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METHOD FOR PRODUCING A PHOTOGRAPHIC ELEMENT

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FIG. 1

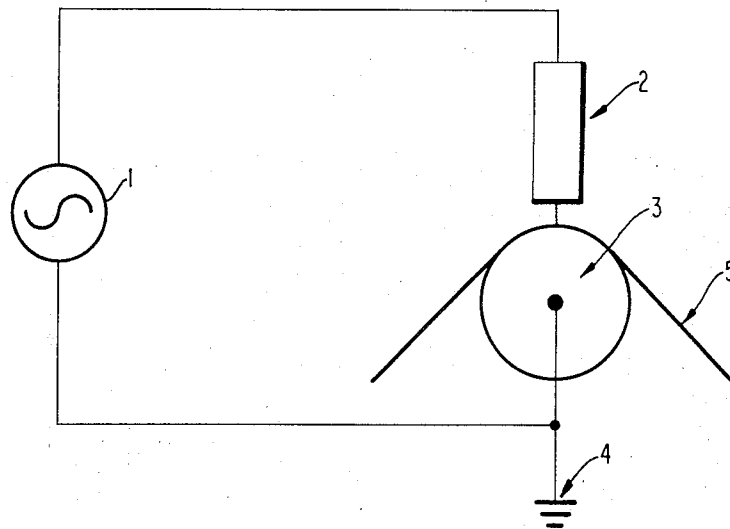
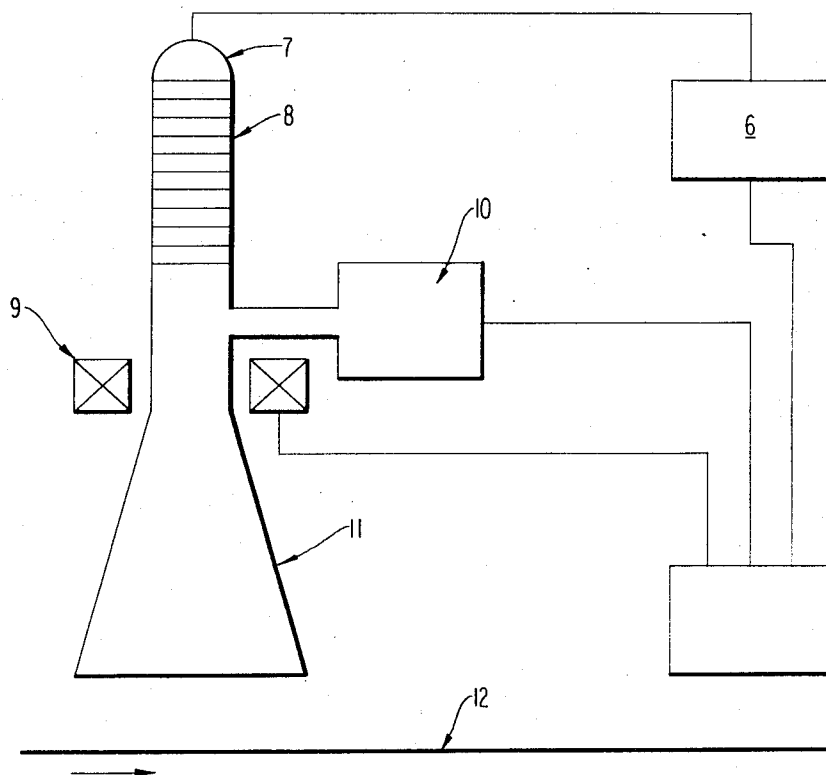


FIG. 2



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3,697,305 METHOD FOR PRODUCING A PHOTOGRAPHIC ELEMENT

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6 Claims

ABSTRACT OF THE DISCLOSURE

A method for producing a useful and practical photographic element having excellent water-resisting properties, dimensional stability and rapid-drying qualities comprising treating a biaxially-stretched and roughed polystyrene film base with a corona discharge or electron irradiation, applying, if necessary, a gelatin layer to said base, and then applying a gelatin-containing photographic emulsion or suspension onto the treated surface of the support.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to a method of producing a photographic element.

Description of the prior art

Baryta paper has generally been used as a photographic support for photographic paper or as the element for a silver salt diffusion transfer process. Baryta paper is produced by applying an aqueous mixture of finely divided barium sulfate and a small quantity of binder such as gelatin on a paper made from pulp. The paper has various disadvantages such as its easy expansion and contraction depending upon moisture variation, especially, shrinkage after development, and its weakness to water.

