



(43) International Publication Date
14 September 2017 (14.09.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/155217 A1

- (51) **International Patent Classification:**
C07C 309/24 (2006.01) *C07C 309/44* (2006.01)
C07C 309/32 (2006.01)
- (21) **International Application Number:**
PCT/KR2017/001584
- (22) **International Filing Date:**
14 February 2017 (14.02.2017)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
10-2016-0029353 11 March 2016 (11.03.2016) KR
- (71) **Applicant:** **CHIROCHEM CO., LTD.** [KR/KR]; 1646,
Yuseong-daero, Yuseong-gu, Daejeon 34054 (KR).
- (72) **Inventors:** **LEE, Ho Seong**; #506-603, 448, Expo-ro,
Yuseong-gu, Daejeon 34049 (KR). **SONG, Jeong Ho**;
#410-2003, 160, Doum 3-ro, Sejong 30063 (KR). **KIM,**
Ho Cheol; #907-303, 151, Maeum-ro, Sejong 30063 (KR).
HAN, Sang Cheol; #301-206, 72, Singeum 1-gil, Gongju-
si, Chungcheongnam-do 32578 (KR). **KIM, Eui Gyun**;
#405-703, 65, Taebong-ro 2-gil, Seocho-gu, Seoul 06764
(KR).
- (74) **Agent:** **PLUS INTERNATIONAL IP LAW FIRM**; 10F,
809, Hanbat-daero, Seo-gu, Daejeon 35209 (KR).

- (81) **Designated States** (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) **Title:** METHOD FOR ACIDIFYING TEREPHTHALYLIDENE DICAMPHOR SULFONIC ACID SALT

(57) **Abstract:** Provided is a method for acidifying a terephthalylidene dicamphor sulfonic acid salt to convert the terephthalylidene dicamphor sulfonic acid salt to a terephthalylidene dicamphor sulfonic acid, and specifically, a method for converting a terephthalylidene dicamphor sulfonic acid salt to a terephthalylidene dicamphor sulfonic acid in the presence of a cation exchange resin, wherein the conversion method of the present invention is a significantly effective method with a high conversion rate by a simple process.



WO 2017/155217 A1

Description

Title of Invention: METHOD FOR ACIDIFYING TEREPHTHALYLIDENE DICAMPHOR SULFONIC ACID SALT

Technical Field

- [1] The present invention relates to a method for acidifying a terephthalylidene dicamphor sulfonic acid salt, and more particularly, to a method for converting a terephthalylidene dicamphor sulfonic acid salt to a terephthalylidene dicamphor sulfonic acid in the presence of a cation exchange resin.

