

Method of Producing Polyphenylene Ether

TECHNICAL FIELD

5 [0001] The present disclosure relates to a method of producing polyphenylene ether (hereinafter, may be abbreviated simply as "PPE"), especially to a production method that allows production of high-quality PPE powder with high production efficiency.

BACKGROUND

10 [0002] Modified PPE resin, in which PPE is a key material, may be processed by various molding methods, such as melting injection molding and melting extrusion molding, to produce products and components of desired shapes. Accordingly, modified PPE resin is widely used as a plastic material for products and components in electrical and electronic fields, automobile
15 fields, and other various industrial material fields.

[0003] Examples of a method of producing PPE include oxidative polymerization of a phenolic compound in the presence of a copper compound and amines in a good solvent for PPE. As a known way to precipitate PPE from the PPE solution obtained by the aforementioned method, PPE particles
20 may be precipitated by adding a poor solvent, such as methanol containing water, for PPE to the PPE solution containing the good solvent for PPE.

In the process of producing PPE, polymerization time and precipitation conditions may be sometimes changed to produce brands having different molecular weights (e.g., PPE having different molecular weights). At the time
25 of changing brands, a transitional product (i.e., an intermediate product that is neither a product obtained before the change nor a product obtained after the change) is generated. Furthermore, the precipitation conditions during the change in brands might be in an unstable state until the compositions in a precipitation tank are replaced.

30 [0004] According to reports on conventional PPE precipitation, although there are many technologies for improving an mean particle size, a fine powder rate, and a particle size, no technology is disclosed for changing brands efficiently and allowing continuous and reliable production even after a change in brands. That is to say, there is currently a need for development of
35 a precipitation method that reduces the transitional product during a change in brands and that allows a change in brands in a stable state.

[0005] Patent Literature 1 describes a method including the step of mixing the concentrated solution with an anti-solvent to precipitate the poly (arylene ether). By adjusting the temperature of the concentrated solution, immediately before being mixed with the anti-solvent, to not less than approximately

5 ($T_{\text{cloud}} - 10\text{ }^{\circ}\text{C}$), the method prevents generation of excessively fine particles.

[0006] Patent Literature 2 describes a method for producing a poly(arylene ether) with improved particle size characteristics, the method including the step of: (a) mixing a first mixture, which contains a poly(arylene ether) and a solvent, with a poor solvent to form a second mixture, which contains the

10 solvent, the poor solvent, and the poly(arylene ether). The step (a) further includes the following processes (b), (c), (d), (e) and (f): (b) adjusting an impeller tip speed to be not more than 6 m/s; (c) adjusting a solids content to be from approximately 10 % by mass to approximately 50 % by mass with respect to the poly(arylene ether) resin; (d) maintaining a temperature of the

15 second mixture to be at least 5 $^{\circ}\text{C}$ lower than the boiling point of the poor solvent; (e) providing a ratio of the poor solvent to the first mixture by mass of approximately from 0.5 : 1 to approximately 4 : 1; and (f) providing the poor solvent containing not more than 5 % by mass of water. The poly(arylene ether) with the improved particle size characteristics (i) includes

20 approximately not more than 50 % by mass of particles having a particle size of less than 38 μm ; and (ii) has a mean particle size of not less than 100 μm .

[0007] Patent Literature 3 describes a method including the steps of preparing a solution of an organic solvent for polyphenylene oxide while maintaining a temperature of from 60 $^{\circ}\text{C}$ to the boiling temperature of the

25 organic solvent for polyphenylene oxide, adding, to the prepared solution, an organic liquid in which polyphenylene oxide is insoluble as soon as possible while maintaining the aforementioned temperature range for precipitation in polyphenylene oxide, and collecting the precipitates and drying the collected precipitates. Thus, the method in Patent Literature 3 reduces the amount of

30 fine particles.

[0008] The technologies described in Patent Literatures 1 and 2 mix PPE, a PPE solution including a good solvent for PPE, and a poor solvent, such as methanol containing a small amount of water, to precipitate PPE.

35 CITATION LIST
Patent Literatures

[0009]

PTL 1: Japanese Unexamined Patent Application Publication No. 2004-531626

PTL 2: Japanese Unexamined Patent Application Publication No.
5 2014-508208

PTL 3: Japanese Examined Patent Publication No. Sho 45-000587

SUMMARY

[0010] The methods described in Patent Literatures 1 and 2 need the use of
10 a mixing tank to add a small amount of water to methanol in advance, and at
the time of changing conditions, such as changing brands, the transitional
product is generated until the compositions in a precipitation tank are
replaced.

The conventional PPE precipitation methods are technologies for
15 regulating the particle size of precipitated PPE and are not sufficient to
address the industrial needs for producing stably high-quality PPE with high
production efficiency.

[0011] Hence, the present disclosure is to provide a method of producing
PPE that allows reliable operation, without causing any troubles, such as an
20 increase in fine powder, scale adhesion and growth in a precipitation tank, and
scale fall-off and contamination into a product, even during operation of the
precipitation tank that may include a change in brands, that significantly
reduces the amount of the transitional product generated at the time of
changing brands, and that allows efficient production of PPE.

[0012] In view of the aforementioned problem, the present inventors have
25 studied the technology that allows operation in the stable state by preventing a
decrease in production efficiency due to the generation of the transitional
product at the time of changing conditions, such as changing brands, in
producing PPE, and that also continues precipitation in a stable state even
30 after a change in brands.

The study has revealed that, at the time of changing conditions, such as
changing brands, precipitation is unstable, and there occur various troubles,
such as an increase in fine powder, scale generation and growth in the
precipitation tank, and significant deterioration in quality of a product due to
35 the scale falling off and contaminating the product.

Thus, the present inventors have studied the conditions for reducing the

transitional product generated due to a change in brands and producing stably high-quality product even after changing conditions by attempting, when adding a poor solvent and water to the precipitation tank, to add the poor solvent and the water separately with use of different pipes of individual systems without mixing the poor solvent with the water in advance. Thus, the present inventors have found the conditions for continuing reliable operation even during a change in brands by regulating the compositions in the precipitation tank when adding a PPE solution to the precipitation tank.

[0013] In other words, the present disclosure is as follows.

(1) A method of producing polyphenylene ether, the method including:

the polymerization step of oxidatively polymerizing a phenolic compound in a polymerization solution containing a good solvent for polyphenylene ether and a catalyst to obtain a polyphenylene ether mixture liquid; and

the precipitation step of adding, into a precipitation tank equipped with a stirrer, the polyphenylene ether mixture liquid, a poor solvent for polyphenylene ether, and water to be mixed and precipitating polyphenylene ether to thereby obtain a slurry liquid containing a polyphenylene ether particulate substance, wherein

in the precipitation step, the poor solvent for polyphenylene ether and the water are added into the precipitation tank through different pipes, and

in the precipitation step, the amount of the water added is from 0.05 to 30 % by mass with respect to 100 % by mass of the poor solvent for polyphenylene ether.

[0014] (2) The method of producing polyphenylene ether according to (1), wherein, in the precipitation step, the ratio by mass of the poor solvent for polyphenylene ether added to the good solvent for polyphenylene ether contained in the polyphenylene ether mixture liquid added, that is to say, the mass of the poor solvent for polyphenylene ether added / the mass of the good solvent for polyphenylene ether contained in the polyphenylene ether mixture liquid added, is from 0.3 to 2.0.

[0015] (3) The method of producing polyphenylene ether according to (1) or (2), wherein the phenolic compound is 2,6-dimethylphenol.

[0016] (4) The method of producing polyphenylene ether according to any one of (1) to (3), wherein a content rate of polyphenylene ether particles

having a particle size of not more than 105 μm in the polyphenylene ether particulate substance is not more than 11 % by mass.

[0017] The method of producing PPE according to the present disclosure allows reliable operation, without causing any troubles, such as an increase in fine powder, scale adhesion and growth in the precipitation tank, and scale fall-off and contamination into a product, even during operation of the precipitation tank that may include a change in brands and significantly reduces the amount of the transitional product generated at the time of changing brands.

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BRIEF DESCRIPTION OF THE DRAWINGS

[0018] In the accompanying drawings:

FIG. 1 is a schematic view illustrating an example of a precipitation tank used in a production method according to one of embodiments; and

15 FIG. 2 is a schematic view illustrating a draft tube disposed in a precipitation tank used in a production method according to one of embodiments as seen from an upper surface of the precipitation tank.