The foregoing disadvantages can be overcome by using a support produced by dipping a polymer film, for example, a polystyrene film, in a solvent or swelling agent and then whitening the treated surface by dipping the film in a non-solvent for the polystyrene. The film has very desirable properties as a photographic support due to its superior water-resisting quality, drying velocity, dimensional stability, stiffness, opacity and the like.

Polystyrene has, however, the disadvantages as a support for photographic paper in that it is difficult to firmly bond a photographic emulsion layer containing hydrophilic gelatin thereto, due to the hydrophobic and chemically-inactive properties of polystyrene.

It is well known that a remarkable improvement in adhesion can easily be obtained by subjecting polyethylene or other film material consisting of hydrophobic polymers to a corona discharge treatment. In the case of polystyrene, however firm adhesion cannot be generally effected even by treating the same with a corona discharge. When a 1-10% aqueous solution of gelatin is applied to a biaxially stretched polystyrene support subsequent to treatment with a corona discharge, the adhesion is so poor that the gelatin layer formed is released naturally from the surface of the support.

As a result of many studies directed toward overcoming the foregoing disadvantages of baryta paper, the present inventors attained the present invention.

An object of the present invention is to obtain a novel photographic paper having excellent water-resistance, dimensional stability and a rapid drying property.

SUMMARY OF THE INVENTION

The present invention provides a method for the production of a photographic element which comprises treating a biaxially stretched roughed polystyrene support with a corona discharge or electron irradiation and, if necessary, applying a gelatin layer thereto, and then applying a photographic emulsion or suspension containing gelatin as a binder, to the treated surface.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1 and 2 represent suitable apparatus for conducting the corona discharge and electron irradiation treatments, respectively.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The phrase "a biaxially stretched roughed polystyrene film," as used herein, refers to a process consisting of biaxially stretching an extruded polystyrene film by a conventional prior art biaxially stretching method, contacting, for 0.5 to 30 seconds, the stretched film with organic solvents capable of dissolving or swelling the polystyrene, such as tetrahydrofuran, methyl acetate, ethyl acetate, acetone, methyl ethyl ketone, methylene chloride, ethylene chloride, cyclohexane, benzene or mixtures thereof to swell the film, then roughing by contacting, for more than one second, the surface of the film with organic solvents which are compatible with the organic solvents used in the swelling treatment but which do not dissolve the polystyrene, such as methanol or ethanol. The contacting of the polystyrene film with the solvents can usually be accomplished by either dipping the film in the organic solvent, applying the organic solvent to the film by a roller applicator or a brush, or spraying the organic solvent onto the film. In general, the most effective roughing process has been a mechanical abrasion or whitening of the whole film by the incorporation of a foaming agent such as a normal alkane capable of generating a gas upon heating rather than the above contacting process with an organic solvent.

The biaxial stretching of the film can be accomplished by stretching both axes of the film at the same time or separately for the purposes of the present invention. Any conventional prior art biaxial stretching process may be employed.

The polystyrene resin may also be used in combination with 5 to 40 weight percent of a white pigment such as, for example, titanium dioxide, barium sulfate, calcium sulfate, barium carbonate, lithopone, alumina white, calcium carbonate, silica white and the like, and, if necessary, a colored pigment. The whitening or the opalizing of said film according to the foregoing process imparts a valid photographic scene to the photographic element produced from the treated support. The polystyrene resin has excellent water-resistance, dimensional stability, stiffness and other advantageous properties, and especially when the film is treated in the foregoing manner, it exhibits superior whiteness and opacity. It may be very desirable as a support for photographic elements. However, it is difficult to bond the polystyrene resin to a hydrophilic gelatin-containing emulsion due to the hydrophobic and chemically inactive properties of the polystyrene as mentioned above.