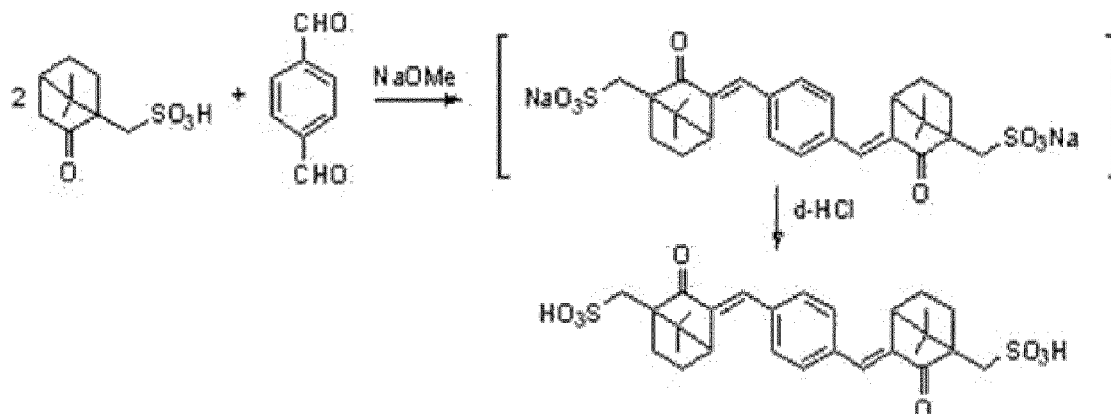
Background Art

- [2] Ultraviolet rays include ultraviolet ray A (320 to 400 nm) and ultraviolet ray B (290 to 320 nm), wherein the ultraviolet ray A occupies 90% or more of the ultraviolet rays. Usually, exposure to the ultraviolet rays occur more frequently during the summertime, for example, the ultraviolet ray B is well-known to be the main cause of erythema, mild burns, etc., while the ultraviolet ray A is known to penetrate the skin and have an effect on cells, and cause photoaging, skin allergy, and even skin cancer, etc. Accordingly, the ultraviolet ray A affects the skin regardless of the season, and thus, more specific care is needed.
- [3] Almost all materials for organic sunscreen that are currently on the market are fat-soluble, and have no solubility to water. Accordingly, cosmetics manufactured using the materials for organic sunscreen that are currently on the market are disadvantageous in that when the cosmetics are applied to the skin, a sense of using is not good. Further, inorganic sunscreens are poorly spread, and causes the skin to feel thick when the sunscreens are applied thereto, which has a bad sense of using.
- [4] On the other hand, a terephthalylidene dicamphor sulfonic acid, which is known from U.S. Patent Publication Nos. 4,585,597 and 5,698,595, is able to protect skin from the ultraviolet ray A to prevent skin aging, and have high solubility to water. Thus, cosmetics including the terephthalylidene dicamphor sulfonic acid have a good spread property to produce products with good sense of using, and are easily washed, which facilitates to maintain pure skin.
- [5] Further, the terephthalylidene dicamphor sulfonic acid is distributed as a 33% aqueous solution as a water-soluble material for organic sunscreen which is able to be produced in various formulations, and is also registered as a 33% aqueous solution.
- [6] A method for producing the terephthalylidene dicamphor sulfonic acid is known in U.S. Patent Publication Nos. 4,585,597 and 4,588,839. As shown in Reaction Scheme 1 below, it is known that 2 moles of 10-dl-camphor sulfonic acid and 1 mole of terephthalaldehyde are subjected to condensation reaction in the presence of a base to obtain

a terephthalylidene dicamphor sulfonic acid salt, and the terephthalylidene dicamphor sulfonic acid salt is acidified by using hydrochloric acid to obtain a terephthalylidene dicamphor sulfonic acid:

[7] [Reaction Scheme 1]

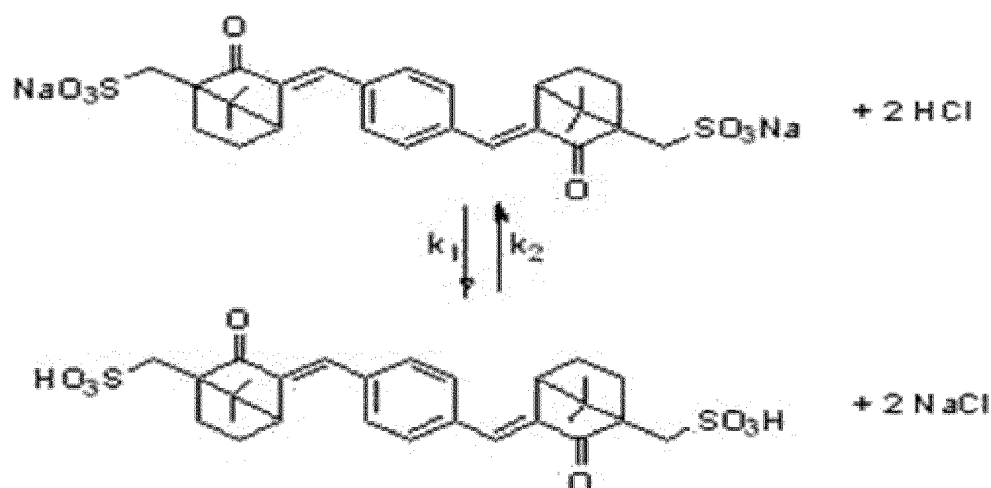
[8]



[9] However, this acidification reaction corresponds to an equilibrium reaction as shown in Reaction Scheme 2 below:

[10] [Reaction Scheme 2]

[11]



[12] Therefore, an excessive amount of acid should be used to achieve the acidification of the terephthalylidene dicamphor sulfonic acid salt, which causes an increase in production cost and requires a separate process for removing the acid used in an excessive amount. In addition, another process for removing water-soluble salts such as NaCl , which is produced as a by-product from the water-soluble terephthalylidene dicamphor sulfonic acid is further required.