DETAILED DESCRIPTION

20 [0019] One of embodiments of the present disclosure (hereinafter, called the "present embodiment") is described in details below. Note that the present disclosure is not limited to the following embodiment and that various modifications may be made without departing from the gist of the present disclosure.

25 [0020] [Method of Producing Polyphenylene Ether]

A method of producing PPE according to the present embodiment includes: the polymerization step of oxidatively polymerizing a phenolic compound in a polymerization solution containing a good solvent for polyphenylene ether and a catalyst to obtain a polyphenylene ether mixture liquid; and

30 the precipitation step of adding, into a precipitation tank equipped with a stirrer, the polyphenylene ether mixture liquid, a poor solvent for polyphenylene ether, and water to be mixed and precipitating polyphenylene ether to thereby obtain a slurry liquid containing a polyphenylene ether particulate substance.

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In the precipitation step, the poor solvent for polyphenylene ether and

the water are added into the precipitation tank through different pipes.

In the precipitation step, the amount of the water added is from 0.05 to 30 % by mass with respect to 100 % by mass of the poor solvent for polyphenylene ether.

5 The method of producing PPE according to the present embodiment is preferably a continuous process.

[0021] In the following, a detailed description is given of each step in the method of producing PPE according to the present embodiment.

(Polymerization Step)

10 In the polymerization step, the phenolic compound may be oxidatively polymerized by, for example, allowing an oxygen-containing gas to flow through the polymerization solution containing the good solvent (such as an aromatic solvent) for PPE, a metal catalyst, a halogen compound, an amine compound, or the like.

15 **[0022]** -Polymerization Solution-
--Phenolic Compound--

Examples of the phenolic compound may include o-cresol, 2,6-dimethylphenol, 2-ethylphenol, 2-methyl-6-ethylphenol, 2,6-diethylphenol, 2-n-propylphenol, 2-ethyl-6-n-propylphenol, 20 2-methyl-6-chlorophenol, 2-methyl-6-bromophenol, 2-methyl-6-isopropylphenol, 2-methyl-6-n-propylphenol, 2-ethyl-6-bromophenol, 2-methyl-6-n-butylphenol, 2,6-di-n-propylphenol, 2-ethyl-6-chlorophenol, 2-methyl-6-phenylphenol, 2-phenylphenol, 2,6-diphenylphenol, 2,6-bis-(4-fluorophenyl)phenol, 2-methyl-6-tolylphenol, 2,6-ditolylphenol, 25 2,5-dimethylphenol, 2,3,6-trimethylphenol, 2,5-diethylphenol, 2-methyl-5-ethylphenol, 2-ethyl-5-methylphenol, 2-allyl-5-methylphenol, 2,5-diallylphenol, 2,3-diethyl-6-n-propylphenol, 2-methyl-5-chlorophenol, 2-methyl-5-bromophenol, 2-methyl-5-isopropylphenol, 2-methyl-5-n-propylphenol, 2-ethyl-5-bromophenol, 30 2-methyl-5-n-butylphenol, 2,5-di-n-propylphenol, 2-ethyl-5-chlorophenol, 2-methyl-5-phenylphenol, 2,5-diphenylphenol, 2,5-bis-(4-fluorophenyl)phenol, 2-methyl-5-tolylphenol, 2,5-ditolylphenol, 2,6-dimethyl-3-allylphenol, 2,3,6-triallylphenol, 2,3,6-tributylphenol, 2,6-di-n-butyl-3-methylphenol, 2,6-di-t-butyl-3-methylphenol, 35 2,6-dimethyl-3-n-butylphenol, and 2,6-dimethyl-3-t-butylphenol.

Especially, due to low cost and widespread availability,

2,6-dimethylphenol, 2,6-diethylphenol, 2,6-diphenylphenol, 2,3,6-trimethylphenol and 2,5-dimethylphenol are preferable, and 2,6-dimethylphenol and 2,3,6-trimethylphenol are more preferable, and 2,6-dimethylphenol is even more preferable.

5 The aforementioned types of the phenolic compound may be used singly or in combination of two or more.

As a combination of two or more types, for example, a combination of 2,6-dimethylphenol and 2,6-diethylphenol, a combination of 2,6-dimethylphenol and 2,6-diphenylphenol, a combination of
10 2,3,6-trimethylphenol and 2,5-dimethylphenol, and a combination of 2,6-dimethylphenol and 2,3,6-trimethylphenol may be considered. The mixture ratio of different types of the phenolic compound may be selected at will.

Additionally, the aforementioned phenolic compound may contain small
15 amounts of m-cresol, p-cresol, 2,4-dimethylphenol, 2,4,6-trimethylphenol, and the like, which are by-products from production.

[0023] --Good Solvent for Polyphenylene Ether--

Examples of the aforementioned good solvent for polyphenylene ether may include an aromatic solvent, such as benzene, toluene, xylene,
20 ethylbenzene, and styrene. From the perspective of ease in removing a residual solvent, toluene is preferable.

The aforementioned types of the good solvent for polyphenylene ether may be used singly or in combination of two or more.

[0024] --Catalyst--

25 As the aforementioned catalyst, any catalyst generally used for polymerizing PPE may be adopted.

Examples of the aforementioned catalyst may include a catalyst containing a metal catalyst, a halogen compound, an amine compound, and a mixture thereof. One example may be a mixture composed of a transition metal
30 ion having a redox ability as the metal catalyst and an amine compound capable of forming a complex with the transition ion. Specific examples may include a mixture composed of a copper compound and an amine compound, a mixture composed of a manganese compound and an amine compound, a mixture composed of a cobalt compound and an amine compound. Among these
35 examples, a mixture composed of a copper compound and an amine compound is preferable.

[0025] --Metal Catalyst--

As the aforementioned metal catalyst in the aforementioned catalyst, a copper compound is preferable.

As the aforementioned copper compound, a cuprous compound, a cupric compound, or a mixture thereof may be used. Examples of the cuprous compound may include cuprous chloride, cuprous bromide, cuprous sulfate, and cuprous nitrate. Examples of the cupric compound may include cupric oxide, cupric chloride, cupric bromide, cupric sulfate, and cupric nitrate. Among these examples, cupric oxide, cuprous chloride, cupric chloride, cuprous bromide, and cupric bromide are preferable.

These types of copper salt may be synthesized at the time of use, from copper oxide (such as cuprous oxide), copper carbonate, copper hydroxide, and the like, and from halogen or acid corresponding thereto, such as from cuprous oxide and hydrogen halide (or a hydrogen halide solution).

These types of the metal catalyst may be used singly or in a combination of two or more.

[0026] --Halogen Compound--

Examples of the halogen compound may include, but not particularly limited to, hydrogen chloride, hydrogen bromide, hydrogen iodide, sodium chloride, sodium bromide, sodium iodide, potassium chloride, potassium bromide, potassium iodide, tetramethylammonium chloride, tetramethylammonium bromide, tetramethylammonium iodide, tetraethylammonium chloride, tetraethylammonium bromide, and tetraethylammonium iodide. Moreover, these types of the halogen compound may be used in the state of an aqueous solution or a solution using an appropriate solvent. Among all, an aqueous solution of hydrogen chloride and an aqueous solution of hydrogen bromide are preferable.

These types of the halogen compound may be used singly or in a combination of two or more.

[0027] --Amine Compound--

Example of the aforementioned amine compound may include a diamine compound, a secondary monoamine compound, and a tertiary monoamine compound. Among these examples, a diamine compound is preferably contained, and a diamine compound, a secondary monoamine compound, and a tertiary monoamine compound are more preferably contained.

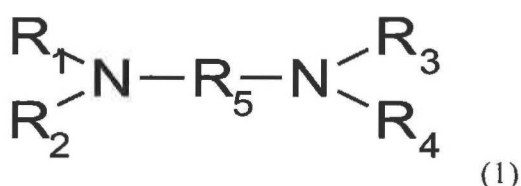
These types of the amine compound may be used singly or in

combination of two or more.

[0028] As the aforementioned diamine compound, the one represented by the following formula (1) is preferably used.

