



(51) International Patent Classification:

C08F 6/02 (2006.01) *C08J 3/09* (2006.01)
C08F 6/12 (2006.01) *C08L 25/18* (2006.01)

(21) International Application Number:

PCT/US2014/048342

(22) International Filing Date:

28 July 2014 (28.07.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/859,397 29 July 2013 (29.07.2013) US

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(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, 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, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, 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, 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: POLYMER PURIFICATION

(57) Abstract: A process for removing silicon impurities from a polymer comprising the steps of (1) dissolving said polymer in a first solvent to make a solution, (2) adding a non-solvent to said solution, and (3) contacting said solution containing said non-solvent with a mixture of acidic cation and basic anion exchange resins, for a sufficient period of time to substantially remove all of said silicon from the solution of step (2).



TITLE

POLYMER PURIFICATION

BACKGROUND OF THE INVENTION

Polymers, including copolymers and terpolymers, when produced from various processes have metal impurities which must be removed or substantially reduced if the polymers are to be used in photoresist applications. Typically, they contain small quantities of a base catalyst, including their sodium salts, which is undesirable in the final polymer when used as a photoresist material. The polymer generally undergoes further processing to remove the residue base catalyst material before its ultimate use. The additional processing usually entails the contact of the polymer containing the base material with an ion exchange resin; this is exemplified in US 7, 312, 281 and US 5,288,850. However, the type of ion exchange resin which is suitable to remove the base catalyst material does not remove all the impurities from the polymer. The main impurity remaining is silicon which is also undesirable if the polymer is to be used as a photoresist material. Other sources of silicon contamination can be from glass reactors, equipment, and the like. The subject of this invention thus pertains to a method of purifying the polymer containing silicon in order to remove this silicon material therefrom.

Davidson, in U. S. Patent 5,945,251, discloses a method of purifying polyhydroxystyrene polymers by adding an amine, a hydrophilic solvent, a hydrophobic solvent, and water to the polymer; separating the aqueous phase; then removing the hydrophilic solvent and the hydrophobic solvent to form the purified polymer.

Zempini, et al, in U.S. 5,5789,522 and U.S. 5,939,511, extracts impurities from phenolic resin by dissolving the resin in a photoresist solvent and extracting the water-soluble impurities therefrom.

U.S. 5,288,850 and U.S. 5,284,930 disclose the use of an ion exchange material to remove impurities such as sodium and like impurities, but not silicon.

A need remains for processes for the efficient and cost effective removal of silicon from polymers.

SUMMARY OF THE DISCLOSURE

The present invention provides a novel process for removing silicon impurities from polymers that have been produced by prior art processes. For example, vinylphenol polymers are very useful materials as photoresists, integrated circuit packaging materials, printed circuit boards, and the like. In order to cope with the recent miniaturization trend in these electronic devices requiring high precision and high electronic performances, all metal contents in materials used therein must be minimized. Accordingly, when such polymers are used in such electronic devices, reduction in contents of these metal impurities, such as silicon in the polymers prepared by conventional processes, to a minimum degree is strongly desired. The object of the present invention is to provide a readily applicable and economical process for the removal of silicon at a high degree of reduction from polymers.

As a result of extensive studies in order to achieve the above object, the present inventors have found that the above object can easily be achieved by contacting the polymer with a solvent and an a non-solvent to form a solution and thereafter contacting the solution with a mixture of an acidic cation and basic anion exchange resin. This finding has led to the completion of the present invention.

Thus, the gist of the present invention resides in a process for removing silicon from a polymer characterized by mixing said polymer with a solvent and a non-solvent to make a solution and contacting said solution with a mixture cation and anion exchange resins.

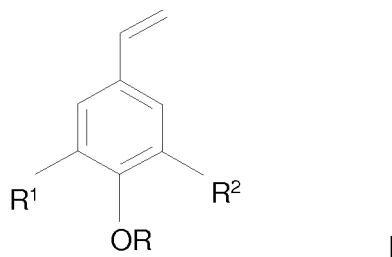
The polymers to be treated are any polymer or polymer blend; however, some exemplary polymers that are susceptible to treatment with the method of this invention are polymers of 4-acetoxystyrene. The 4-acetoxystyrene derived polymers are then transesterified to 4-hydroxyphenyl-containing polymers useful in paints, resins, thickening agents, and in photoresist compositions. As previously described in the prior art, the polymer after polymerization, with or without the presence of a chain transfer agent(CTA) such as those that are described in WO 98 01478 and WO 99 31144, is further processed, for example, separated from the solvent by filtration, centrifugation,

decantation, or the like. After the polymer is prepared, the polymer is subject to the present invention process to remove silicon impurities.