[13] Further, even if a substantially excessive amount of acid is used, the acidification reaction into the terephthalylidene dicamphor sulfonic acid is not completed. In other words, according to the existing methods using general inorganic acids or general organic acids, the acidification reaction process is also complicated, and it is economically inefficient, and the terephthalylidene dicamphor sulfonic acid also has a

very low yield.

- [14] Therefore, there is a need for research on a method for acidifying a terephthalylidene dicamphor sulfonic acid salt including a simple and efficient reaction process.

Disclosure of Invention

Technical Problem

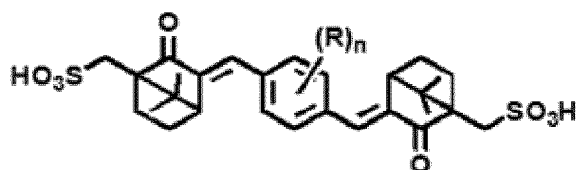
- [15] The present inventors researched an acidification reaction of a terephthalylidene dicamphor sulfonic acid salt to solve the above-described problems, and completed the present invention.
- [16] An object of the present invention is to provide a method for converting a terephthalylidene dicamphor sulfonic acid salt to a terephthalylidene dicamphor sulfonic acid in a very economical manner with high yield and high purity by a simple process.

Solution to Problem

- [17] In one general aspect, there is provided a method for converting a terephthalylidene dicamphor sulfonic acid salt to a terephthalylidene dicamphor sulfonic acid with high yield and high purity by a simple process, which is unlike the related art. The conversion method of the present invention includes converting a terephthalylidene dicamphor sulfonic acid salt represented by Chemical Formula 2 below to a terephthalylidene dicamphor sulfonic acid represented by Chemical Formula 1 below in the presence of a cation exchange resin:

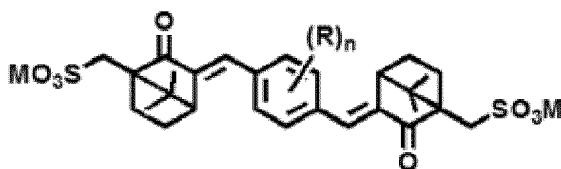
- [18] [Chemical Formula 1]

[19]



- [20] [Chemical Formula 2]

[21]



- [22] in Chemical Formulas 1 and 2,
- [23] M is an alkali metal or $N(R^1)(R^2)(R^3)(R^4)$, and R^1 to R^4 are each independently hydrogen or (C1-C7)alkyl;
- [24] R is (C1-C7)alkyl or (C1-C7)alkoxy; and
- [25] n is an integer of 0 or 1 to 4, and when n is 2 or more, R may be the same as or different from each other.
- [26] In Chemical Formula 2 according to an exemplary embodiment of the present

invention, M may be Na, and n may be 0.

[27] The cation exchange resin according to an exemplary embodiment of the present invention may be an H-type cation exchange resin, and a sulfonated styrene-based resin crosslinked with divinylbenzene, and may have an ion exchange capacity of 1 to 3 meq/ml.

[28] The conversion method according to an exemplary embodiment of the present invention may use an aqueous solution of terephthalylidene dicamphor sulfonic acid salt in which the terephthalylidene dicamphor sulfonic acid salt represented by Chemical Formula 2 is dissolved in water, and the aqueous solution of terephthalylidene dicamphor sulfonic acid salt may be produced by using 500 to 1000 parts by weight of water with respect to 100 parts by weight of the terephthalylidene dicamphor sulfonic acid salt.

Advantageous Effects of Invention

[29] According to the conversion method of the present invention, the terephthalylidene dicamphor sulfonic acid salt is converted to the terephthalylidene dicamphor sulfonic acid in the presence of the cation exchange resin. Therefore, a conversion rate is significantly high even in the presence of a small amount of the cation exchange resin, and thus, almost all amounts of the terephthalylidene dicamphor sulfonic acid salt are acidified, and the produced salts are significantly easily removed.

[30] Further, the conversion method of the present invention is able to obtain the terephthalylidene dicamphor sulfonic acid in an aqueous solution state, and thus, it is easy to obtain a 33% aqueous solution of terephthalylidene dicamphor sulfonic acid, which is possible to be manufactured as products that are able to be immediately distributed without separate processes.