The present invention overcomes these disadvantages in the treatment of the roughed polystyrene film with a corona discharge or with electron irradiation. According to our reliable studies, the present inventors have found that roughed polystyrene film, without being subjected to a corona discharge treatment or electron irradiation, has a contact angle to water of 80°-90°, that film treated with a corona discharge or electron irradiation according to

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the present invention results in decreased values of the contact angle of 5-6° and 35-50° respectively, and that said treatments make the surface of the polystyrene film remarkably hydrophilic. Furthermore, test results demonstrate that, although in the case of a biaxially stretched non-roughed polystyrene film, the contact angle is decreased to 5 to 50° by treatment with a corona discharge or electron irradiation, it is difficult to effect a firm adhesion between the film and a coating of an emulsion consisting essentially of gelatin. When, however, the roughed, biaxially stretched polystyrene film is treated with a corona discharge or electron irradiation, the adhering strength between the film coating of the emulsion containing gelatin and the treated film surface is markedly greater in both the dry state and the wet state during development.

For example, even if the exfoliation at the boundary surfaces of the two phases between said film and said film coating are done in the dry state, the adhesion between the two is so strong that the cohesive failure is in the internal film without releasing said film coating from said film. In this case, the cohesive failure strength is sufficient to provide the good adhering strength required between the film coating and the support, such as the photographic emulsion layer or an image-receiving layer.

Furthermore, the adhering strength between the support and the film coating does not deteriorate even after standing for a long period of time.

The corona discharge treatment according to the present invention can be accomplished by utilizing the apparatus shown in FIG. 1.

In FIG. 1, 1 is a high frequency generator; 2 is an electrode; 3 is a treatment roller whose surface is coated with chlorosulfonated polyethylene (Hypalon) or with a polyester film; 4 is a ground; and 5 is the film base to be treated. The corona discharge treatment is carried out while the film base is travelling between 2 and 3. The voltage across the electrodes is usually from 5 kv. to 500 kv. but is not necessarily limited to this range. The electrode distance can be varied depending on the thickness of the film base to be treated, but a range between 0.5 mm. and 10 mm. is generally preferred. The velocity of the film base is generally between 1 and 20 mm./min., but can be properly varied depending on the kind of apparatus used and the treating effect.

The electron irradiation may be conducted by utilizing the apparatus shown in FIG. 2. In FIG. 2, 6 is a high voltage generator; 7 is an electron gun; 8 is an accelerator; 9 is a scanning coil; 10 is a vacuum pump; 11 is a scanning tube; and 12 is the film base to be treated. An electron beam generated by electron gun 7 is accelerated through accelerator 8, and exposed to the film base 12 with scanning through scanning coil 9. At this time, a maximum voltage of about 300 kv. is functionally and economically advantageous to effect this purpose. The beam electric current is 20 to 50 ma., and a desirable velocity of the film base is from 4 to 20 m./min.

In the present invention, the terminology "emulsion or suspension containing gelatin as a binder" or "gelatin containing layer" indicates, for example, an aqueous emulsion or suspension of gelatin prepared by optionally adding thereto silver halides such as silver chloride, silver chlorobromide and silver iodobromide; a photosensitive diazo compound; development nuclei of an image-receiving element used in a silver salt diffusion transfer process or various other components.

If necessary, a silver halide emulsion may be coated onto the gelatin emulsion layer so that the gelatin emulsion layer is an undercoating layer for the silver halide emulsion.

In the present invention, the adherence of the aqueous gelatin layer film coating to the support is problematic, and it may not be important whether any component is emulsified or suspended in the aqueous gelatin solution.

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For this reason, although the present invention is primarily directed toward photographic elements, the nature of the present invention suggests that it would be sufficiently applicable to the other technical fields which are concerned with the adhesion between a gelatin membrane and a roughed, biaxially-stretched polystyrene film.

The following tests and examples more specifically set forth the present invention. In addition, the adhesion tests between the polystyrene film support and the film coating in the examples was performed by the following methods.

(1) DRY STATE ADHESION TEST

A 0.14 mm. thick cellulose triacetate film was coated onto a specimen with an epoxy type adhesive and allowed to stand at 23° C. and at a relative humidity of 65%; then cut into a long strip-like shape, 1 cm. wide and 15 cm. long; thereafter, said film was released at a drawing velocity of 7.38 cm./min. The releasing strength was measured with a strain gauge. In the examples, the term "good adhesion" in test tested specimen refers to a releasing strength greater than 8 g./mm., which is satisfactory for a photographic element.