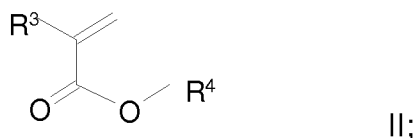
As described herein, any polymer may be used as the starting material for the removal of silicon therefrom. In addition to the polymers described below, polymers to be treated, include without limitation, (1) the high chi polymers described in provisional patent applications serial nos. 61/597530; 61/597558; and 61/597583, all filed on February 10, 2012; (2) the copolymers or block copolymers described in US 6,136,500; (3) the fluorinated polymers described in US 7,696,292 and US 8,034,534; and (4) the poly (meth) acrylates described in US 6,777,511. All of the references described herein are incorporated herein (in toto) by reference.

DETAILED DESCRIPTION OF THE INVENTION

This invention provides a process for the silicon removal from a wide variety of polymers, but for exemplary purposes, we have chosen those polymers derived from the monomer I,



wherein R is either $-C(O)R^5$ or $-R^5$; as a homopolymer or a copolymer typically with one or more of the following monomers:
an acrylate monomer having the formula II,



and/or with one or more ethylenically unsaturated copolymerizable monomers (EUCM) selected from the group consisting of styrene, 4-methylstyrene, styrene alkoxide wherein the alkyl portion is $C_1 - C_5$ straight or branch chain, tert.-butylstyrene, 4-tert.-butoxystyrene,

cyclohexyl acrylate, tert.-butyl acrylate, tert.-butyl methacrylate, maleic anhydride, dialkyl maleate, dialkyl fumarate and vinyl chloride,

wherein:

i) R^1 and R^2 are the same or different and independently selected from the group consisting of:

hydrogen;

fluorine, chlorine or bromine;

alkyl or fluoroalkyl group having the formula $C_nH_xF_y$ where n is an integer from 1 to 4, x and y are integers from 0 to $2n+1$, and the sum of x and y is $2n+1$; and

phenyl or tolyl;

ii) R^3 is selected from the group consisting of:

hydrogen; and

methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl or tert.-butyl;

iii) R^4 is methyl, ethyl, n-propyl, iso-propyl, n-butyl, i-butyl, tert.-butyl, t-amyl, benzyl,

cyclohexyl, 9-anthracenyl, 2-hydroxyethyl, cinnamyl, adamantyl, methyl or

ethyl or hydroxyl adamantyl, isobornyl, 2-ethoxyethyl, n-heptyl, n-hexyl,

2-hydroxypropyl, 2-ethylbutyl, 2-methoxypropyl, 2-(2-methoxyethoxy),

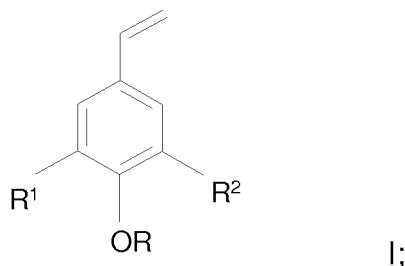
oxotetrahydrofuran, hydroxy-trimethylpropyl, oxo-oxatricyclo non yl, 2-

naphthyl, 2-phenylethyl, phenyl, and the

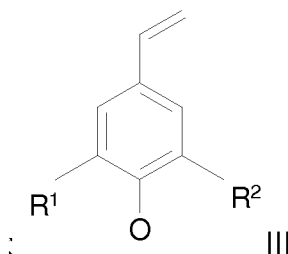
like; and

iv) R^5 is C_1 - C_4 alkyl,

typically manufactured by subjecting a monomer of formula I,



or a monomer of the formula I and/or monomer II, and/or one or more of said copolymerizable monomers (EUCM) to suitable polymerization conditions in a first solvent and in the presence of a free radical initiator at suitable temperature for a sufficient period of time to produce a polymer of corresponding composition. The polymer is then transesterified to a polymer containing the monomer of formula III:



by (1) subjecting said polymer to transesterification conditions in said first solvent in the presence of catalytic amounts of a base catalyst at suitable temperature such that the transesterified by-product ester formed is continuously removed from the reaction mixture to form the homopolymer of I or the copolymer of I, and/or II, and/or said copolymerizable monomer, (EUCM) or (2) subjecting the polymer to acidic hydrolysis with a strong acid. The polymer is then optionally passed through an ion-exchange bed to remove said base or acid catalyst.