As the aforementioned catalyst, for example, the one containing a copper compound, a halogen compound, and a diamine compound represented by the following general formula (1) may be used. Using such a catalyst tends to increase a polymerization rate and further reduce polymerization time. Furthermore, controlling a catalyst amount, an oxygen feed amount, and polymerization time tends to make it easier to control the molecular weight after the polymerization.

[Formula 1]



(In the formula (1), R_1 , R_2 , R_3 and R_4 each independently represent a hydrogen atom, or a straight-chain or a branched-chain alkyl group having a carbon number of 1 to 6, and all of these are not simultaneously hydrogen atoms. R_5 represents a straight-chain or branched chain alkylene group having a carbon number of 2 to 5.)

[0029] Examples of the diamine compounds represented by the aforementioned general formula (1) may include, but not particularly limited to, N,N,N',N'-tetramethylethylenediamine, N,N,N'-trimethylethylenediamine, N,N'-dimethylethylenediamine, N,N-dimethylethylenediamine, N-methylethylenediamine, N,N,N',N'-tetraethylethylenediamine, N,N,N'-triethylethylenediamine, N,N'-diethylethylenediamine, N,N-diethylethylenediamine, N-ethylethylenediamine, N,N-dimethyl-N'-ethylethylenediamine, N-n-propylethylenediamine, N,N'-dimethyl-N-ethylethylenediamine, N-i-propylethylenediamine, N,N'-di-n-propylethylenediamine, N-n-butylethylenediamine, N,N'-di-i-propylethylenediamine, N-i-butylethylenediamine, N,N'-di-n-butylethylenediamine, N-t-butylethylenediamine, N,N'-di-i-butylethylenediamine, N,N,N',N'-tetramethyl-1,3-diaminopropane, N,N'-dimethyl-1,3-diaminopropane, N,N'-trimethyl-1,3-diaminopropane, N,N'-dimethyl-1,3-diaminopropane,

N-methyl-1,3-diaminopropane,
N,N,N',N'-tetramethyl-1,3-diamino-1-methylpropane,
N,N,N',N'-tetramethyl-1,3-diamino-2-methylpropane,
N,N,N',N'-tetramethyl-1,4-diaminobutane, and
5 N,N,N',N'-tetramethyl-1,5-diaminopentane. Among all, a diamine compound whose R₅ in the formula (1) is an alkylene group having a carbon number of 2 or 3 is preferable.

The aforementioned types of the diamine compound may be used singly or in combination of two or more.

10 The amount of the aforementioned diamine compound used is not particularly limited to any amount and is preferably from 0.01 to 10 mol with respect to 100 mol of the aforementioned phenolic compound.

[0030] The tertiary monoamine compound is not particularly limited to any compound and may be, for example, an aliphatic tertiary amine, including
15 an alicyclic tertiary amine. Examples of the tertiary monoamine compound may include, but not particularly limited to, trimethyl amine, triethylamine, tripropylamine, tributylamine, triisobutylamine, dimethylethylamine, dimethylpropylamine, aryldiethylamine, N-butyl-dimethylamine, diethylisopropylamine, and N-methylcyclohexylamine.

20 These examples of the tertiary monoamine compound may be used singly or in combination of two or more.

The amount of the tertiary monoamine compound used is not particularly limited to any amount and is preferably not more than 15 mol with respect to 100 mol of the aforementioned phenolic compound.

25 [0031] The whole amount of the aforementioned tertiary monoamine compound may be added before polymerization. Alternatively, a part of the tertiary monoamine compound may be added before polymerization, and the remaining monoamine compound may be added successively during polymerization. The aforementioned tertiary monoamine may also be mixed
30 with the phenolic compound before being added to the polymerization solution simultaneously with start of polymerization.

[0032] The aforementioned secondary monoamine is not particularly limited to any compound and may be, for example, a secondary aliphatic amine. Examples of the secondary aliphatic amine may include, but not
35 particularly limited to, dimethyl amine, diethylamine, di-n-propylamine, di-i-propylamine, di-n-butylamine, di-i-butylamine, di-t-butylamine,

dipentylamine, dihexylamine, dioctylamine, didecylamine, dibenzylamine, methyl ethyl amine, methylpropylamine, methylbutylamine, and cyclohexylamine.

As the aforementioned secondary monoamine compound, the one
5 containing an aromatic may be used. Examples of the secondary monoamine compound containing an aromatic may include, but not particularly limited to: N-(substituted or unsubstituted phenyl)alkanamine, such as N-phenylmethanolamine, N-phenylethanolamine, N-phenylpropanolamine, N-(m-methylphenyl)ethanolamine, N-(p-methylphenyl)ethanolamine,
10 N-(2',6'-dimethylphenyl)ethanolamine, and N-(p-chlorophenyl)ethanolamine; and N-hydrocarbon substituted aniline, such as N-ethylaniline, N-butaniline, N-methyl-2-methylaniline, N-methyl-2,6-dimethylaniline, and diphenylamine.

These examples of the secondary monoamine compound may be used singly or in combination of two or more.

15 The amount of the secondary monoamine compound used is not particularly limited to any amount and is preferably not more than 15 mol with respect to 100 mol of the aforementioned phenolic compound.

[0033] Additionally, a surfactant, which is conventionally known to provide the effect of improving polymerization activity, may further be added
20 to the polymerization solvent.

Examples of the aforementioned surfactant may include trioctylmethylammonium chloride known by the product names Aliquat 336 (manufactured by Henkel Corporation) and CapRiquat (manufactured by Dojindo Laboratories).

25 The amount of the aforementioned surfactant used is preferably in the range not more than 0.1 % by mass with respect to the entire amount of the aforementioned polymerization solution.

[0034] --Aeration by Oxygen-Containing Gas--

In the aforementioned polymerization step, the phenolic compound may
30 be polymerized while an oxygen-containing gas is allowed to flow through. Timing of initiating the aeration by (i.e., the flow of) the oxygen-containing gas is not particularly limited to any time. However, in adjustment of the polymerization solution, it is preferable to initiate the flow of the oxygen-containing gas after introducing, into the reactor, any one of the
35 phenolic compound, the aromatic solvent, and the catalyst.

[0035] The oxygen-containing gas is not particularly limited to any type of gas and may be, for example, a mixture of oxygen and any inert gas, air, or a

mixture of air and any inert gas. The inert gas is not particularly limited to any type of inert gas and may be, for example, any inert gas which does not significantly affect polymerization reaction. Nitrogen is a typical inert gas.

[0036] From the perspective of further efficient polymerization, the amount of the oxygen-containing gas flown in the aforementioned polymerization step is preferably from 3 to 14 NL/minute and more preferably from 6 to 13 NL/minute with respect to 1 kg of the phenolic compound subjected to the polymerization reaction.

[0037] In the production method according to the present embodiment, any method of polymerizing PPE may be used. Examples of the aforementioned method of polymerizing PPE may include the method described in U.S. Patent No. 3,306,874, in which 2,6-xylenol is oxidatively polymerized with use of a complex of cuprous salt and amine as a catalyst, and the methods described in U.S. Patent No. 3,306,875, U.S. Patent No. 3,257,357, U.S. Patent No. 3,257,358, Japanese Examined Patent Publication No. Sho 52-017880, Japanese Unexamined Patent Application Publication No. Sho 50-051197, and Japanese Unexamined Patent Application Publication No. Sho JP 63-152628.

[0038] Examples of the method of polymerizing PPE may include precipitation polymerization and solution polymerization methods. The production method according to the present embodiment is preferably the one that precipitates PPE obtained by the solution polymerization method. The solution polymerization method is a polymerization method in which polymerization is performed in a good solvent for PPE, and no precipitate is yielded during the polymerization. In the solution polymerization method, all the PPE molecules are dissolved, and the molecular weight distribution tends to be wide.

[0039] After the aforementioned polymerization step, a catalyst extraction step may also be conducted. In the catalyst extraction step, a chelating agent solution is added to the PPE mixture liquid to extract the metal catalyst to the chelating agent solution, and by the liquid-liquid separation between an aromatic solvent phase and a chelating agent solution phase, the metal catalyst in the PPE mixture liquid is removed. In the aforementioned catalyst extraction step, water may be additionally added to the PPE mixture liquid resulting from the liquid-liquid separation after the addition of the chelating agent. By thus repeating the liquid-liquid separation, the catalyst may be further extracted. Additionally, the PPE mixture liquid after the catalyst is

extracted in the catalyst extraction step may also be called the "polyphenylene ether mixture liquid" or the "PPE mixture liquid" herein.