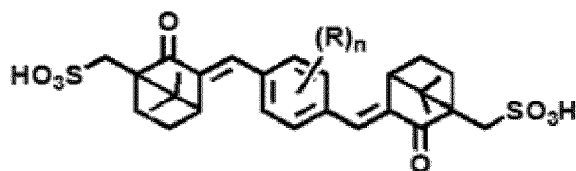
[31] In addition, the conversion method of the present invention is a significantly economical and efficient method since almost all amounts of the terephthalylidene dicamphor sulfonic acid salt are converted to the terephthalylidene dicamphor sulfonic acid, and the used cation exchange resin is able to be recovered and reused.

Best Mode for Carrying out the Invention

[32] The present invention provides a method for converting a terephthalylidene dicamphor sulfonic acid salt represented by Chemical Formula 2 below to a terephthalylidene dicamphor sulfonic acid represented by Chemical Formula 1 below in the presence of a cation exchange resin:

[33] [Chemical Formula 1]

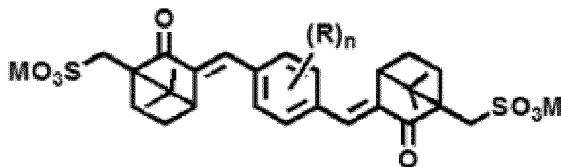
[34]



[35]

[Chemical Formula 2]

[36]



[37]

in Chemical Formulas 1 and 2,

[38]

M is an alkali metal or $N(R^1)(R^2)(R^3)(R^4)$, and R^1 to R^4 are each independently hydrogen or (C1-C7)alkyl;

[39]

R is (C1-C7)alkyl or (C1-C7)alkoxy; and

[40]

n is an integer of 0 or 1 to 4, and when n is 2 or more, R may be the same as or different from each other.

[41]

According to the conversion method of the present invention, almost all amounts of the terephthalylidene dicamphor sulfonic acid salt may be converted by using the cation exchange resin without using an inorganic acid or an organic acid which is the conventional method, and even though a small amount of the cation exchange resin is used as compared to the conventional method of using the inorganic acid or the organic acid, the conversion method is a very economical method due to a high conversion rate.

[42]

Further, salts that are produced as by-products may be easily removed, and thus, a separate process for removing the salts is not required.

[43]

The conversion methods using the inorganic acid or the organic acid known in the art commonly have problems in that excessive amounts of acids are required to be removed and salts corresponding to the respective acids produced as by-products are required to be removed. In addition, an acidification degree may vary depending on kinds of acid used at this time, and accordingly, a content of terephthalylidene dicamphor sulfonic acid is greatly deteriorated by the conventional methods using general acids.

[44]

On the other hand, the conversion method for acidifying the terephthalylidene dicamphor sulfonic acid salt to convert the terephthalylidene dicamphor sulfonic acid salt to the terephthalylidene dicamphor sulfonic acid according to the present invention uses the cation exchange resin, and thus, an excessive amount of acid is not required to be used, a separate process for removing the salt is not required, and the terephthalylidene dicamphor sulfonic acid is obtained in an aqueous solution state, thereby man-

ufacturing a product that is able to be immediately distributed only when a concentration thereof is set to 33%.