It is also within the scope of the present invention to prepare a homopolymer of Formula I from the monomer of Formula III. As another embodiment, polyhydroxystyrene (PHS) can be prepared from acetoxystyrene monomer (ASM).

The scope of the present invention thus covers (a) a homopolymer of Formula I derived from Formula III monomer; (b) a copolymer derived from Formula II and Formula III monomers; (c) a copolymer derived from Formula III monomers and the EUCM; and (d) a terpolymer derived from monomers of Formula II, Formula III, and EUCM. It is also within the scope of the present invention to use other monomers such as norbornene monomers, fluorine monomers and the like to form a polymer product to be treated by the novel processes of the present invention.

In conjunction with Formula II (an acrylate monomer) set forth herein, some preferred acrylate monomers are (1) MAA-methyl adamantyl, (2) MAMA-methyl adamantyl methacrylate, (3) EAA-ethyl adamantyl acrylate, (4) EAMA- ethyl adamantyl methacrylate, (5) ETCDA- ethyl tricyclodecanyl acrylate, (6) ETCDMA- ethyl tricyclodecanyl methacrylate, (7) PAMA- propyl adamantyl methacrylate, (8) MBAMA- methoxybutyl adamantyl methacrylate, (9) MBAA- methoxybutyl adamantyl acrylate, (10) isobornylacrylate, (11) isobornylmethacrylate, (12) cyclohexylacrylate, and (13) cyclohexylmethacrylate. Other preferred acrylate monomers which can be used are (14) 2-methyl-2-adamantyl methacrylate; (15) 2-ethyl-2-adamantyl methacrylate; (16) 3-hydroxy-1-adamantyl methacrylate; (17) 3-hydroxy-1-adamantyl acrylate; (18)

2-methyl-2-adamantyl acrylate; (19) 2-ethyl-2-adamantyl acrylate; (20) 2-hydroxy-1, 1, 2-trimethylpropyl acrylate; (21) 5-oxo-4-oxatricyclo-non-2-yl acrylate; (22) 2-hydroxy-1, 1,2-trimethylpropyl 2-methacrylate; (23) 2-methyl-2-adamantyl 2-methacrylate; (24) 2-ethyl-2-adamantyl 2-methacrylate; (25) 5-oxotetrahydrofuran-3-yl acrylate; (26) 3-hydroxy-1-adamantyl 2-methylacrylate; (27) 5-oxotetrahydrofuran-3-yl 2-methylacrylate; (28) 5-oxo-4-oxatricyclo-non-2-yl 2 methylacrylate.

Additional acrylates and other monomers that may be used in the present invention with the substituted styrene and CTA to form various copolymers include the following materials:

Monodecyl maleate; 2-hydroxy ethyl methacrylate; isodecyl methacrylate; hydroxy propyl methacrylate; isobutyl methacrylate; lauryl methacrylate; hydroxy propyl acrylate; methyl acrylate; t-butylaminoethyl methacrylate; isocyanatoethyl methacrylate; tributyltin methacrylate; sulfoethyl methacrylate; butyl vinyl ether blocked methacrylic acid; t-butyl methacrylate; 2-phenoxy ethyl methacrylate; acetoacetoxyethyl methacrylate; 2-phenoxy ethyl acrylate; 2-ethoxy ethoxy ethyl acrylate; B-carboxyethyl acrylate; maleic anhydride; isobornyl methacrylate; isobornyl acrylate; methyl methacrylate; ethyl acrylate; 2-ethyl hexyl methacrylate; 2-ethyl hexyl acrylate; glycidyl methacrylate; N-butyl acrylate; acrolein; 2-diethylaminoethyl methacrylate; allyl methacrylate; vinyl oxazoline ester of tall meso methacrylate; itaconic acid; acrylic acid; N-butyl methacrylate; ethyl methacrylate; hydroxy ethyl acrylate; acrylamide oil; acrylonitrile; methacrylic acid; and stearyl methacrylate. Some preferred acrylate monomers are (1) MAA-methyl adamantyl, (2) MAMA-methyl adamantyl methacrylate, (3) EAA-ethyl adamantyl acrylate, (4) EAMA- ethyl adamantyl methacrylate, (5) ETCDA- ethyl tricyclodecanyl acrylate, (6) ETCDMA- ethyl tricyclodecanyl methacrylate, (7) PAMA- propyl adamantyl methacrylate, (8) MBAMA-methoxybutyl adamantyl methacrylate, (9) MBAA- methoxybutyl adamantyl acrylate, (10) isobornylacrylate, and (11) isobornylmethacrylate.