[0040] In the aforementioned catalyst extraction step, a chelating agent solution may be added to the PPE mixture liquid resulting from the polymerization step and stirred to extract the metal catalyst, which is used as the aforementioned catalyst, to the chelating agent solution, and by the liquid-liquid separation between the polyphenylene ether mixture liquid and the chelating agent solution, the metal catalyst in the PPE mixture liquid may be removed.

10 Examples of the chelating agent used in the aforementioned chelating agent solution may include: an acid, such as hydrochloric acid and acetic acid; ethylenediaminetetraacetic acid (EDTA) and salt thereof; and nitrilotriacetic acid and salt thereof. Although the aforementioned chelating agent may be added in the form of the chelating agent alone, it is preferable to add the chelating agent in the form of a chelating agent aqueous solution or the like, by dissolving the chelating agent in a solvent, such as water, that has a low dissolution ability for PPE and that phase-separates from an aromatic solvent, which is the good solvent for PPE. When the chelating aqueous solution is used, the metal catalyst, after being coupled with the chelating agent and deactivated, is extracted to a water phase. This allows separation of PPE included in an organic phase from the metal catalyst.

[0041] In the aforementioned catalyst extraction step, by repeating the liquid-liquid separation process by additionally adding water to the PPE mixture liquid resulting from the liquid-liquid separation after the addition of the chelating agent, the metal catalyst may be further extracted.

[0042] Two-phase separation in the catalyst extraction step or in a washing step, which is described later, may be settled separation or may be conducted by using a liquid-liquid separation device.

[0043] After the polymerization step or the catalyst extraction step described above, a condensation step may also be conducted. In the condensation step, the concentration of PPE contained in the PPE mixture liquid resulting from the polymerization step is regulated by vaporizing a part of the good solvent. Additionally, the PPE mixture liquid after PPE is condensed in the condensation step may also be called the "polyphenylene ether mixture liquid" or the "PPE mixture liquid" herein. Either one or both of the catalyst extraction step and the condensation step described above may be

conducted.

The concentration of PPE in the PPE mixture liquid after the concentration is preferably more than 30 % by mass and preferably not more than 50 % by mass. The concentration of PPE in the PPE mixture liquid is
5 more preferably not more than 48 % by mass and even more preferably not more than 45 % by mass.

A concentration of PPE in the PPE mixture liquid of not more than 30 % by mass is not preferable because it makes the dispersibility of the PPE mixture liquid in the precipitation tank excessively high, causing an increase
10 in fine powder. A concentration of PPE in the PPE mixture liquid of more than 50 % by mass decreases the dispersibility of the PPE mixture liquid in the precipitation tank, causing the poorly dispersed PPE mixture liquid to adhere to a wall surface, a stirring shaft, baffles, or the like to form scale. Another unfavorable issue is that the liquid viscosity is increased, leading to an
15 increase in equipment expenses of peripherals, such as pumps.

[0044] (Precipitation Step)

The production method according to the present embodiment includes the precipitation step of mixing the PPE mixture liquid resulting from the polymerization step, the catalyst extraction step, or the condensation step,
20 with a poor solvent, such as methanol, for PPE, and water for solidification to thereby obtain a slurry liquid containing a polyphenylene ether particulate substance. The aforementioned precipitation step may be, for example, the step, performed after condensation or the like as needed, of adding, to the PPE mixture liquid, a poor solvent for PPE, such as ketones having a carbon
25 number of 1 to 10 and alcohols having a carbon number of 1 to 10, and water to be mixed and precipitating PPE to thereby obtain a slurry liquid containing the PPE particulate substance.

Since, in the production method according to the present embodiment, the poor solvent for PPE and the water are added through different pipes,
30 scale generation and growth after production are prevented. Furthermore, after a change in brands, the generation of the transitional product is reduced due to a reduction in time in which the transitional product may be generated, and the generation of fine powder PPE and the generation of scale are reduced.

[0045] (Poor Solvent for PPE)

35 Examples of the aforementioned poor solvent for PPE may include a polar solvent, such as ketones having a carbon number of 1 to 10 and alcohols

having a carbon number of 1 to 10. Examples of the aforementioned polar solvents may include methanol, ethanol, propanol, isopropanol, n-butanol, 2-butanol, pentanol, hexanol, ethyleneglycol, acetone, and methylethylketone. Among these examples, methanol, ethanol, isopropanol, n-butanol, 2-butanol, acetone, and methylethylketone are preferable. As the aforementioned polar solvent, alcohol having a carbon number of 1 to 10 is also preferable.

The aforementioned types of the polar solvent may be used singly or in combination of two or more.

[0046] In the aforementioned precipitation step, from the perspectives of further reducing the generation of the transitional product at the time of changing brands and further reducing the generation of fine powder PPE, the amount of the water added is from 0.05 to 30 % by mass, preferably from 1 to 25 % by mass, and more preferably from 3 to 20 % by mass with respect to 100 % by mass of the poor solvent for PPE.

When the amount of the water added is not more than 30 % by mass, the particle size of the resultant PPE is unlikely to be enlarged.

[0047] In the following, a description is given of the precipitation tank used in the precipitation step.

In the aforementioned precipitation step, the precipitation tank equipped with a stirrer is used. The stirrer herein preferably includes at least one-stage stirring blade that is disposed in the precipitation tank and that is selected from an inclined paddle blade, a screw blade, and a ribbon blade. From the perspective of enhancing miscibility, the stirrer also preferably includes one or more baffles, and the stirring blade is preferably adapted for downward discharge.

[0048] FIGs. 1 and 2 illustrate an example of the precipitation tank used in the production method according to the present embodiment.

A precipitation tank 1 may include a draft tube 2, at least one-stage stirring blade 3, which is disposed in the draft tube 2 and which is selected from an inclined paddle blade, a screw blade, and a ribbon blade, and one or more baffles 4 (four baffles 4 in FIGs. 1 and 2), which are disposed on the outer side of the draft tube 2.

The draft tube 2 is a partition wall disposed in the precipitation tank 1, and the draft tube 2 may have a substantially cylindrical shape, a substantially polygonal tubular shape, or the like. The draft tube 2 is preferably disposed concentrically with the precipitation tank 1.

When the stirring blade 3 is an inclined paddle blade, the stirring blade 3 is preferably the one in which an ordinary paddle is inclined from 5 to 85 degrees, more preferably from 35 to 55 degrees, with respect to a rotational direction. When the stirring blade 3 is a screw blade, the stirring blade 3 is preferably the one having a shape similar to that of a screw used in, for example, ships. When the stirring blade 3 is a ribbon blade, the stirring blade 3 is preferably a helical stirring blade of single blade type or double blade type.

The baffles 4 are baffle plates fixed in the draft tube 2 to control the flow. In the precipitation tank, the mixture liquid of the PPE mixture liquid, the poor solvent for PPE, and the water is flown toward the tank bottom or a liquid level 8 while swirling in the draft tube 2, and then, flows between the draft tube 2 and a wall of the precipitation tank 1 substantially perpendicularly toward the liquid level 8 or the tank bottom to circularly flow inside and outside the draft tube 2. The circulation direction of the mixture liquid depends on the rotational direction of the stirring blade 3 and the shape of the stirring blade 3. The production method according to the present embodiment preferably involves the circulation flow in which the mixture liquid flows toward the tank bottom while swirling in the draft tube 2 and flows between the draft tube 2 and the wall of the precipitation tank 1 substantially perpendicularly toward the liquid level 8. The production method according to the present embodiment may employ a stirring blade adapted for downward discharge to generate flow toward the tank bottom within the draft tube 2 and may also employ a ribbon blade adapted for upward discharge to generate flow toward the liquid level 8 outside the draft tube 2.

[0049] In the production method according to the present embodiment, the poor solvent for PPE and the water are added into the precipitation tank through different pipes. It is especially preferable that the PPE mixture liquid, the poor solvent for PPE, and the water are added into the precipitation tank through different pipes.

The PPE mixture liquid is added into the precipitation tank 1 through a PPE mixture liquid supply port 5. Preferably, the PPE mixture liquid supply port 5 is arranged above the liquid level 8, and the PPE mixture liquid is added into the precipitation tank 1 dropwise. From the perspective of further reducing the generation of scale, the PPE mixture liquid is preferably dropped

to a part of the circulation flow that flows toward the tank bottom.