- [45] In a specific embodiment, first, a column is filled with the cation exchange resin, and then, the terephthalylidene dicamphor sulfonic acid salt dissolved in water is passed through the column, almost all amounts of the terephthalylidene dicamphor sulfonic acid salt are acidified even using only the cation exchange resin having an equivalent ratio which is much smaller than a used amount of general inorganic acid or general organic acid. In addition, the salts that are produced as by-products are easily removed, and the terephthalylidene dicamphor sulfonic acid in an aqueous solution state is obtained, and thus, a product that is able to be immediately distributed is manufactured only when a concentration thereof is set to 33%.
- [46] Therefore, the conversion method of the terephthalylidene dicamphor sulfonic acid salt to the terephthalylidene dicamphor sulfonic acid of the present invention is a significantly efficient method since the process is very simple and the conversion rate and purity are high.
- [47] The conversion method of the terephthalylidene dicamphor sulfonic acid salt to the terephthalylidene dicamphor sulfonic acid using the cation exchange resin according to an exemplary embodiment of the present invention may acidify the terephthalylidene dicamphor sulfonic acid salt by adding the cation exchange resin to an aqueous solution of terephthalylidene dicamphor sulfonic acid salt. However, preferably, the terephthalylidene dicamphor sulfonic acid salt may be acidified by filling the column with the cation exchange resin and then, passing the aqueous solution of terephthalylidene dicamphor sulfonic acid salt, in view of an increase in yield, simplification of the process, and economical efficiency.
- [48] Compounds represented by Chemical Formulas 1 and 2 described in the present invention include all isomers in cis-trans forms, etc., with respect to each double bond. 「alkyl」 and 「alkoxy」 used in the present invention include both linear and branched forms, and have 1 to 7 carbon atoms, preferably, 1 to 5 carbon atoms, and more preferably, 1 to 3 carbon atoms.
- [49] The alkali metal, which is the M according to an exemplary embodiment of the present invention may be any alkali metal within the scope recognized by those skilled in the art. Examples of the alkali metal may include Li, Na, K, etc., and preferably, Na, in view of a reaction efficiency.
- [50] The R according to an exemplary embodiment of the present invention may be (C1-C5)alkyl or (C1-C5)alkoxy, and preferably (C1-C5)alkyl, and n may be zero when phenylene has no substituent.
- [51] The cation exchange resin according to an exemplary embodiment of the present invention is obtained by binding a sulfonic acid group ($-\text{SO}_3\text{H}$), a carboxyl group

(-COOH), or the like, as an exchange group, to a basic polymer matrix having a network structure, and exchanges cations such as Ca^{2+} , Na^+ , H^+ , etc. The cation exchange resin may be a strongly acidic cation exchange resin or a weakly acidic cation exchange resin, and preferably an H-type cation exchange resin capable of exchanging the cation of H^+ .

[52] Specifically, the cation exchange resin according to an exemplary embodiment of the present invention may include, as the matrix, a copolymer of divinylbenzene and styrene or divinylbenzene and acrylate, or a tetrafluoroethylene polymer and include, as the exchange group, a sulfonic acid or a carboxylic acid, and preferably, the sulfonic acid. More preferably, the cation exchange resin may be a sulfonated styrene-based resin crosslinked with divinylbenzene in view of a reaction efficiency.

[53] Preferably, the cation exchange resin according to an exemplary embodiment of the present invention may be the H-type cation exchange resin, and the sulfonated styrene-based resin crosslinked with divinylbenzene, and may have an ion exchange capacity of 1 meq/ml or more, preferably, 1 to 3 meq/ml, and more preferably 1.5 to 3 meq/ml.

[54] The ion exchange capacity described in the present invention is measured as a number equivalent of ions that may be exchanged, and may be expressed as a polymer volume (an ion exchange capacity per volume, i.e., a volume capacity), and preferably means a milliequivalent of an exchange capacity per a swelling volume of a wetted bed (wetted polymer).

[55] Specifically, when the cation exchange resin is filled in a column and used, the cation exchange resin may have an amount corresponding to 2 to 6 times a volume ratio with respect to a weight of the terephthalylidene dicamphor sulfonic acid salt, and may be regenerated using dilute hydrochloric acid and used repeatedly. Regarding an elution rate of the column, a reaction solution having an amount of 0.2 to 2 times per hour with respect to a volume of the cation exchange resin filled in the column may be passed.

[56] All of the aqueous solution of terephthalylidene dicamphor sulfonic acid eluted from the column may be concentrated to obtain a target compound, i.e., the terephthalylidene dicamphor sulfonic acid, in a brown solid form. In addition, some of water in the aqueous solution of terephthalylidene dicamphor sulfonic acid eluted from the column may be distilled off, and quantified with 0.1 mol of potassium hydroxide to produce a 33% aqueous solution, which is able to be manufactured as a ready-to-market product.

[57] Preferably, the conversion method of the present invention may use an aqueous solution of terephthalylidene dicamphor sulfonic acid salt in which the terephthalylidene dicamphor sulfonic acid salt represented by Chemical Formula 2 is dissolved in water, and the aqueous solution may be produced by using 500 to 1000 parts by

weight, and preferably 700 to 1000 parts by weight of water with respect to 100 parts by weight of the terephthalylidene dicamphor sulfonic acid salt.

