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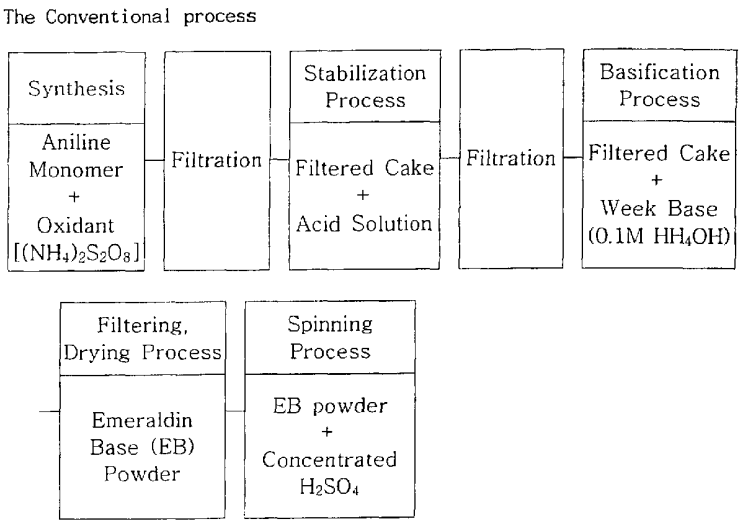
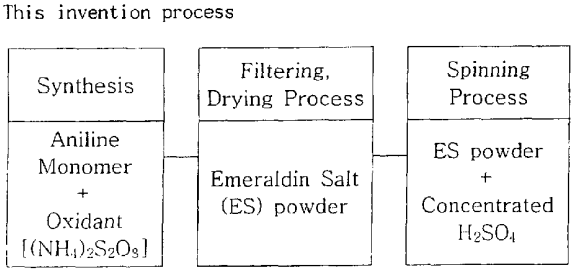
(54) Title: FABRICATION METHOD OF CONDUCTIVE POLYANILINE SPINNING SOLUTION





(57) Abstract: This invention refers to the fabrication method of conductive polymer polyaniline and polynaniline blend spinning solution, the fabrication method of spinning solution using polyaniline salts in detail. This method is characterized by the dissolution of polyaniline salt instead of EB(emeraldine base), in concentrated sulfuric acid for fabrication of polyaniline spinning solution. There are two ways for preparation of spinning solution. There are two ways for preparation of spinning solution, the dissolution of pure polyaniline salt, the dissolution of polyaniline salt and aramidor nylon in concentrated sulfuric acid(polyaniline blend).

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FABRICATION METHOD OF CONDUCTIVE POLYANILINE SPINNING SOLUTION

Technical Field

This invention relates to fabricate conductive polyaniline and polyaniline-blend spinning solutions.

Background Art

This invention refers to the fabrication method of conductive polymer polyaniline and polyaniline blend spinning solution, the fabrication method of spinning solution using polyaniline salts in detail.

Generally, the polymer referred to as "Polyaniline" is all the base form of the polymer which has the complicated process of preparation as follows. Polyaniline salt was prepared when oxidant was added to aniline monomer in aqueous acid solution and filtered. This salt was treated in aqueous acid solution and filtered again. Polyaniline salt was converted to base form Emeraldine Base(EB) after neutralizing with weak base and vacuum drying. Then, EB was used for fabrication of spinning solution.

It was disclosed that polyaniline or polyaniline blend fibers are processed from solutions in concentrated sulfuric acid in Polymer Commun. 31. 275(1990). Polyaniline and poly(p-phenylene terephthalamide) (aramid) blend fiber was processed from solution in concentrated sulfuric acid(98 wt %). This blend fiber had the improved mechanical properties whereas kept the conductivity of pure polyaniline. In this method, dissolve polyaniline base in concentrated sulfuric acid.

For example, MacDiarmid et. al. disclosed the processing of high molecular weight polymer solution in concentrated sulfuric acid or 1-methyl-2-pyrrolidinone(NMP) was drawn into the amorphous pure polyaniline fiber(U. S. PAT. No. 5,177,187). The same method is applied as previously described. For polyaniline and poly(p-phenylene terephthalamide) blend fiber, Jen et al. in U. S. Pat. No. 5,069,820(melt spinning), Smith et al. in U. S. Pat. No. 5,196,144(solution spinning from 96% sulfuric acid solutions) and Elsenbaumer in U. S. Pat. No. 5,160,457(spinning from solutions and doping) also disclosed the same way of fabrication using the polyaniline base form of EB.