In one embodiment of the present invention, co-polymers having polyhydroxystyrene (PHS) and/or poly (4-hydroxystyrene), and one or more of the above acrylate monomers are some of the materials that can be purified by the novel processes of the present invention. It is to be understood that the purification processes set forth herein

can be used to purify other monomer classes which have been polymerized. These monomer classes include, without limitation, vinyl acetate, acrylics, styrenes, styrenes-acrylics, olefins such as ethylene and propylene, acrylonitrile, maleic anhydride, and mixtures thereof. The polymerization (including the transesterification and catalyst removal) of these monomers can be carried out by the processes described in US 7,148,320 and US 7,312,281, which are incorporated herein by reference.

For example, in the transesterification step, the polymer from the polymerization step is subjected to said transesterification conditions in an alcoholic solvent in the presence of catalytic amounts of a base catalyst. (It is to be understood that after the polymerization step set forth above, there still remains some alcoholic solvent mixed with the desired polymer, but additional solvent can be added in order to keep the polymer in a fluid state. The transesterification could be conducted without the addition of this additional solvent, but the reaction would be more difficult and possibly take longer.) The base catalyst is such that it will not substantially react with said alkyl acrylate monomer II, or with said co-polymerizable monomers (EUCM). The base catalyst is either an alkalic metal hydroxide or an alkalic metal alkoxide. The base catalyst is selected from the group consisting of lithium hydroxide, lithium methoxide, lithium ethoxide, lithium isopropoxide, sodium hydroxide, sodium methoxide, sodium ethoxide, sodium isopropoxide, potassium hydroxide, potassium methoxide, potassium ethoxide, potassium isopropoxide, cesium hydroxide, cesium methoxide, cesium ethoxide, cesium isopropoxide, and combinations thereof.

If a hydrolysis is utilized to effect removal of the phenol blocking group, the acid should be a member of the strong acids, as for example hydrochloric acid, hydrobromic acid, sulfuric acid, or the like.

After the polymer is formed and there is used a metal (for example, sodium) containing catalyst, the polymer is subjected to an ion exchange resin treatment to remove the sodium metal ions.

It is be noted that the prior art cited above discloses that the polymerization and/or transesterification steps are carried out on an anhydrous basis (i.e. < about 5,000 ppm - parts per million-water).

Thus and according to the method of this invention, after polymerization , transesterification, and catalyst removal from the polymer, the polymer containing the silicon impurities, about 100 to about 1000 ppb, is subjected to the novel process which then provides a substantially purified polymer having substantially little, if any, silicon materials or impurities therein, that is less than about 75 ppb (parts per billion).

At this point, it has been found that there exists substantial quantities of silicon in the polymer material and which must be removed if the polymer is to be used as a photoresist material.

Thus, the uniqueness of the present invention is the provision of an process for the removal of the silicon impurity from the polymer. The polymer containing these silicon impurities is mixed with a solvent and a non-solvent to provide a solution which is then contacted with a mixture of an acidic cation and a basic anion exchange resin.

Thereafter, the polymer solution is separated from the exchange resin and can be precipitated into water, filtered and dried, or the polymer solution can undergo a solvent swap with a photoresist solvent and directly used as such as photoresist solution.

The removal of silicon from the polymer solution according to the present invention comprises dissolving the polymer into a first solvent and adding a non-solvent to make a solution and contacting the solution with blend of an acidic cation and a basic anion exchange resin. Regarding the first solvent, solvents which are capable of dissolving polymers, stable without being deteriorated or decomposed when contacted with ion exchange resin, and unreactive with polymers, can be selected. Although depending on the types of polymers and the operation conditions, solvents satisfying these requirements include, but not limited to, alcohols, e.g., methanol, ethanol, isopropanol, etc.; esters, e.g., ethyl acetate, ethyl lactate, etc.; cyclic ethers, e.g., tetrahydrofuran, dioxane, etc.; ketones, e.g., acetone, methyl ethyl ketone, etc.; alkylene glycol ethers or esters, e.g., ethylene glycol ethyl ether, ethylene glycol ethyl ether acetate, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, propylene glycol monomethyl ether acetate, etc.; and the like.

The first solvent is generally an alcohol having 1 to 4 carbon atoms and is selected from the group consisting of methanol, ethanol, propanol, isopropanol, t-butanol, and combinations thereof. However, other solvents such as ethyl acetate, methyl ethyl

ketone, tetrahydrofuran , and the like can be used and this depends upon the polymer. The amount of solvent used is not critical and can be any amount which accomplishes the desired end result.