[58] Hereinafter, the present invention is described in more detail with reference to the following Examples, but the present invention is not limited by the Examples below.

[59] [Example 1] Production of terephthalylidene dicamphor sulfonic acid

[60] 12 g (20 mmol) of disodium terephthalylidene dicamphor sulfonate was dissolved in 100 ml of water, and then, 200 ml (1.8 meq/ml) of a cation exchange resin, i.e., TRILITE SCR-BH (Samyang Corp.) was added and stirred at room temperature for 5 hours. The resin was removed by filtration, and the product was washed with 50 ml of water. The water was removed by distillation under reduced pressure, and the resulting solid was dried under reduced pressure to obtain 10.4 g (yield: 93.4%) of a terephthalylidene dicamphor sulfonic acid in a brown solid form, as a target compound.

[61] 1 g of the solid that was precisely weighed was dissolved in 50 ml of water, and titrated with 0.1 mol of potassium hydroxide solution (indicator: 1 ml of phenolphthalein solution). Upon calibration with a blank test by using the same method, a content of the terephthalylidene dicamphor sulfonic acid in an acidified solid form was 89.7%.

[62] [Example 2] Production of terephthalylidene dicamphor sulfonic acid

[63] Example 2 was performed in the same manner as in Example 1 except that 12.7 g of dipotassium terephthalylidene dicamphor sulfonate was used, thereby obtaining 10.5 g of terephthalylidene dicamphor sulfonic acid in a brown solid form, as a target compound. A content of the terephthalylidene dicamphor sulfonic acid in the solid form was 89.6%.

[64] [Example 3] Production of terephthalylidene dicamphor sulfonic acid

[65] Example 3 was performed in the same manner as in Example 1 except that 11.9 g of diammonium terephthalylidene dicamphor sulfonate was used, thereby obtaining 10.4 g of terephthalylidene dicamphor sulfonic acid in a brown solid form, as a target compound. A content of the terephthalylidene dicamphor sulfonic acid in the solid form was 89.5%.

[66] [Example 4] Production of terephthalylidene dicamphor sulfonic acid

[67] 20 L (1.8 meq/ml) of a cation exchange resin, i.e., TRILITE SCR-BH (Samyang Corp.) was filled in a column. 4 kg (6.6 mol) of disodium terephthalylidene dicamphor sulfonate dissolved in 28 L of water was eluted at a rate of 9 L/hr. The eluted product was washed with 16 L of water to obtain a reaction solution, and water was removed from the reaction solution by distillation under reduced pressure, and the produced solid was dried under reduced pressure to obtain 3.6 kg (yield: 97%) of a terephthalylidene dicamphor sulfonic acid in a brown solid form, as a target compound.

[68] 1 g of the solid that was precisely weighed was dissolved in 50 ml of water, and

titrated with 0.1 mol of potassium hydroxide solution (indicator: 1 ml of phenolphthalein solution). Upon calibration with a blank test by using the same method, a content of the terephthalylidene dicamphor sulfonic acid was 99.9%.

[69] $^1\text{H-NMR}(\text{CD}_3\text{OD})\delta(\text{ppm})$: 0.83(s, 6H), 1.18(s, 6H), 1.61(m, 2H), 1.71(m, 2H), 2.32(m, 2H), 2.73(m, 2H), 2.98(d, 2H), 3.18(m, 2H), 3.48(d, 2H), 7.22(s, 2H), 7.59(s, 4H)

[70] [Example 5] Production of 33% aqueous solution of terephthalylidene dicamphor sulfonic acid

[71] Only two-thirds of water was removed from the resulting liquid obtained after practicing the same method as in Example 4 to obtain 10.7 kg of a brown aqueous solution. Quantification was performed as the same as in Example 4 to confirm a content, thereby obtaining a 33% aqueous solution of terephthalylidene dicamphor sulfonic acid.

[72] [Comparative Example 1] Acidification using hydrochloric acid

[73] 12 g (20 mmol) of disodium terephthalylidene dicamphor sulfonate was dissolved in 30 ml of water and 30 ml of concentrated hydrochloric acid (360 mmol). After refluxing for 1 hour, the product was concentrated and cooled, and the resulting solid was filtered. The filtered solid was washed with 6N hydrochloric acid, dried under reduced pressure at 80, and dried under reduced pressure at 100 to obtain 7.02 g of a solid.