As earlier explained, the fabrication of the above method has the disadvantages of complicate procedures and high cost of production where the use of base form of polyaniline, EB.

Disclosure of Invention

In order to solve the above problems, this invention relates to the fabrication method of polyaniline, polyaniline-blend spinning solution using the product of polyaniline salt in the first step of polyaniline preparation.

The present inventor has found a fabrication method of polyaniline spinning solution with dissolving directly polyaniline salt(hydrochloride, sulfate) in concentrated sulfuric acid.

The present inventor has also found a method for polyaniline blend spinning solution by mixing polyaniline spinning solution with blend solution in concentrated sulfuric acid.

Following detailed explanations are based on the attached figure. As described in Figure 1, the existing procedure is made up of complicated multi-steps. However, in the present invention, spinning solution is easily prepared applying EB salt directly in concentrated aqueous acid solution instead of first three steps in the existing process.

Generally, hydrochloric acid and sulfuric acid are used for the preparation of polyaniline. The first products of the process is polyaniline-hydrochloride salt or polyaniline-H_2SO_4 salt.

For polyaniline-hydrochloride salt, when it reacts with

concentrated sulfuric acid, polyaniline-hydrochloride salt changes into polyaniline-H_2SO_4 salt. Additionally, hydrogenchloride gas is generated, whish is easily evaporated on the way of preparation of spinning solution.

For polyaniline-H_2SO_4 salt, it is easily dissolved in concentrated sulfuric acid and spinning solution is also easily fabricated.

Brief Description of Drawings

Figure 1 illustrates the comparison of the process between the existing and the present invention fabrication method of polyaniline and polyaniline blend spinning solution. Figure 1 illustrates the comparison of the process of the fabrication method of polyaniline, polyaniline blend spinning solution.

Best Mode for Carrying Out the Invention

The composition of matter and process of this invention are further illustrated in the following examples.

Example 1. Preparation of polyaniline spinning solution from polyaniline hydrochlride salt.

40ml(0.22 mol) of purified aniline was added in 1M aqueous hydrochloric acid solution and kept at 0℃. 23g of oxidant $(NH_4)_2S_2O_8$ was added and kept at 0℃ in 400ml of 1M aqueous hydrocholric acid solution. Then oxidant solution was gradually added into aniline solution for 2 minutes, when two solutions reached at temperature equilibrium. After stirring for 90 minutes at 0℃, polyaniline-hydrochloride salt was filtered and dried. After dissolving 15g of polyaniline hydrochloride salt in 85g concentrated sulfuric acid(above 98% w/w), hydrogen chloride gas was evaporated in air-free bath. Then, polyaniline fiber was obtained by spinning under nitrogen gas pressure in coagulating bath including distilled water and air dried for 2 days. The fiber prepared exhibited a conductivity of 10 S/cm.

Example 2. Preparation of polyaniline spinning solution from polyaniline-H_2SO_4 salt.

40ml(0.22 mol) of purified aniline was added in 1M aqueous sulfuric acid solution and kept at 0 degree C. 23g of oxidant $(NH_4)_2S_2O_8$ was added and kept at 0℃ in 400ml of 1M aqueous sulfuric acid solution. Then oxidant solution was gradually added into aniline solution for 2 minutes, when two

solutions reached at temperature equilibrium. After stirring for 90 minutes at 0℃, polyaniline-H_2SO_4 salt was filtered and dried. After dissolving 15g of polyaniline-H_2SO_4 salt in 85g concentrated sulfuric acid(above 98% w/w), polyaniline fiber was obtained by spinning under nitrogen gas pressure in coagulating bath including distilled water and air dried for 2 days. The fiber prepared exhibited a conductivity of 10 S/cm.

Example 3. Preparation of polyaniline blend spinning solution from polyaniline hydrochloride salt.