(2) WET STATE ADHESION TEST

The same surface of the above specimen, after developing, fixing or water-washing, was bonded in a wet state, with a cyanoacrylate type adhesive, a cellulose triacetate film in the same manner as in (1) and the releasing strength was measured. In this case, "good adhesion" refers to a releasing strength greater than 2 g./mm., which is sufficient for a photographic element.

In the following examples, "part" is "by weight."

EXAMPLE 1

A biaxially stretched 0.1 mm. thick polystyrene support was dipped in a solution consisting of 7 parts ethyl acetate and 1 part ethanol for 3 seconds and then dipped in methanol for an additional 30 seconds to whiten and opalize the support. The roughed polystyrene support was subjected to a corona discharge treatment using a corona discharger (Model HFSG-1 produced by Lepel High Frequency Laboratories) under the following conditions.

Distance between electrodes	----- (mm.)	0.8
Length of electrode	----- (mm.)	300
Thickness of electrode	----- (mm.)	10
Frequency	----- (mc.)	1
Feeding speed of support	----- (m./min.)	2
Discharging electric power	----- (w.)	12-175

After the corona discharge and roughing treatments, the polystyrene support surface was coated with a gelatin-silver halide photographic emulsion having the following composition per 1 m.² of film.

		G.
Silver chlorobromide (chlorine:bromine=3 mole:7 mole)	-----	3.5
Gelatin	-----	13.0
Formalin (hardener)	-----	0.1
Saponin	-----	0.03

The adhesion between the emulsion layer and the film base, as confirmed by the releasing test results shown in the table below is large enough, such that it does not result in exfoliation at the boundary surface.

In the dry state, the releasing test leads to a cohesive failure at the internal film with a cohesive failure strength greater than 8 g./mm. which is satisfactory for a photographic element.

Further, in the wet state, the boundary surface between the emulsion layer and the support was not released; the break occurred in the internal emulsion layer. The adhesion between the emulsion layer and the film base was greater than 2 g./mm. which is satisfactory for a photo-

graphic element, and furthermore the adhesion had not deteriorated even after standing for a long time.

On the other hand, when a roughed polystyrene support, which had not been subjected to a corona discharge treatment was coated with the emulsion in like manner as above, the adhesion was extremely inferior in both the dry and the wet states, and was below 2 g./mm. in the dry state and nearly 0 g./mm. in the wet state.

A transparent polystyrene film, which was treated with a corona discharge in like manner as above, but not roughened, was extremely inferior in its adhesion in both the dry and the wet states with both releasing tests resulting in a release strength of 0 g./mm.

EXAMPLE 4

A biaxially stretched 0.2 mm. thick polystyrene film base was dipped in a solution consisting of 15 parts ethylene chloride, 15 parts ethanol and 1 part water for 3 seconds and then dipped in methanol for 30 seconds to obtain a whitened and opalized film base with a porous layer on the surface. The roughed polystyrene support was subjected to a corona discharge treatment under the same conditions as in Example 1, and then a gelatin-silver halide color photographic emulsion having the following composition was applied thereto per 1 m.² of film.

Discharge electric power (w.).	0	12	20	32	50	100	175
Dry state releasing strength (g./mm.).	1.8	28.1	23.2	20.8	22.0	20.2	20.6
Released position	Emulsion layer/ support. ¹	At the internal support. ²	At the internal support.	At the internal support.	At the internal support.	At the internal support.	At the internal support.
Wet state releasing strength (g./mm.).	0	4.0	3.8	4.6	5.2	4.1	4.8
Released position	Emulsion layer/ support.	At the internal emulsion layer.	At the internal emulsion layer.	At the internal emulsion layer.	At the internal emulsion layer.	At the internal emulsion layer.	At the internal emulsion layer.

¹ Emulsion layer/support refers to the exfoliation at the boundary surface between the emulsion layer and the backing surface.

² "At the internal support" refers to the cohesive failure of the support.

EXAMPLE 2

A biaxially stretched 0.1 mm. thick polystyrene support was dipped in a solution consisting of 1 part acetone and 1 part methyl ethyl ketone for 3 seconds and then dipped in methanol for 30 seconds to obtain a whitened, opalized support with a minute porous layer on the surface. The roughed polystyrene layer was subjected to a corona discharge treatment under the same conditions as in Example 1, and thereafter was coated with the following aqueous gelatin solution per 1 m.² of said film.