The poor solvent for PPE is added into the precipitation tank 1 through a poor solvent supply port 6. The poor solvent supply port 6 is preferably arranged directly in the wall of the precipitation tank 1 above the liquid level 8, or between the draft tube 2 and the wall of the precipitation tank 1 above the liquid level 8.

The water is added into the precipitation tank 1 through a water supply port 7. Since the water and the poor solvent for PPE are not mixed before being added into the precipitation tank 1, the generation of the transitional product at the time of changing brands is even further reduced, the generation of fine powder PPE is even further reduced, and the generation of scale is even further reduced. The water supply port 7 is preferably arranged directly in the wall of the precipitation tank 1 above the liquid level 8, or between the draft tube 2 and the wall of the precipitation tank 1 above the liquid level 8.

The poor solvent supply port 6, the water supply port 7, and the PPE mixture liquid supply port 5 are preferably arranged so that the poor solvent for PPE, the water, and the PPE mixture liquid are added, for example, in this order during circulation flow. For example, the poor solvent supply port 6, the water supply port 7, and the PPE mixture liquid supply port 5 are preferably arranged in this order from the upstream to the downstream of the circulation flow. In cases of the circulation flow flowing toward the tank bottom while swirling in the draft tube 2 and flowing between the draft tube 2 and the wall of the precipitation tank 1 substantially perpendicularly toward the liquid level 8, the poor solvent supply port 6, the water supply port 7, and the PPE mixture liquid supply port 5 are preferably arranged in this order from the wall of the precipitation tank 1 toward the center of the precipitation tank 1 above the liquid level 8.

The slurry solution may be expelled through an outlet 9 and collected.

[0050] From the perspective of reducing time required for changing brands, residence time in the precipitation tank 1 is preferably from 0.2 to 2 minutes and more preferably from 0.5 to 1.7 minutes.

[0051] In the precipitation step, from the perspectives of further reducing the generation of the transitional product at the time of changing brands, further reducing the generation of fine powder PPE, and further reducing the generation of scale, the amount of the aforementioned poor solvent for polyphenylene ether added is preferably as follows. That is to say, the ratio by

mass of the aforementioned poor solvent for polyphenylene ether added to the
aforementioned good solvent for polyphenylene ether contained in the
aforementioned polyphenylene ether mixture liquid added (the mass of the
aforementioned poor solvent for polyphenylene ether added / the mass of the
5 aforementioned good solvent for polyphenylene ether contained in the
aforementioned polyphenylene ether mixture liquid added) is preferably from
0.3 to 2.0 and more preferably from 0.5 to 2.0.

[0052] The temperature of the PPE mixture liquid immediately before
being added into the precipitation tank 1 is preferably not less than 60 °C and
10 not more than 100 °C. The temperature of the PPE mixture liquid is more
preferably not more than 90 °C and even more preferably not more than 80 °C.
The temperature of the PPE mixture liquid is still even more preferably not
less than 65 °C.

A temperature of the PPE mixture liquid of less than 60 °C decreases the
15 dispersibility of the PPE mixture liquid in the precipitation tank 1, causing the
poorly dispersed PPE mixture liquid to adhere to the wall surface, the stirring
shaft, baffles, or the like and often form scale. Another unfavorable issue is
that the liquid viscosity is increased, leading to an increase in equipment
expenses of peripherals, such as pumps. A temperature of the PPE mixture
20 liquid of more than 100 °C is not preferable because it makes the
dispersibility of the PPE mixture liquid in the precipitation tank 1 excessively
high, causing an increase in fine powder.

[0053] The stirring rate of the precipitation tank 1 is preferably from 500
to 3000 rpm.

25 The amount of solution added into the precipitation per unit time
preferably equals the amount of solution expelled from the precipitation tank
1 per unit time.

The precipitation tank 1 may have a capacity of 500 mL to 3 kL for
resident liquid, and the production method according to the present
30 embodiment may be applied to a wide range of production of PPE.

[0054] From the perspective of the quality of PPE produced, the content
rate (fine powder rate) of polyphenylene ether particles having a particle size
of not more than 105 μm in the polyphenylene ether particulate substance
contained in the slurry liquid is preferably not more than 11 % by mass, more
35 preferably not more than 10.5 % by mass, and more preferably not more than
10.0 % by mass.

The fine powder rate may be measured by using the method described in Examples below.

5 The production method according to the present embodiment significantly reduces the generation of the transitional product at the time of changing brands and allows reliable production of PPE after a change in brands within a short period of time. In detail, for example, PPE having a fine powder rate of not more than 11 % by mass may be produced with 8 to 11 substitutions after a change in brands.

10 Herein, one substitution after a change in brands refers to replacement of contents in the precipitation tank 1 by adding a solution in a volume corresponding to a volume of liquid that may reside in the precipitation tank 1 after the change in brands. For example, when resident time is 1.9 minutes, time required for one substitution after a change in brands is 1.9 minutes, and time required for two substitutions after a change in brands is 3.8 minutes.

15 **[0055]** The slurry liquid containing the PPE particulate substance obtained after the aforementioned precipitation step is in the form of a slurry liquid (suspension liquid), in which the PPE particulate substance is present in the mixture liquid containing an aromatic solvent as the good solvent and a polar solvent as the poor solvent. In the production method according to the present
20 embodiment, a solid-liquid separation step may also be conducted, for example, after the aforementioned precipitation step to subject the precipitated slurry liquid to solid-liquid separation, and thus, wet PPE particles may be obtained from the aforementioned slurry solution.

Examples of a device that may be used in the solid-liquid separation may
25 include, but not particularly limited to, a centrifugal separator (of a vibration-type, a screw-type, a decanter-type, a basket-type, or the like), a vacuum filter (such as a drum-type filter, a belt filter, a rotary vacuum filter, a Young filter, and a Nutsche filter), a filter press, and a roll press.

[0056] The wet PPE particles separated in the aforementioned solid-liquid
30 separation step are impregnated with a lot of components of the good solvent, such as an aromatic solvent. In the production method according to the present embodiment, a washing step may also be conducted, for example, after the aforementioned solid-liquid separation step to wash the wet PPE particles with a washing liquid containing the aforementioned good solvent, which at
35 least contains an aromatic solvent, and the aforementioned poor solvent, which at least contains a polar solvent. By thus repeating the solid-liquid

separation step, the PPE particles may also be obtained. By washing the wet PPE particles with the washing liquid containing an aromatic solvent and a polar solvent, the content of the good solvent components in the wet PPE particles may be reduced.

5 The slurry liquid may also be separated into the solvent and the wet PPE particles by the solid-liquid separation step after the aforementioned washing step. At this time, the process of, for example, washing the wet PPE particles with the poor solvent to perform solid-liquid separation may also be repeated.

[0057] The obtained wet PPE particles may be crushed by a crusher for
10 regulating the fine powder rate. As the aforementioned crusher, for example, a jaw crusher, a cone crusher, a hammer mill, a feather mill, a ball mill, a high-speed rotation mill, and a jet mill may be used.

[0058] In the production method according to the present embodiment, a
15 drying step may also be conducted, for example, after the washing step or the solid-liquid separation step, to dry the PPE particles.

 The drying step may be conducted after crushing or without crushing.

 The drying temperature is preferably not less than 60 °C, more preferably not less than 80 °C, even more preferably not less than 120 °C, still even more preferably not less than 140 °C, and most preferably not less than
20 150 °C. When the drying temperature is less than 60 °C, the content, in PPE, of the good solvent, such as aromatic hydrocarbon, for PPE sometimes fails to be reduced to less than 1.5 % by mass efficiently.

 To increase the yield of PPE after the drying step, a method of rising the drying temperature, a method of allowing an inert gas, such as nitrogen, to
25 flow during drying, a method of increasing the degree of vacuum during drying, and a method of performing stirring during drying are preferably adopted.

 The drying step preferably employs a dryer having a mixing function. Examples of the dryer having the mixing function may include a stirring-type
30 and a tumbling-type dryer. The use of such a dryer helps increase the processing amount and maintain high productivity.

[0059] In the following, a detailed description is given of PPE obtained by the production method according to the present embodiment.