It is also preferred in both the use of the first solvent and non solvent that these materials/liquids have a boiling point that is lower than the boiling point of the photoresist compatible solvent, herein after described.

However, the quantity of first solvent used is generally from about 20 percent to about 50 percent by weight of the total weight of the resultant solution.

The quantity of polymer dissolved in the first solvent is from about 10 per cent to about 50 percent by weight of the total weight of the resultant solution.

The non-solvent is selected from the group consisting of water, hexanes, heptanes, toluene, and mixtures thereof. Generally, water is the preferred non-solvent and is present in the resultant solution in an amount of from 0.0001 percent to about 1.00 percent by weight of the total weight of the resultant solution. The resultant solution, containing the non- solvent, thus provides the silicon in the form of a silica species selected from at least one of soluble ionic bisilicates, monosilicic acid, soluble polymeric silica or colloidal silica. Water is the preferred non-solvent since it provides a mechanism whereby the silicon is in an ionic form, thus making it suitable for sequestering with the ion exchange resins/material, described herein. This is a theory regarding the silicon in the resultant solution containing said non solvent and the inventors do not want to be limited in any way by this theory.

As mentioned above, some polymer solutions already contain some quantities of water therein and hence there is no need to add the non-solvent to the polymer solution, since the said first solvent inherently contains sufficient quantities of said non-solvent therein .

The first solvent is used for dissolving the polymers generally in an amount to make the viscosity of the resulting solution 10 poise or less at the temperature at which it is contacted with the mixture of ion exchange resins. Lowering the viscosity of the solution by the use of a large amount of first solvent can make the rate of silicon

removal higher. According, the viscosity of the solution less than about 1 poise can remove silicon at a remarkably high level. Therefore, a preferable amount of first solvent is the amount sufficient to make the viscosity of the solution 1 poise or less at the temperature at which it is contacted with the ion exchange resins. There are no specific limitations as to the larger side amounts of the solvents used, although the use of an excessive amount is not economical. Thus, the amount of the solvents to make the viscosity about 0.1 poise is generally and fully sufficient, and therefore, preferable viscosity range is between 0.1 and 1 poise.

Commercially available acidic cation and basic anion exchange resins are used in the present invention. Among the mixture of resins, cation exchange resins of sulfonated styrene-divinylbenzene cross-linked polymer are preferred. There are two types of strongly acidic cation exchange resins, one is the porous type made of porous resins and the other one is the gel type which is made of nonporous resins. The gel type can be used in the present invention as well as the porous-type. In the mixture of resins, basic anion exchange resins are used together with the acidic cation exchange resin. These mixed ion exchange resins, (that is, the acidic cation and basic anion exchange resin) are used and are commercially under the trademark , Amberlite TM IRN 150 ion exchange resin.

It is desirable to treat or wash the ion exchange resins with deionized (DI) water, and then a first solvent to remove residual water prior to use in order to control the amount of water and any impurities therein.

The batch agitation method and the fixed-bed flow method are applicable to the contact of polymer solution with the mixed acidic cation and basic anion exchange resins, with the latter being more preferable.

The period of time required for the contact is usually in the range in terms of liquid hourly space velocity (LHSV) of 0.2 to 5 hr.sup.-1 on the basis of the solution of the polymer, in the case of the fixed-bed flow method, even though there are no specific need that the range must be maintained. The temperature at which the materials are contacted is preferably 0 C to 100 C, and more preferably 10 C to 50 C. The rate of

silicon removal is lowered at a low temperature, since the solution of polymers has a high viscosity at low temperatures, requiring a large amount of solvent to reduce the viscosity to a suitable range. On the other hand, a higher temperature may impair qualities of the polymers or the solvent, may cause release of acids from the acidic cation exchange resin, or may deteriorate the acidic cation exchange resin, even though the low viscosity requirement for easy removal of silicon is satisfied at a high temperature.

Microfilters may be provided before and after the ion exchange resin treatment in order to remove by filtration insoluble impurities contained in the polymers or fine particles which might be flown out from the ion exchange resins; however, as described below, the use of microfilters to remove silicon from the polymer did not work..

The polymers from which silicon has been removed by the process described above can be directed to various uses as a photoresist solution, described below.

Alternatively, the polymers can be precipitated by pouring the solution into purified water, collection of the precipitate by filtration, and drying the precipitate or a process comprising heat-treating the solution under vacuum to remove the solvent and drying the polymer.