Gelatin	g--	10
Water	g--	190
Formalin (20% aqueous solution)	cc--	4

The gelatin-silver halide photographic emulsion as mentioned in Example 1 was applied to said gelatin layer. It exhibited a good adhesion strength of greater than 20 g./mm. in the dry state and greater than 5 g./mm. in the wet state. On the other hand, the adhesion obtained by applying the foregoing gelatin solution to the roughed film base without the corona discharge treatment was inferior.

EXAMPLE 3

A biaxially stretched 0.2 mm. thick polystyrene support was dipped in a solution consisting of 1 part benzene and 1 part acetone for 2 seconds and then dipped in methanol for an additional 30 seconds to obtain a whitened, opalized film base with a porous layer on the surface. The roughed polystyrene support was subjected to a corona discharge treatment under the same condition as in Example 1 and thereafter was coated with a solution for an image-receiving layer, which was used in a silver salt diffusion transfer process, having the following composition per 1 m.² of said film.

Gelatin	G.	3
Ag ₂ S colloid		0.001
Phenylmercaptotetrazole		0.01
Saponin		0.02

The releasing test for the image-receiving material was performed, and the adhesion was found to be 15 g./mm. in the dry state at a discharge electric power of 50 w., and 5.0 g./mm. in the wet state. It exhibited an adhesive strength which is satisfactory for an image-receiving material for a silver salt diffusion transfer process.

On the other hand, there was no adhesion obtained by applying the coating solution for the image-receiving layer to the roughed film base without subjecting the film base to a corona discharge treatment.

Silver chlorobromide (chlorine:bromine=3 mole:7 mole)	g--	3.0
Gelatin	g--	3.5
Emulsified dispersion containing benzoylaceto-2-chloro-5-dodecyloxycarbonyl anilide as a yellow coupler	g--	14.0
Triethylene phosphamide (3% acetone solution)	ml--	3.0
Polyvinylpyrrolidone	g--	0.7

The releasing test of the film coated with said color photographic emulsion was performed, and the adhering strength was found to be greater than 12 g./mm. in the dry state and greater than 4 g./mm. in the wet state. It exhibited an adhering strength which is satisfactory for a photographic element.

On the other hand, the adhesion obtained by applying the gelatin-silver halide color photographic emulsion to said roughed film base without first subjecting the film base to a corona discharge treatment, was extremely poor.

EXAMPLE 5

A biaxially stretched 0.1 mm. thick polystyrene film was dipped in a solution consisting of 7 parts ethyl acetate and 1 part ethanol for 3 seconds and successively dipped in methanol for 30 seconds to whiten and opalize the film. The roughed film was then treated with electron irradiation under the following conditions by means of an electron accelerating apparatus (300 ev. transformer type electron accelerating apparatus manufactured by Nisshin Electric Works, Ltd.).

Voltage used	kv--	300
Beam electric current	ma--	25
Dosage:		
(1)	M rad--	1
(2)	M rad--	2
(3)	M rad--	4
(4)	M rad--	8

The resulting film was successively coated with a silver halide photographic emulsion having the following composition per 1 m.² of said film.

Silver chlorobromide	G.	3.5
Gelatin (binder)		13.0
Formalin (hardener)		0.1
Saponin (wetting agent for coating)		0.03
Filled up to 130 cc. with water.		

The releasing test of the film coated with said emulsion was performed and the releasing strength for all of the

treating conditions was found to be greater than 10 g./mm. in the dry state and greater than 2 g./mm. in the wet state. The adhesion strength of said emulsion layer to said film base is satisfactory for a photographic element. Furthermore, these adhering strengths were not deteriorated even after standing for a long time.

On the other hand, when a roughed polystyrene support which had not been first treated with electron irradiation, was coated with said emulsion, the adhesion was extremely poor in both the dry and the wet states, and the releasing strength was below 2 g./mm. in the dry state and nearly 0 g./mm. in the wet state. Furthermore, when a transparent polystyrene film, which has been treated with electron irradiation but not roughed, is coated with said emulsion, the adhesion was extremely inferior in both the dry and the wet states, with releasing strengths of 0 g./mm. for both states.

From the result of this example, it was confirmed that both the roughing and the electron irradiation treatment of the polystyrene film is substantially essential for imparting a releasing strength satisfactory for a photographic element.