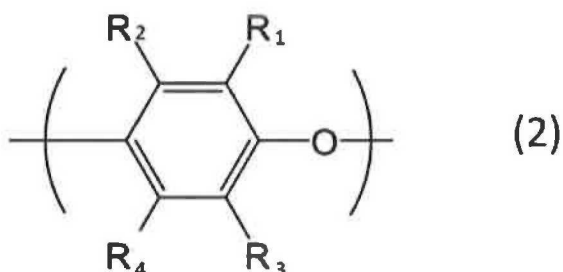
[Polyphenylene Ether]

35 PPE obtained by the production method according to the present embodiment is a homopolymer and/or a copolymer having a repeating unit

structure represented by the following general formula (2).

Additionally, herein, PPE obtained by the production method according to the present embodiment may also be called PPE according to the present embodiment.

5 [Formula 2]



In the formula (2), R₁, R₂, R₃, and R₄ are each independently selected from the group consisting of a hydrogen atom, a halogen atom, an alkyl group having a carbon number of 1 to 7, a phenyl group, a haloalkyl group, an aminoalkyl group, a hydrocarbon oxy group, and a halohydrocarbon oxy group in which a halogen atom is separated from an oxygen atom by at least two carbon atoms.

[0060] Examples of the aforementioned PPE homopolymer may include, but not particularly limited to, poly(2,6-dimethyl-1,4-phenylene)ether, poly(2-methyl-6-ethyl-1,4-phenylene)ether, poly(2,6-diethyl-1,4-phenylene)ether, poly(2-ethyl-6-n-propyl-1,4-phenylene)ether, poly(2,6-di-n-propyl-1,4-phenylene)ether, poly(2-methyl-6-n-butyl-1,4-phenylene)ether, poly(2-ethyl-6-isopropyl-1,4-phenylene)ether, poly(2-methyl-6-hydroxyethyl-1,4-phenylene)ether, and poly(2-methyl-6-chloroethyl-1,4-phenylene)ether. Among these examples, poly(2,6-dimethyl-1,4-phenylene)ether is preferable in terms of low cost and widespread availability.

[0061] Examples of the aforementioned PPE copolymer may include, but not particularly limited to, a copolymer of 2,6-dimethylphenol and 2,3,6-trimethylphenol, a copolymer of 2,6-dimethylphenol and o-cresol, and a copolymer of 2,6-dimethylphenol, 2,3,6-trimethylphenol, and o-cresol. Among these examples, a copolymer of 2,6-dimethylphenol and 2,3,6-trimethylphenol is preferable in terms of low cost and widespread

availability.

[0062] The reduced viscosity, measured at 30 °C with use of a 0.5 g/dL chloroform solution, of PPE according to the present embodiment is preferably from 0.25 to 0.70 dL/g and more preferably 0.25 to 0.60 dL/g.

5 When the aforementioned reduced viscosity is less than 0.25 dL/g, the dispersibility of the PPE good solvent solution in the precipitation tank is excessively high, and fine powder is increased, which is not preferable. Furthermore, satisfactory mechanical properties cannot be achieved. When the
10 aforementioned reduced viscosity is more than 0.70 dL/g, the dispersibility of the PPE good solvent solution in the precipitation tank is decreased, and the poorly dispersed PPE good solvent solution adheres to the wall surface, the stirring shaft, the baffles, or the like to form scale. Furthermore, the liquid viscosity is increased, possibly posing the need for enhancing the abilities of peripherals of the polymerization tank. This decreases polymerization
15 efficiency. Furthermore, a melt viscosity is increased, and post-processing and processability are deteriorated.

Additionally, the aforementioned reduced viscosity may be obtained by preparing the 0.5 g/dL chloroform solution of PPE and measuring the reduced viscosity, in η_{sp}/c (dL/g), of the prepared chloroform solution as a sample at
20 30 °C with use of a Ubbelohde viscometer tube.

[0063] The content (fine powder rate) of polyphenylene ether particles having a particle size of not more than 105 μm in the polyphenylene ether particulate substance contained in the slurry liquid obtained by the production method according to the present embodiment is preferably not more than 35 %
25 by mass, more preferably not more than 30 % by mass, even more preferably not more than 11 % by mass, still even more than not more than 10.5 % by mass, and most preferably not more than 10 % by mass.

The fine powder rate may be measured by using the method described in Examples below.

30 [0064] The average particle size of PPE according to the present embodiment is preferably not less than 250 μm and more preferably not less than 280 μm .

Additionally, the average particle size of PPE may be measured as a volume average particle size according to a wet process (methanol solvent)
35 with use of a laser diffraction scattering particle size distribution measurement device, which is a particle size distribution analyzer according

to the laser diffraction scattering method manufactured by Shimadzu Corporation.

From a cumulative curve of particle size distribution of the volume average particle size, a particle size (median diameter) corresponding to a center cumulative value is defined as the average particle size (μm). Similarly, the content (% by mass), in powder, of particles having a particle size of not more than 105 μm obtained from the cumulative curve of particle size distribution of the volume average particle size is calculated as the fine powder rate.

10

EXAMPLES

[0065] The present embodiment will now be described in detail based on Examples and Comparative Examples. However, the scope of the present embodiment is not limited to these Examples.

15 To start with, methods of measuring the physical properties and characteristics applied to the Examples and Comparative Example are as follows.

[0066] (1) Concentration of PPE in PPE Mixture Liquid

A PPE mixture liquid after polymerization or a PPE mixture liquid after the condensation step, was measured and transferred to an aluminum plate and dried at a room temperature for 60 minutes. The sample, whose surface was in a dried state, was placed into a vacuum dryer, together with the aluminum plate, and the temperature of the vacuum dryer was set to 180 °C. Then, vacuum drying was performed for 120 minutes at a reduced pressure of 10 torr. From the amounts of the sample before and after the drying, the concentration (% by mass) of PPE in the PPE mixture liquid was calculated.

25

[0067] (2) Reduced Viscosity

The reduced viscosity (η_{sp}/c) [dL/g] at 30 °C of a 0.5 g/dL chloroform solution was obtained with use of an Ubbelohde viscometer tube.

30

[0068] (3) Condition of Scale Adhesion

During production of a slurry liquid, scale that was present approximately 20 minutes after a change in brands was visually observed and evaluated according to the following criteria.

Good: Condition of scale adhesion to a degree that does not interfere with operation, and scale does not grow.

35

Medium: Although scale adheres and grows, operation may be continued.

Bad: PPE is wrapped around the stirring shaft and forms a large clot therearound. During operation, the clot falls and is crushed by stirring and mixed into a product.

[0069] (4) Fine Powder Rate

5 By using the obtained slurry liquid, the content of particles having a particle size of not more than 105 μm in PPE particles contained in the slurry liquid, obtained from the cumulative curve of particle size distribution of the volume average particle size with use of a laser diffraction particle size distribution measurement device (Model SALD-3100, manufactured by
10 Shimadzu Corporation), was calculated as the fine powder rate (% by mass).

[0070] <Production Example 1>

While nitrogen gas was blown at a flow rate of 500 ml/minute into a 40-liter jacketed polymerization tank, which included, on the bottom thereof, a stirring turbine blade, and baffles for introducing an oxygen-inclusive gas
15 and which also included, on a vent gas line on the upper portion thereof, a reflux condenser, 4.57 g of cupric oxide, 24.18 g of a 47 % by mass hydrogen bromide aqueous solution, 11.00 g of di-t-butylethylenediamine, 62.72 g of di-n-butylamine, 149.92 g of butyldimethylamine, 20.65 kg of toluene, and 3.12 kg of 2,6-dimethylphenol were added and stirred until a uniform solution
20 was formed and the internal temperature of the polymerization tank reached 25 °C.

Subsequently, dried air was started to be introduced from the sparger into the polymerization tank at a flow rate of 32.8 L/minute to start polymerization. The dried air was allowed to flow for 140 minutes, and thus, a
25 polymerization mixture was obtained. Additionally, the internal temperature during the polymerization was controlled at 40 °C. The polymerization liquid at the end of the polymerization was in the form of a uniform solution.