In another embodiment of the present invention, there is provided a solvent swap after the purification step described above. In this solvent swap step, the first solvent (containing the purified polymer) is then exchanged with an aprotic/organic solvent which is a photoresist compatible solvent, and the first solvent is removed by distillation. The term "photoresist compatible solvent" is one that is commonly used in the photoresist art as demonstrated in US 5,945,251 (column 4, lines 17-27), US 5,789,522 (column 13, lines 7-18) and US 5,939,511, all of which mention PGMEA. All of these patents are incorporated herein by reference in toto. This photoresist compatible solvent can be a member selected from the group glycol ethers, glycol ether acetates and aliphatic esters having no hydroxyl or keto group. Examples of the solvent include glycol ether acetates such as ethylene glycol monoethyl ether acetate and propylene glycol monomethyl ether acetate (PGMEA), and ethyl lactate.

The silicon content contained in polymers can be reduced by the process of the present invention. In particular, when the process is applied at a viscosity of the solutions of 1 poise or less, all silicon impurities can be reduced to a concentration of several ppb, generally less than about 75 ppb. The high purity products manufactured by the process of the present invention is suitably used as materials for precision devices, especially for electronic devices, such as photoresists, integrated circuit packaging materials, printed circuit boards, adhesives, and the like.

This invention is further illustrated by the following examples that are provided for illustration purposes and in no way limits the scope of the present invention.

EXAMPLE 1

Into a 50 liter reactor fitted with an agitator, there were charged 8 kilograms of polymer (poly hydroxy styrene homopolymer), 19 kilograms of methanol, and 0.189 kilograms of water. The ingredients were agitated for 2 hours to make a solution analyzed as 29.55%, by weight, polymer, 0.70%, by weight, water, and containing 274 ppb silicon. The polymer was prepared by the process set forth in US 7,312,281.

Separately, there was prepared a 500 gram Amberlite™ IRN 150 ion exchange resin bed, containing both acidic cation and basic anion resins, by adding the Amberlite resin to a two inch column having a length of 24 inches. The Amberlite material was washed with 5 kilograms of deionized water followed by a rinse with 20 kilograms of methanol to remove the residual water.

The polymer solution/mixture described above was passed through the rinsed Amberlite™ IRN150 column at a flow rate of 1.2 kilograms per hour. The process was carried out at ambient temperature, 20C. A post ion exchange sample was collected every hour for subsequent silicon analysis. The post ion exchange samples were then further precipitated into ten times its volume of water followed by vacuum drying. The

dried polymer samples were submitted for silicon analysis and the results are set forth below.

Operational time, hours running	Silicon analyzed, ppb
0 (initial)	274
1	27
7	39
11	24
17	25
21	23
23	21

The silicon analyses were conducted by **graphite furnace atomic absorption** spectrometry (GFAAS), also known as Electrothermal Atomic Absorption Spectrometry (ETAAS); note ASTM E1184-10 and ASTM D3919-08.

EXAMPLE 2

Example 1 above was repeated with the following exceptions. The Amberlite [™] IRN 150 ion exchange resin was contained in an one inch column, 24 inches in height. The resin was first rinsed with methanol washes (20 milliliters) three times to insure that there was substantially no silicon present. The methanol samples were combined and analyzed for silicon content which was found to be 2 ppb, indicating that there was no substantial silicon pickup from the resin itself. The next procedure was to analyze a new polymer in solution (prior to the resin treatment) for silicon content. This was found to have 85ppb. The polymer in solution was then passed through the resin as described above in Example 1. The resultant treated polymer solution was analyzed to have 19 ppb silicon.

EXAMPLE 3

Example 2 above was repeated with the exception that additional water was added to the new polymer in solution; the water was present in 0.5 per cent by weight of the polymer solution. The treated solution was analyzed to have 14 ppb silicon versus 19 ppb in Example 2 above.. This then demonstrates the significance of adding water to the polymer solution.

EXAMPLE 4

Into a one liter reactor fitted with an agitator, there were charged 300 grams of polymer (poly hydroxy styrene homopolymer), 700 grams of methanol , and 0.19 grams of water. The ingredients were agitated for 1 hours to make a solution analyzed as 30.0 %, by weight, polymer, 0.50%, by weight, water, and containing 301 ppb silicon. The polymer was prepared by the process set forth in US 7,312,281. Separately, there was prepared a 25 gram Amberlite [™] IRN150 ion exchange resin bed, containing both acidic cation and basic anion resins, by adding the Amberlite resin to a one inch column having a length of 24 inches. The Amberlite material was washed with 1 kilogram of deionized water followed by a rinse with 320 kilograms of methanol .