[74] 1 g of the solid that was precisely weighed was dissolved in 50 ml of water, and titrated with 0.1 mol of potassium hydroxide solution (indicator: 1 ml of phenolphthalein solution). Upon calibration with a blank test by using the same method, a content of the terephthalylidene dicamphor sulfonic acid in the solid acidified with hydrochloric acid was 33.6%.

[75] [Comparative Example 2] Acidification using methanesulfonic acid

[76] 6.06 g (10 mmol) of disodium terephthalylidene dicamphor sulfonate was dissolved in 50 ml of water, 17.29 g (180 mmol) of methanesulfonic acid was added and stirred at room temperature for 2 hours. The reaction solution was concentrated, and water was completely removed with 100 ml of toluene, using a Dean-Stark apparatus. A solid produced by cooling was filtered, and the filtered solid was washed with toluene, dried under reduced pressure at 80, and dried under reduced pressure at 100 to obtain 7.68 g of a solid.

[77] Upon quantification as in Comparative Example 1 in consideration that sodium methanesulfonate was included, a content of the terephthalylidene dicamphor sulfonic acid in the solid acidified with methanesulfonic acid was about 22.5%.

[78] [Comparative Example 3] Acidification using trifluoroacetic acid

[79] Comparative Example 3 was performed in the same manner as in Comparative

Example 2 except that 20.52 g (180 mmol) of trifluoroacetic acid was added after 6.06 g (10 mmol) of disodium terephthalylidene dicamphor sulfonate was dissolved in 50 ml of water, thereby obtaining 5.91 g of a solid.

[80] Upon quantification as in Comparative Example 1 in consideration that sodium trifluoroacetate was included, a content of the terephthalylidene dicamphor sulfonic acid in the solid acidified with trifluoroacetic acid was about 7.5%.

[81] [Comparative Example 4] Acidification using sulfuric acid

[82] Comparative Example 4 was performed in the same manner as in Comparative Example 2 except that 8.82g (90 mmol) of sulfuric acid was added after 6.06 g (10 mmol) of disodium terephthalylidene dicamphor sulfonate was dissolved in 50 ml of water, thereby obtaining 6.44g of a solid.

[83] Upon quantification as in Comparative Example 1 in consideration that sodium sulfate was included, a content of the terephthalylidene dicamphor sulfonic acid in the solid acidified with sulfuric acid was about 19.7%.

[84] It could be appreciated that the conversion rate of the terephthalylidene dicamphor sulfonic acid produced in Examples 1 to 4 was much higher than that of Comparative Example 1. Further, Examples 1 to 4 did not require a separate process for removing the salts, and thus, the process was simpler and the purity was higher than that of Comparative Example 1.

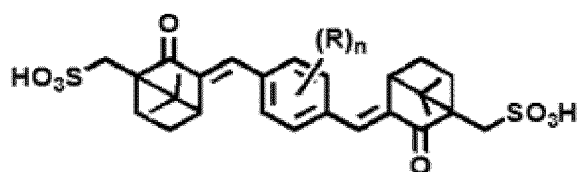
[85] In addition, it could be appreciated that in Comparative Examples 2 to 4, the conversion rate was low, and the terephthalylidene dicamphor sulfonic acid including the salts corresponding to respective organic acid and inorganic acid was obtained, and thus, the purity was low and the separate process for removing the salts was required.

[86] In conclusion, it could be appreciated that the conversion method of the terephthalylidene dicamphor sulfonic acid salt to the terephthalylidene dicamphor sulfonic acid in the presence of the cation exchange resin of the present invention not only has a higher conversion rate and a higher purity, but also has a simpler conversion process, which is an economical and efficient method as compared to the conventional methods.