The flow of the dried air was stopped, and 10 kg of a 2.5 % by mass aqueous solution of ethylenediaminetetraacetic acid tetrasodium salt
30 (manufactured by Dojindo Laboratories) was added into the PPE mixture liquid resulting from the polymerization. The PPE mixture liquid was stirred at 70 °C for 150 minutes and subsequently, left standing for 20 minutes and separated into an organic phase and an aqueous phase through liquid-liquid separation, to collect the organic phase. The concentration of PPE in thus obtained PPE
35 mixture liquid was 13.1 % by mass. The obtained PPE mixture liquid was defined as the PPE mixture liquid (1).

By using a part of the obtained PPE mixture liquid (1), slurry, in which PPE was precipitated, was prepared by controlling the PPE mixture liquid (1) to a room temperature and subsequently by adding excess methanol and a small amount of water. After that, the aforementioned slurry was filtered with
5 use of a basket-type centrifuge (Model 0-15, manufactured by Tanabe Willtec Inc.). After the filtration, excess methanol and a small amount of water were added into the basket-type centrifuge, and filtration was performed again to obtain wet PPE particles.

Subsequently, the wet PPE particles were placed into a vacuum dryer and
10 held at 150 °C and at 1 mmHg for 1.5 hours to thereby obtain dried polyphenylene ether particles. The reduced viscosity of the obtained PPE particles was 0.502 dL/g.

[0071] <Production Example 2>

A PPE mixture liquid was produced in the same manner as in Production
15 Example 1 except that dried air was allowed to flow for 90 minutes. The concentration of PPE in the obtained PPE mixture liquid was 13.1 % by mass. The obtained PPE mixture liquid was defined as the PPE mixture liquid (2).

The reduced viscosity of the dried polyphenylene ether particles obtained in the same manner as in Production Example 1 from a part of the
20 obtained PPE mixture liquid (2) was 0.323d L/g.

[0072] <Production Example 3>

A PPE mixture liquid was produced in the same manner as in Production
Example 1 except that dried air was allowed to flow for 110 minutes. The concentration of PPE in the obtained PPE mixture liquid was 13.1 % by mass.
25 The obtained PPE mixture liquid was defined as the PPE mixture liquid (3).

The reduced viscosity of the dried polyphenylene ether particles obtained in the same manner as in Production Example 1 from a part of the obtained PPE mixture liquid (3) was 0.404 dL/g.

[0073] <Production Example 4>

30 A PPE mixture liquid was produced in the same manner as in Production Example 1 except that dried air was allowed to flow for 180 minutes. The concentration of PPE in the obtained PPE mixture liquid was 13.1 % by mass. The obtained PPE mixture liquid was defined as the PPE mixture liquid (4).

The reduced viscosity of the dried polyphenylene ether particles
35 obtained in the same manner as in Production Example 1 from a part of the obtained PPE mixture liquid (4) was 0.609 dL/g.

[0074] [Example 1]

The PPE mixture liquid (1) obtained in Production Example 1 was placed into a jacketed stirred tank 1 and heated by letting a heating medium at 120 °C flow around the jacket. Generated vapor, which contained toluene as the main component, was cooled by a condenser, and the condensed toluene was extracted out of the system. The condensation was continued until the concentration of polymer in the stirred tank reached 35 % by mass. The aforementioned operation was repeated to prepare 10 Kg of a PPE mixture liquid (1), in which the concentration of polymer was 35 % by mass. Similarly, the PPE mixture liquid (2) obtained in Production Example 2 was placed into a jacketed stirred tank 2, and 10 Kg of a PPE mixture liquid (2), in which the concentration of polymer was 35 % by mass, was prepared.

In the subsequent precipitation step, as illustrated in FIGs. 1 and 2, a jacketed precipitation tank, which included a draft tube 2, provided on the outer side thereof with four baffles, and four inclined paddle blades, was used. The capacity of liquid that might reside in the precipitation tank was 1232 mL. Into the precipitation tank, 500 g of toluene and 500 g of methanol were fed and stirred at 1700 rpm. The stirred tank was provided with an overflow line and adapted to expel liquid inside the tank when the amount of the liquid exceeded 1232 mL, which was an overflow level. The circulation flow, flowing toward the tank bottom while swirling in the draft tube and flowing between the draft tube and the wall of the precipitation tank substantially perpendicularly toward the liquid level, was adopted. Regarding feed line positions, the PPE mixture liquid supply port was arranged above the liquid level and inside the draft tube so that the PPE mixture liquid was added to a portion flowing toward the tank bottom during the circulation flow. The poor solvent supply port and the water supply port were arranged between the draft tube and the wall of the precipitation tank above the liquid level. Furthermore, the water supply port was arranged on the inner side of the poor solvent supply port so that water might be dropped after the poor solvent for PPE was dropped (refer to FIG. 1). Three liquid addition nozzles were disposed at different locations above the liquid level, and into the tank, the PPE mixture liquid (1) was added through the first nozzle (i.e., the PPE mixture liquid supply port) at a flow rate of 445 g/minute, methanol was added through the second nozzle (i.e., the poor solvent supply port) at a flow rate of 188 g/minute, and water was added through the third nozzle (i.e., the water supply

port) at a flow rate of 15 g/minute. The temperature of the PPE mixture liquid (1), immediately before being added, was 65 °C. The stirrer was continued to rotate at 1700 rpm. The slurry liquid was expelled at a flow rate of 648 g/minute, and the slurry liquid overflowed and expelled from the precipitation tank was received in a washing tank (1). After continuous operation for approximately 20 minutes, the stirred tank 1 was switched to a stirred tank 2, and the overflowed slurry liquid expelled from the precipitation tank was switched to a washing tank (2). Then, into the precipitation tank, the PPE mixture liquid (2) was added through the aforementioned first nozzle at 386 g/minute, methanol was added thorough the aforementioned second nozzle at 239 g/minute, and water was added through the aforementioned third nozzle at 15 g/minute, to change brands. The temperature of the PPE mixture liquid (2), immediately before being added, was 65 °C. The stirrer was continued to rotate at 1700 rpm. The slurry liquid was expelled at 640 g/minute (with a resident time of approximately 1.9 minutes), and the slurry liquid overflowed and expelled from the precipitation tank was sampled after one substitution after the change in brands, after two substitutions after the change in brands, after three substitutions after the change in brands, and approximately 20 minutes after the change in brands. Thus obtained slurry liquid samples were subjected to measurements according to the aforementioned methods. Table 1 shows results.

Additionally, the slurry liquid was sampled after one substitution after the change in brands, after two substitutions after the change in brands, after three substitutions after the change in brands, and approximately 20 minutes after the change in brands, and a part of each slurry liquid sample was filtrated with use of the basket-type centrifuge (Model 0-15, manufactured by Tanabe Willtec Inc.). After the filtration, excess methanol and a small amount of water were added into the basket-type centrifuge, and filtration was performed again to obtain wet PPE particles. Subsequently, the wet PPE particles were placed into a vacuum dryer and held at 150 °C and at 1 mmHg for 1.5 hours, and the reduced viscosity of thus obtained dried polyphenylene ether particles was measured. The four slurry liquid samples exhibited substantially the same measurement values and demonstrated reliable production of polyphenylene ether even after the change in brands. Meanwhile, the reduced viscosity of the dried polyphenylene ether particles was measured in the same manner as described above for the slurry liquid, which was

obtained by adding, into the precipitation tank, the PPE mixture liquid (2) through the first nozzle at 386 g/minute, methanol through the second nozzle at 239 g/minute, and water through the third nozzle at 15 g/minute from the start. It was confirmed that the measured reduced viscosity was substantially equal to the reduced viscosity of the dried polyphenylene ether after the change in brands.

[0075] [Comparative Example 1]

The same processing as in Example 1 was performed except for the following points. Two liquid addition nozzles were disposed at different locations above the liquid level, and into the tank, the PPE mixture liquid (1) was added through the first nozzle at 445 g/minute, and a mixture solution of methanol and water was added through the second nozzle at 203 g/minute. After continuous operation for approximately 20 minutes, the PPE mixture liquid (2) was added into the tank through the first nozzle at 386 g/minute, and a mixture liquid of methanol and water was added into the tank thorough the second nozzle at 254 g/minute, to change brands. The resulting slurry liquid was subjected to measurements according to the aforementioned methods. Table 1 shows results.

