0.01m/sec (13.6 FPM) (ft/min), with a wind-up speed
✓ of 0.2m/sec (40 FPM). The fiber was washed with water
and drawn approximately 4X across a hot bar to give 2.1
dpf fiber with T/E/M=5.5 gpd/32%/94gpd.



The claims defining the invention are as follows:-

1. A process for preparing poly(m-phenylene isophthalamide) filaments comprising:

a) reacting m-phenylene diamine with isophthaloyl chloride in an amide solvent to produce poly(m-phenylene isophthalamide) in an HCl-containing amide solution;

b) passing the polymer solution through a bed of ion exchange resin in base form to remove HCl and collecting an amide solution of the polymer as effluent;

c) removing amide solvent from the effluent as necessary to attain suitable viscosity and concentration of the solution for spinning; and

d) spinning the solution to form filaments.

2. A process according to Claim 1 wherein the amide solvent is dimethyl acetamide.

3. A process according to Claim 1 wherein the ion exchange resin has tertiary amine functional groups.

4. A process for preparing poly(m-phenylene isophthalamide) filaments comprising:

a) reacting m-phenylene diamine with isophthaloyl chloride in an amide solvent to produce poly(m-phenylene isophthalamide) in an HCl-containing amide solution;

b) passing a major portion of the polymer solution through a bed of ion exchange resin in base form to remove HCl and combining the HCl-free effluent of polymer in amide solvent with the remaining HCl-containing polymer solution;

c) neutralizing the HCl of the combined solutions by addition of lime;

d) removing solvent as necessary to attain suitable viscosity and concentration of the solution for spinning; and

e) spinning the solution to form filaments.

5. A process for preparing poly(m-phenylene isophthalamide) filaments comprising;



a) reacting in an amide solvent, isophthaloyl chloride with a stoichiometric excess of m-phenylene diamine to produce an HCl-containing solution of low molecular weight polymer having an excess of amine ends;

b) passing the polymer solution through a bed of ion exchange resin in base form to remove HCl and recovering the HCl-free effluent of polymer in amide solvent;

c) adding isophthaloyl chloride to the effluent to form high molecular polymer and byproduct HCl;

d) neutralizing the HCl by addition of lime;

e) removing solvent as necessary to attain suitable viscosity and concentration of the solution for spinning; and

f) spinning the solution to form filaments.

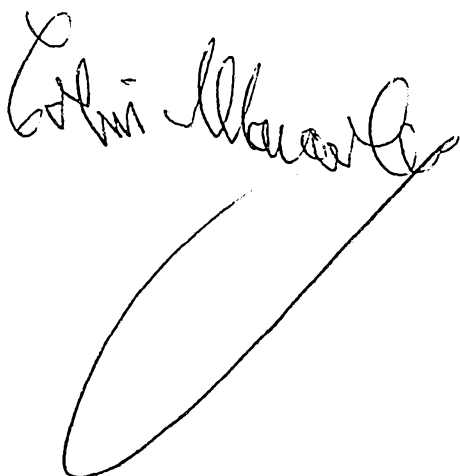
6. A method of removing HCl from a solution of poly(m-phenylene isophthalamide) in an HCl-containing amide solvent, comprising passing the solution through a bed of ion exchange resin in base form and recovering the HCl-free amide solution of the polymer.

DATED this 19th day of April, 1996.

E.I. DU PONT DE NEMOURS AND COMPANY

By their Patent Attorneys:

CALLINAN LAWRIE



INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/US 94/03145

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 D01F6/60 C08G69/32

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 5 D01F C08G

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 practical, 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.
A	DATABASE WPI Section Ch, Week 7919, Derwent Publications Ltd., London, GB; Class A, AN 79-36489B & SU,A,494 036 (SOKOLOV L B) 20 November 1978 see abstract ---	1-7
A	US,A,3 063 966 (STEPHANIE LOUISE KWOLEK ET AL.) 13 November 1962 see example 14 ---	1-7
A	US,A,3 498 955 (HERBERT S. MORGAN ET AL.) 3 March 1970 see the whole document ---	1-7
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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- *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
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- * & * document member of the same patent family

Date of the actual completion of the international search

8 July 1994

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 94/03145

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE, A, 23 13 308 (FARBWERKE HOECHST AG) 19 September 1974 see the whole document ---	1-7
A	DATABASE WPI Section Ch, Week 9207, Derwent Publications Ltd., London, GB; Class A, AN 92-053123 & JP, A, 3 296 530 (TORAY IND INC) 27 December 1991 see abstract ---	1-7
A	US, A, 4 342 715 (KEIZO SHIMADA ET AL.) 3 August 1982 -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. Application No

PCT/US 94/03145

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3063966		NONE	
US-A-3498955	03-03-70	BE-A- 71/686 DE-A- 1770799 FR-A- 1571904 GB-A- 1215185 LU-A- 56431 NL-A- 6809577	06-01-69 13-01-72 20-06-69 09-12-70 21-05-69 08-01-69
DE-A-2313308	19-09-74	FR-A, B 2221541 JP-A- 49128096 US-A- 3991037 US-I- B451308	11-10-74 07-12-74 09-11-76 17-02-76
US-A-4342715	03-08-82	NONE	