40ml(0.22 mol) of purified aniline was added in 1M aqueous hydrochloric acid solution and kept at 0℃. 23g of oxidant $(NH_4)_2S_2O_8$ was added and kept at 0℃. in 400ml of 1M aqueous hydrocholric acid solution. Then oxidant solution was gradually added into aniline solution for 2 minutes, when two solutions reached at temperature equilibrium. After stirring for 90 minutes at 0℃, polyaniline hydrochloride salt was filtered and dried. After dissolving 15g of polyaniline hydrochloride salt in 85g concentrated sulfuric acid(above 98% w/w), hydrogen chloride gas was evaporated in air-free bath.(solution A)

Dissolve 15g of Aramid pulp in 85g of concentrated sulfuric acid(above 98% w/w).(solution B)

Mix solution A and solution B at the ratio of 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8 and 1:9, respectively. Polyaniline aramid fiber was obtained by spinning under nitrogen gas pressure in coagulating bath including distilled water. The composite fibers were dried in the air for 2 days and had the conductivity as illustrated in Table 1. The conductivity studies indicated that there wasn't any variation among fibers up to 5:5 ratio, there was a sudden drop above that ratio, according to the increase of aramid.

Example 4. Preparation of polyaniline blend spinning solution from polyaniline-H_2SO_4 salt.

40ml(0.22 mol) of purified aniline was added in 1M aqueous sulfuric acid solution and kept at 0℃. 23g of oxidant $(NH_4)_2S_2O_8$ was added and kept at 0℃. in 400ml of 1M aqueous sulfuric acid solution. Then oxidant solution was gradually added into aniline solution for 2 minutes, when two solutions reached at temperature equilibrium. After stirring for 90 minutes at 0℃, polyaniline sulfate was filtered and dried. After dissolving 15g of

polyaniline-H_2SO_4 salt in 85g concentrated sulfuric acid(above 98% w/w).(solution A)

Dissolve 15g of Aramid pulp in 85g of concentrated sulfuric acid(above 98% w/w).(solution B)

Mix solution A and solution B at the ratio of 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8 and 1:9, respectively. Polyaniline aramid fiber was obtained by spinning under nitrogen gas pressure in coagulating bath including distilled water. The composite fibers were dried in the air for 2 days and had the conductivity as illustrated in Table 1. The conductivity studies indicated that there wasn't any variation among fibers up to 5:5 ratio, there was a sudden drop above that ratio, according to the increase of aramid.

Industrial Applicability

As mentioned before, the present invention relates to the fabrication method of polyaniline, polyaniline blend spinning solution using the product of polyaniline salt. That is, this invention refers to the fabrication method of conductive polymer fibers which is characterized by the simplicity of process and cut down expenses using the first polyaniline salt in the first step of polyaniline preparation. Besides, fibers that have various

conductivity can be prepared by the same process.

Table 1. Electrical Conductivities of the various spinning polyaniline and polyaniline-blend Fibers

polyaniline salt(%)	aramid (%)	electrical conductity(S/cm)	
		Polyaniline-HCl salt	Polyaniline-H_2SO_4 salt
100	0	9.99	10.25
90	10	6.74	5.75
80	20	4.64	6.94
70	30	6.81	3.78
60	40	2.39	3.46
50	50	1.30	2.92
40	60	0.51	0.46
30	70	0.30	0.44
20	80	0.28	0.33
10	90	0.02	0.07

What is claimed is:

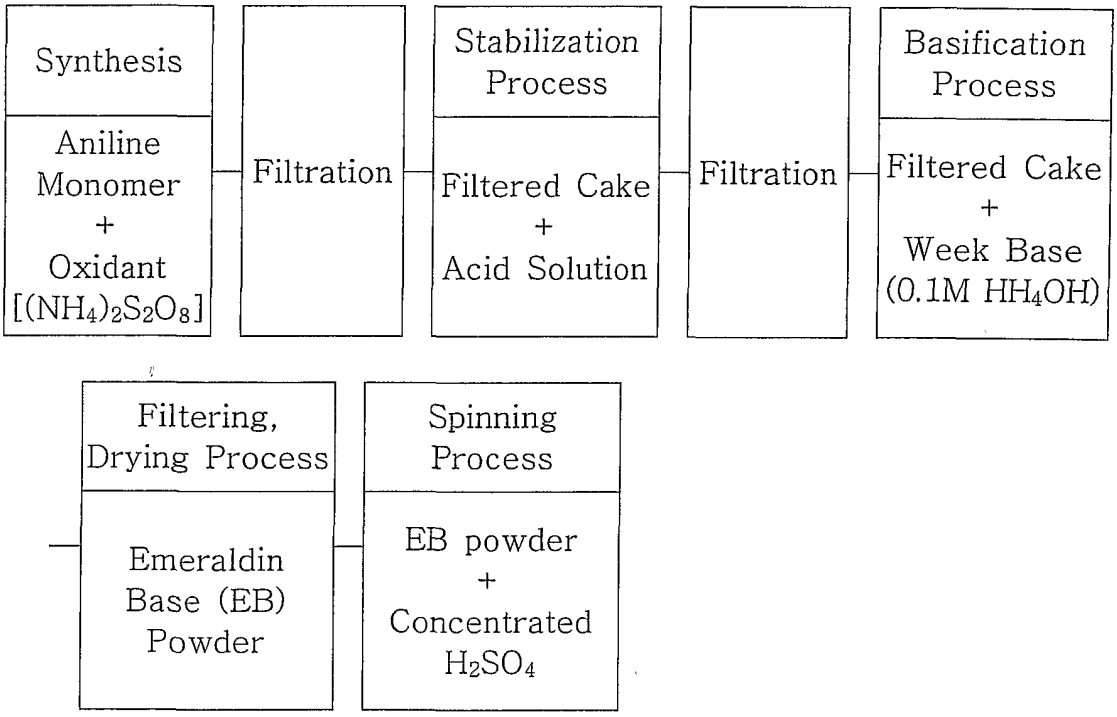
1. The fabrication method to make electrically conductive polyaniline spinning solution with dissolving directly polyaniline salt(polyaniline hydrochloride salt, polyaniline-H_2SO_4 salt, et. al.) instead of EB(emeraldine base) in concentrated sulfuric acid(above 98% w/w).

2. The fabrication method to make electrically conductive polyaniline-blend(Nylon, aramid) spinning solution with dissolving directly polyaniline salt(polyaniline hydrochloride salt, polyaniline-H_2SO_4 salt, et. al.) instead of EB(emeraldine base) in concentrated sulfuric acid(above 98% w/w).

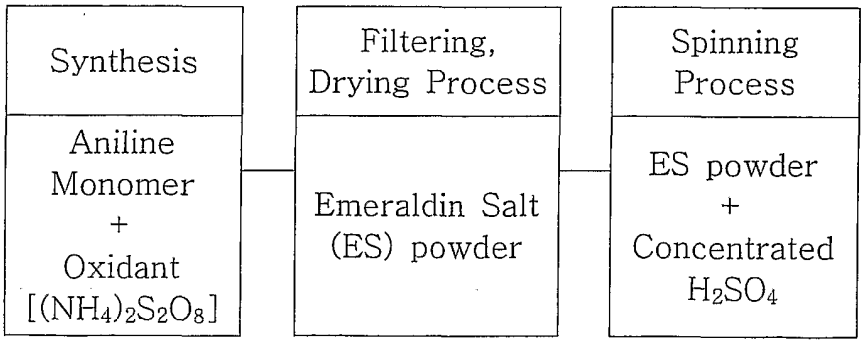
3. The weight % of polyaniline salt in the spinning solution is from 1 to 99.9 on weight % of blend material(Nylon, aramid)

Figure 1.

The Conventional process



This invention process



INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

IPC7 D01F 2/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimun documentation searched (classification system followed by classification symbols)

IPC7 D01F

Documentation searched other than minimun documentation to the extent that such documents are included in the fileds searched

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US, 5788897 A (E. I. DUPONT CO.) 4 AUGUST 1998(Family None) see examples 1 - 4, claim 1	3 1 - 2
X A	US, 5911930 A (MONSANTO CO.) 15 JUNE 1999(Family None) see the whole document	3 1 - 2
A	US, 5160457 A (ALLIED SIGNAL INC.) 3 NOVEMBER 1992(Family None) see the whole document	1 - 3
A	US, 5069820 A (ALLIED SIGNAL INC.) 3 DECEMBER 1991(Family None) see the whole document	1 - 3
A	US, 6001475 A (E. I. DUPONT CO.) 14 DECEMBER 1999(Family None) see abstract	1 - 3

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search	Date of mailing of the international search report
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