Similarly to Example 1, the slurry liquid was collected after one substitution after the change in brands, after two substitutions after the change in brands, after three substitutions after the change in brands, and approximately 20 minutes after the change in brands, and the reduced viscosity of the dried polyphenylene ether particles was measured. Substantially the same measurement values were obtained. Meanwhile, it was confirmed that the obtained measurement values were substantially equal to the reduced viscosity of the dried polyphenylene ether particles in the slurry liquid, which was obtained by adding the PPE mixture liquid (2) through the first nozzle at 386 g/minute and the mixture liquid of methanol and water through the second nozzle at 254 g/minute from the start.

[0076] [Example 2]

The PPE mixture liquid (3) obtained in Production Example 3 was placed into the jacketed stirred tank 1 and heated by letting the heating medium at 120 °C flow around the jacket. Generated vapor, which contained toluene as the main component, was cooled by the condenser, and the condensed toluene was extracted out of the system. The condensation was continued until the concentration of polymer in the stirred tank reached 40 %

by mass. The aforementioned operation was repeated to prepare 10 Kg of the PPE mixture liquid (3), in which the concentration of polymer was 40 % by mass. Similarly, the PPE mixture liquid (4) obtained in Production Example 4 was placed into the jacketed stirred tank 2, and 10 Kg of a PPE mixture liquid (4), in which the concentration of polymer was 40 % by mass, was prepared.

Into the tank, the PPE mixture liquid (3) was added through the first nozzle at 541 g/minute, methanol was added thorough the second nozzle at 535 g/minute, and water was added through the third nozzle at 27 g/minute. The temperature of the PPE mixture liquid (3), immediately before being added, was 75 °C. After continuous operation for approximately 20 minutes, the stirred tank 1 was switched to the stirred tank 2. Then, into the tank, the PPE mixture liquid (4) was added through the first nozzle at 595 g/minute, methanol was added thorough the second nozzle at 482 g/minute, and water was added through the third nozzle at 26 g/minute, to change brands. The temperature of the PPE mixture liquid (4), before being charged, was 75 °C. Except for the aforementioned points, the same processing as in Example 1 was performed. The obtained slurry liquid was subjected to measurements according to the aforementioned methods. Table 1 shows results.

Similarly to Example 1, the slurry liquid was collected after one substitution after the change in brands, after two substitutions after the change in brands, after three substitutions after the change in brands, and approximately 20 minutes after the change in brands, and the reduced viscosity of the dried polyphenylene ether particles was measured. Substantially the same measurement values were obtained. Meanwhile, it was confirmed that the obtained measurement values were substantially equal to the reduced viscosity of the dried polyphenylene ether particles in the slurry liquid, which was obtained by adding the PPE mixture liquid (4) through the first nozzle at 595 g/minute, methanol through the second nozzle at 482 g/minute, and water through the third nozzle at 26 g/minute from the start.

[0077] [Comparative Example 2]

The same processing as in Example 2 was performed except for the following points. Two liquid addition nozzles were disposed at different locations above the liquid level, and into the tank, the PPE mixture liquid (3) was added through the first nozzle at 541 g/minute, and the mixture solution of methanol and water was added through the second nozzle at 562 g/minute. After continuous operation for approximately 20 minutes, the PPE mixture

liquid (4) was added into the tank through the first nozzle at 595 g/minute, and the mixture liquid of methanol and water was added into the tank thorough the second nozzle at 508 g/minute, to change brands. The obtained slurry liquid was subjected to measurements according to the aforementioned methods. Table 1 shows results.

Similarly to Example 1, the slurry liquid was collected after one substitution after the change in brands, after two substitutions after the change in brands, after three substitutions after the change in brands, and approximately 20 minutes after the change in brands, and the reduced viscosity of the dried polyphenylene ether particles was measured. Substantially the same measurement values were obtained. Meanwhile, it was confirmed that the obtained measurement values were substantially equal to the reduced viscosity of the dried polyphenylene ether particles in the slurry liquid, which was obtained by adding the PPE mixture liquid (4) through the first nozzle at 595 g/minute and the mixture liquid of methanol and water through the second nozzle at 508 g/minute from the start.

[0078]

[Table 1]

					Example 1	Example 2	Comparative Example 1	Comparative Example 2	
Before change in brands	Condensation step	PPE mixture liquid		-	Liquid (1)	Liquid (3)	Liquid (1)	Liquid (3)	
		Good solvent for PPE		-	Toluene	Toluene	Toluene	Toluene	
		Temperature of jacket		°C	120	120	120	120	
		Concentration of polymer		% by mass	35	40	35	40	
	Precipitation step	First nozzle	PPE mixture liquid	g/ minute	445	541	445	541	
			Addition temperature	°C	65	75	65	72	
		Second nozzle	Methanol	g/ minute	188	535	-	-	
			Methanol / water	g/ minute	-	-	203	562	
		Third nozzle	Water	g/ minute	15	27	-	-	
		Overflow	Slurry liquid	g/ minute	648	1103	648	1103	
After change in brands	Condensation step	PPE mixture liquid		-	Liquid (2)	Liquid (4)	Liquid (2)	Liquid (4)	
		Good solvent for PPE		-	Toluene	Toluene	Toluene	Toluene	
		Temperature of jacket		°C	120	120	120	120	
		Concentration of polymer		% by mass	35	40	35	40	
	Precipitation step	First nozzle	PPE mixture liquid	g/ minute	386	595	386	595	
			Addition temperature	°C	65	75	65	75	
		Second nozzle	Methanol	g/ minute	239	482	-	-	
			Methanol / water	g/ minute	-	-	254	508	
		Third nozzle	Water	g/ minute	15	26	-	-	
		Overflow	Slurry liquid	g/ minute	640	1103	640	1103	
Evaluation	(2) Reduced viscosity	After one substitution		dL/ g	0.323	0.609	0.323	0.609	
		After two substitutions		dL/ g	0.323	0.609	0.323	0.609	
		After three substitutions		dL/ g	0.323	0.609	0.323	0.609	
		After approximately 20 minutes		dL/ g	0.323	0.609	0.323	0.609	
	(3) Condition of Scale Adhesion			-	Good	Good	Bad	Medium	
	(4) Fine powder rate		After one substitution		% by mass	12.1	12.3	25.5	20.4
			After two substitutions		% by mass	11.4	11.7	22.7	20.1
			After three substitutions		% by mass	11.2	11.3	19.0	15.9
			After approximately 20 minutes		% by mass	10.9	10.0	12.2	12.1
			Time required for fine powder rate to reach not more than 11.0 % by mass		Minutes	14.5	12.1	21.5	21.9

INDUSTRIAL APPLICABILITY

[0079] Polyphenylene ether obtained by the production method according to the present disclosure has industrial applicability as a material for automobile components, heat resistant components, electronic device components, industrial components, coating agents, insulating films, and so forth.

CLAIMS

1. A method of producing polyphenylene ether, the method comprising:

5 the polymerization step of oxidatively polymerizing a phenolic compound in a polymerization solution containing a good solvent for polyphenylene ether and a catalyst to obtain a polyphenylene ether mixture liquid; and

10 the precipitation step of adding, into a precipitation tank equipped with a stirrer, the polyphenylene ether mixture liquid, a poor solvent for polyphenylene ether, and water to be mixed and precipitating polyphenylene ether to thereby obtain a slurry liquid containing a polyphenylene ether particulate substance, wherein

15 in the precipitation step, the poor solvent for polyphenylene ether and the water are added into the precipitation tank through different pipes, and

in the precipitation step, the amount of the water added is from 0.05 to 30 % by mass with respect to 100 % by mass of the poor solvent for polyphenylene ether.

20 2. The method of producing polyphenylene ether according to claim 1, wherein, in the precipitation step, the ratio by mass of the poor solvent for polyphenylene ether added to the good solvent for polyphenylene ether contained in the polyphenylene ether mixture liquid added, that is to say, the mass of the poor solvent for polyphenylene ether added / the mass of the good
25 solvent for polyphenylene ether contained in the polyphenylene ether mixture liquid added, is from 0.3 to 2.0.

30 3. The method of producing polyphenylene ether according to claim 1 or 2, wherein the phenolic compound comprises 2,6-dimethylphenol.

4. The method of producing polyphenylene ether according to any one of claims 1 to 3, wherein a content rate of polyphenylene ether particles having a particle size of not more than 105 μm in the polyphenylene ether particulate substance is not more than 11 % by mass.

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