EXAMPLE 6

A biaxially stretched 0.1 mm. thick polystyrene film was dipped in a solution consisting of 1 part of acetone and 1 part of methyl ethyl ketone for 3 seconds and successively dipped in methanol for 30 seconds to obtain a whitened and opalized film. Said roughed polystyrene film base was treated with electron irradiation under the same conditions as in Example 5 and an aqueous gelatin solution having the following composition per 1 m.² of said film was applied.

Gelatin (component for undercoat) -----g--	10
Formalin (20% aqueous solution hardener) -----cc--	4
Water -----g--	190

The same silver halide photographic emulsion used in Example 5 was applied to the gelatin layer, and the thus-obtained photographic element exhibited very good adhering strengths greater than 15 g./mm. in dry state and greater than 3 g./mm. in wet state.

On the other hand, the adhesion obtained by applying said gelatin solution to said roughed film base without the electron irradiation treatment was poor.

EXAMPLE 7

A biaxially stretched 0.2 mm. thick polystyrene film was dipped in a solution consisting of 1 part of benzene and 1 part of acetone for 2 seconds and then dipped in methanol for 30 seconds to obtain a whitened and opalized film with a porous layer on the surface. Said roughed polystyrene film was treated with electron irradiation under the same conditions as in Example 5, and successively was coated with a solution for forming an image-receiving layer, which was used in a silver salt diffusing transfer process, having the following composition per 1 m.² of said film.

Gelatin (binder) -----G.	3
Silver sulfide colloid (developing nucleus) -----	0.001
Phenylmercaptotetrazole (color toning agent) -----	0.01
Saponin (wetting agent) -----	0.02

The releasing test for said image-receiving material was performed and confirmed to be satisfactory for an image-receiving material for a silver salt diffusing transfer process in both the dry and the wet states.

On the other hand, there was no adhesion obtained by applying the coating solution to said roughed film base for forming an image-receiving layer, without subjecting the film base to an electron irradiation treatment.

EXAMPLE 8

A biaxially stretched 0.2 mm. thick polystyrene film was dipped in a solution consisting of 15 parts of ethylene chloride, 15 parts of ethanol and 1 part of water for 3 seconds and successively dipped in methanol for 30 seconds to obtain a whitened and opalized film with a porous layer on the surface. Said roughed polystyrene was treated with electron irradiation under the same conditions as in Example 5, and successively was coated with a silver halide color photographic emulsion having the following composition per 1 m.² of said film.

Silver chlorobromide -----g--	3.0
Gelatin -----g--	3.5
Emulsified dispersion containing benzoylacetate-2-chloro-5-dodecyloxycarbonyl anilide (yellow coupler) -----g--	14.0
Triethylene phosphamide (3% acetone solution) -----ml--	3.0
Polyvinylpyrrolidone -----g--	0.7

The releasing test of the film coated with said color photographic emulsion was performed, and it was found to have satisfactory adhering strength for a color photographic element in both the dry and the wet states.

On the other hand, the adhesion obtained by applying the foregoing silver halide color photographic emulsion to said roughed film base, without subjecting the film base to an electron irradiation treatment, was poor.

What is claimed is:

1. A method for producing a photographic element comprising biaxially stretching a polystyrene support, roughing the surface of said polystyrene support, subjecting the resulting polystyrene support to the action of a corona discharge or electron irradiation and applying a gelatin-containing emulsion layer onto said support.

2. The method of claim 1 wherein said gelatin emulsion contains silver ion precipitants as physical-development nuclei.

3. The method of claim 1 wherein said roughing comprises treating said polystyrene support with a first organic solvent capable of swelling the polystyrene and then treating said polystyrene support with a second organic solvent compatible with said first organic solvent but which does not swell the polystyrene.

4. The method of claim 3 wherein said first organic solvent is tetrahydrofuran, methyl acetate, ethyl acetate, acetone, methyl ethyl ketone, methylene chloride, ethylene chloride, cyclohexane, benzene or mixtures thereof.

5. The method of claim 3 wherein said second organic solvent is methanol or ethanol.

6. The method of claim 3 wherein said polystyrene support is first contacted with said first organic solvent for from 0.5 to 30 seconds and then contacted with said second organic solvent for a period of time of more than 1 second.

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RONALD H. SMITH, Primary Examiner

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