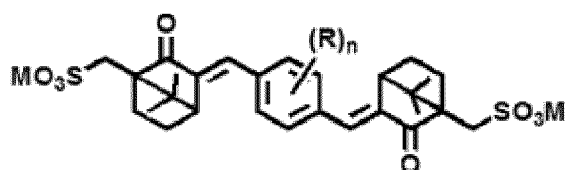
Claims

- [Claim 1] A method for acidifying a terephthalylidene dicamphor sulfonic acid salt, comprising:
converting a terephthalylidene dicamphor sulfonic acid salt represented by Chemical Formula 2 below to a terephthalylidene dicamphor sulfonic acid represented by Chemical Formula 1 below in the presence of a cation exchange resin:

[Chemical Formula 1]



[Chemical Formula 2]



in Chemical Formulas 1 and 2,

M is an alkali metal or $N(R^1)(R^2)(R^3)(R^4)$, and R^1 to R^4 are each independently hydrogen or (C1-C7)alkyl;

R is (C1-C7)alkyl or (C1-C7)alkoxy; and

n is an integer of 0 or 1 to 4, and when n is 2 or more, R may be the same as or different from each other.

- [Claim 2] The method of claim 1, wherein M is Na, and n is 0.
- [Claim 3] The method of claim 1, wherein the cation exchange resin is an H-type cation exchange resin.
- [Claim 4] The method of claim 3, wherein the cation exchange resin is a sulfonated styrene-based resin crosslinked with divinylbenzene.
- [Claim 5] The method of claim 4, wherein the cation exchange resin has an ion exchange capacity of 1 to 3 meq/ml.
- [Claim 6] The method of claim 1, wherein the method uses an aqueous solution of terephthalylidene dicamphor sulfonic acid salt in which the terephthalylidene dicamphor sulfonic acid salt represented by Chemical Formula 2 is dissolved in water.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2017/001584**A. CLASSIFICATION OF SUBJECT MATTER****C07C 309/24(2006.01)i, C07C 309/32(2006.01)i, C07C 309/44(2006.01)i**

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C 309/24; C07C 143/52; C07C 51/347; A61K 7/42; C07C 143/78; C07C 67/30; A61K 2/44; A61K 31/185; C07C 309/32; C07C 309/44

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & STN(Registry, Caplus) & Google & Keywords: terephthalylidene dicamphor sulfonic acid, salt, cation exchange resin**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4585597 A (LANG, G. et al.) 29 April 1986 See claim 1; columns 9, 10, example 19; column 11, lines 3-7; and column 13, line 65 - column 14, line 16.	1-6
Y	US 3439026 A (PATTON, J. W. et al.) 15 April 1969 See claim 1; and column 2, lines 15, 16.	1-6
A	US 4588839 A (LANG, G. et al.) 13 May 1986 See claim 1; column 5; and column 20, line 64 - column 21, line 17.	1-6
A	US 2009-0076297 A1 (BOGAN, JR., L. E. et al.) 19 March 2009 See the whole document.	1-6
A	US 5698595 A (BOELLE, J. P. et al.) 16 December 1997 See the whole document.	1-6



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

17 May 2017 (17.05.2017)

Date of mailing of the international search report

17 May 2017 (17.05.2017)

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea



Facsimile No. +82-42-481-8578

Authorized officer

LEE, Ki Cheul

Telephone No. +82-42-481-3353



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2017/001584

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4585597 A	29/04/1986	CA 1204779 A FR 2528420 A1 JP 03-042255 B2 JP 59-005136 A US 4654434 A US 4663088 A	20/05/1986 16/12/1983 26/06/1991 12/01/1984 31/03/1987 05/05/1987
US 3439026 A	15/04/1969	None	
US 4588839 A	13/05/1986	CA 1211451 A JP 03-032539 B2 JP 59-031756 A	16/09/1986 13/05/1991 20/02/1984
US 2009-0076297 A1	19/03/2009	CN 101391949 A CN 101391949 B EP 2036879 A1 EP 2036879 B1 JP 2009-067775 A JP 2014-015474 A KR 10-0999425 B1 KR 10-2009-0029164 A TW 200914413 A TW I368608 B US 7754916 B2	25/03/2009 05/09/2012 18/03/2009 16/06/2010 02/04/2009 30/01/2014 09/12/2010 20/03/2009 01/04/2009 21/07/2012 13/07/2010
US 5698595 A	16/12/1997	CN 1116924 A EP 0671160 A1 EP 0671160 B1 FR 2717078 A1 JP 08-020511 A JP 2930533 B2 KR 10-0176280 B1	21/02/1996 13/09/1995 07/08/1996 15/09/1995 23/01/1996 03/08/1999 20/03/1999