The polymer solution/mixture described above was passed through the rinsed Amberlite [™] IRN 150 column at a flow rate of 5 grams per minute. The process was carried out at ambient temperature, 20C. A post ion exchange sample was collected at different through-put levels for subsequent silicon analysis. The post ion exchange samples were then further precipitated into ten times its volume of water followed by vacuum drying. The dried polymer samples were submitted for silicon analysis and the results are set forth below.

Operational through-put

total gms of solution	Silicon analyzed, ppb
0 (initial)	301
150	36
300	48
500	39
800	41
1000	52

EXAMPLE 5 (Comparative Example)

Example 1 was repeated but instead of using the Amberlite™ IRN 150 ion exchange resin, a polymer solution (200 grams of polymer and 700 grams methanol) was passed through Meissner Chemdyne polypropylene filters with pore sizes of 0.1 and 0.04 μm at a rate of 10 grams per minute at an ambient temperature in an attempt to remove the silicon impurities. The initial silicon level in the polymer solution (pre-treatment) was 294 ppb. After filtration, the level using the 0.1 μm filter was 307 ppb, and the silicon level using the 0.04 μm filter was 289ppb. The results showed the silicon level did not change on the post-filtration samples, suggesting that the use of a filtration technique does not work.

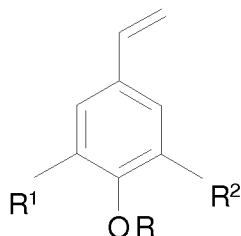
The results demonstrate that the present invention process readily removes silicon impurities from a polymer containing the same, and results in that the treated polymer that can be directly used as a photoresist material.

While specific reaction conditions, reactants, and equipment are described above to enable one skilled in the art to practice the invention, one skilled in the art will be able to make modifications and adjustments which are obvious extensions of the present inventions. Such obvious extensions of or equivalents to the present invention are

intended to be within the scope of the present invention, as demonstrated by the claims which follow.

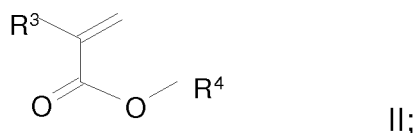
WHAT IS CLAIMED IS:

1. A process for removing silicon impurities from a polymer, containing the same, comprising the steps of (1) dissolving said polymer in a first solvent to make a solution, (2) adding a non-solvent to said solution, and (3) contacting said solution from step (2) with a mixture of acidic cation and basic anion exchange resins, for a sufficient period of time to substantially remove said silicon from said solution of step (2).
2. The process as set forth in claim 1 wherein the polymer has been prepared from a monomer or combination of monomers selected from the group consisting of styrenes, styrenes-acrylics, olefins, vinyl acetate, anhydrides, acrylics, acrylates, norbornenes, fluorinated acrylates, fluorinated methacrylates, acrylonitriles, maleic anhydrides, and mixtures thereof.
3. The process as set forth in claim 1 wherein the first solvent is selected from a class of liquids wherein the polymer is at least 25% by weight thereof is dissolved therein.
4. The process as set forth in claim 1 wherein the non solvent is selected from a class of liquids wherein the polymer is at most 25% by weight thereof is dissolved therein.
5. The process as set forth in claim 1 wherein the non solvent used therein is from about 0.0001 percent, by weight, to about 1.00 percent by weight, of the solution contacted with said resins.
6. The process as set forth in claim 3 wherein the first solvent is selected from the group consisting of methanol, ethyl acetate, methyl ethyl ketone, tetrahydrofuran, and mixtures thereof.
7. The process as set forth in claim 4 wherein the non solvent is selected from the group consisting of water, and hexanes, heptanes, methanol, toluene, and mixtures thereof.
8. A method of purifying polymers derived from acyloxystyrene or alkoxy styrene of the group consisting of



wherein R is either $-\text{C}(\text{O})\text{R}^5$ or $-\text{R}^5$; as a homopolymer or a copolymer with one or more of the following monomers:

an acrylate monomer having the formula II,



and/or with one or more ethylenically unsaturated copolymerizable monomers taken from the group consisting of styrene, 4-methylstyrene, styrene alkoxide wherein the alkyl portion is $\text{C}_1 - \text{C}_5$ straight or branch chain, tert.-butylstyrene, cyclohexyl acrylate, tert.-butyl acrylate, tert.-butyl methacrylate, maleic anhydride, dialkyl maleate, dialkyl fumarate and vinyl chloride, wherein:

i) R^1 and R^2 are the same or different and independently selected from the group consisting of:

hydrogen,

fluorine, chlorine, bromine,

alkyl and fluoroalkyl group having the formula $\text{C}_n\text{H}_x\text{F}_y$ where n is an integer from 1 to 4, x and y are integers from 0 to $2n+1$, and the sum of x and y is $2n+1$,

phenyl, and tolyl;

ii) R^3 is selected from the group consisting of:

hydrogen.

methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, and tert.-butyl;

iii) R^4 is methyl, ethyl, n-propyl, iso-propyl, n-butyl, i-butyl, tert.-butyl, t-amyl, benzyl, cyclohexyl, 9-anthacenyl, 2-hydroxyethyl, cinnamyl, adamantyl, methyl or ethyl or

hydroxyl adamantyl, isobornyl, 2-ethoxyethyl, n-heptyl, n-hexyl, 2-hydroxypropyl, 2-ethylbutyl, 2-methoxypropyl, 2-(2-methoxyethoxy), oxotetrahydrofuran, hydroxy trimethylpropyl, oxo-oxatricyclo non yl, 2-naphthyl, 2-phenylethyl, phenyl.

and mixtures thereof; and

iv) R⁵ is C₁-C₄ alkyl

consisting essentially of subjecting said polymer containing silicon impurities therein, after polymerization thereof, to a process comprising the steps of (1) dissolving said polymer in a first solvent to make a solution, (2) adding a non-solvent to said solution, and (3) contacting said solution with a mixture of acidic cation and basic anion exchange resins for a sufficient period of time, whereby said silicon impurities are substantially removed from said solution of step (2).

9. The process as set forth in claim 8 wherein the first solvent is selected from the group consisting of ethyl acetate, methyl ethyl ketone, tetrahydrofuran, methanol, ethanol, propanol, isopropanol, t-butanol and mixtures thereof.

10. The process as set forth in claim 8 wherein the acyloxystyrene is acetoxystyrene monomer and is the only monomer used.

11. The process as set forth in claim 10 wherein the acetoxystyrene polymer in purified form has less than about 75 parts per billion of silicon materials therein based upon the weight of the polymer.

12. The process as set forth in claim 11 wherein the first solvent is methanol.

13. The process as set forth in claim 8 wherein after said polymerization there is an additional step of transesterification of the polymer which is conducted by adding additional first solvent and in the presence of catalytic amounts of a catalyst.

14. The process as set forth in claim 13 wherein after the transesterification step, there is an additional step of removing the catalyst from the reaction mixture of the transesterified product in said alcoholic solvent by passing said mixture through an ion-exchange bed in order to remove said catalyst therefrom.

15. The process as set forth in claim 14 wherein the process is conducted on an anhydrous basis, before the silicon removal step thereof.

16. The process as set forth in claim 15 wherein the polymer contains 200 ppb to 1000 ppb of silicon impurities

17. The process as set forth in claim 16 wherein after the silicon removal step, there is an additional step wherein said first solvent is removed and replaced by a photoresist compatible solvent.

18. The process as set forth in claim 17 wherein the photoresist compatible solvent is selected from the group consisting of glycol ethers, glycol ether acetates, aliphatic esters having no hydroxyl or keto group, and mixtures thereof.

19. The process as set forth in claim 18 wherein the photoresist compatible solvent is either propylene glycol monomethyl ether acetate or ethyl lactate.

20. The process as set forth in claim 1 wherein there is no addition of said non-solvent to the polymer solution, since the said first solvent contains sufficient quantities of said non-solvent therein .

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/048342

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08F6/02 C08F6/12 C08F8/14 C08J3/09
ADD. C08L25/18

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)

C08F C08J

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

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

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 544 324 A1 (MARUZEN PETROCHEM CO LTD [JP]) 2 June 1993 (1993-06-02) page 2, line 32 - page 3, line 57; claim 8	1-20
X	& US 5 288 850 A (MATSUMOTO TADASHI [JP] ET AL) 22 February 1994 (1994-02-22) cited in the application -----	1-20
X	US 2010/297551 A1 (TERANISHI TADASHI [JP]) 25 November 2010 (2010-11-25) paragraphs [0007] - [0012], [0077] - [0126]; claims 1-9; examples 1-6 -----	1-20

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Further documents are listed in the continuation of Box C.

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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

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"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

7 October 2014

Date of mailing of the international search report

14/10/2014

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/048342

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