United States Patent Office 3,723,159
Patented Mar. 27, 1973

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3,723,159
METHOD FOR THE PRODUCTION OF A PHOTOGRAPHIC ELEMENT

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No Drawing. Filed Jan. 14, 1971, Ser. No. 106,595
Claims priority, application Japan, Jan. 14, 1970, 45/4,163
Int. Cl. G03c *1/78*
U.S. Cl. 117—47 A **12 Claims**

ABSTRACT OF THE DISCLOSURE

A method for the production of a photographic element which comprises ozone-oxidizing a roughened, biaxially stretched polystyrene film and applying thereon a suspension containing gelatin as the binder, and photographic element thus formed.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to a method for the production of a photographic element strengthened in adhesion between a film support consisting of polystyrene (so-called "polystyrene synthetic paper") and a photographic emulsion containing gelatin as a binder.

Description of the prior art

Heretofore, as the known support for photographic paper, there has been used a baryta paper prepared by coating a paper from pulp with barium sulfate. This paper however, has various defects, such as easy expansion and contraction thereof depending on the moisture present, shrinkage thereof after the development, a requirement of a long period for drying subsequent to development, and weakness to water.

As a result of numerous attempts to overcome the foregoing disadvantages known to baryta paper, the inventors have herein attained the present invention.

SUMMARY OF THE INVENTION

It is, therefore, an object of the present invention to provide a method for the production of a photographic element.

Still another object of the present invention is to provide an improved method for the production of the same by using a roughened, biaxially stretched polystyrene film support after oxidizing it with ozone.

Yet another object of the present invention is to provide a useful and practical photographic element having an excellent whiteness, opacity and a strong adhesion strength between the support and the photographic emulsion layer or the image-accepting layer in both dry and wet states.

Accordingly, the present invention is directed to a method for the production of a photographic element which comprises placing a roughened, biaxially stretched polystyrene film in an ozone atmosphere and then applying an emulsion or a suspension containing gelatin as the binder to said film.

The term, "emulsion or suspension containing gelatin as the binder," used hereinafter, is intended to cover an aqueous emulsion or suspension of gelatin prepared by the addition or without the addition of silver halides, such as, silver chloride, silver bromide, silver chlorobromide, silver iodobromide, etc.; a sensitive diazo compound, a developing nucleus for an image-accepting element used in a silver salt diffusion transfer process or other necessary components to an aqueous solution containing gelatin.

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DETAILED DESCRIPTION OF THE INVENTION

The present invention will be more adequately set forth as follows:

The "roughened, biaxially stretched polystyrene film" can be prepared by stretching a film made up previously of a polystyrene resin by the conventionally known process for biaxial stretching of plastics and subjecting the so obtained stretched film to various roughening treatments. The practice of the biaxial stretching may be successful in either a simultaneous stretching or a consecutive stretching. The roughening process may be effected by contacting the stretched film with organic solvents which can dissolve or swell[1] the polystyrene resin. Illustrative of these are tetrahydrofuran, methyl ethyl ketone, methyl isobutyl ketone, methylene chloride, ethylene chloride, cyclohexane, dimethyl formamide, acetone, acetonyl acetone, amyl acetate, amyl propionate, amyl toluene, benzene, n-butanol, iso-butanol, sec-butanol, n-butyl acetate, n-butyl lactate, iso-butyl acetate, sec-butyl acetate, n-butyl propionate, carbon tetrachloride, chlorobenzene, chloroform, cumene, cyclohexanone, cyclohexyl acetate, cyclopentadiene, cymene, di-iso-butyl ketone, dioxane, ethyl acetate, ethylene dichloride, ethylene glycol diacetate, ethylene glycol monoacetate, ethylene glycol acetate, 2-ethylhexyl acetate, ethyl lactate, hexyl acetate, isophorone, mesityl oxide, 3-methoxy butyl acetate, methyl acetate (80%), methyl amyl acetate, methyl n-butyl ketone, methyl chlorohexane, methyl iso-butyl ketone, methyl chlorohexanone, methylene chloride, methyl cyclohexyl acetate, methyl glycol acetate, methyl n-propyl ketone, pentachlorethane, n-propyl acetate, iso-propyl acetate, solvent naphtha (from coal), tetrachlorethane, tetrachlorethylene, tetrahydronaphthalene, toluene, trichlorethane, trichlorethylene, xylene, or mixtures of same to swell said film. The swelled film is further contaced with another organic solvent having a good compatibility with the organic solvents used in the foregoing swelling treatment, and yet not capable of dissolving polystyrene, or with water to roughen the surface of said film. Illustrative of these are amyl alcohol, benzyl alcohol, butylene glycol, butyl glycol, cyclohexanol, diacetone, diethylene glycol, diethyl glycol, diluol-3, dipentene, ethanol, ethyl diglycol, ethylene glycol, ethyl glycol, hexylene glycol, methanol, methyl iso-butyl carbinol, methyl chlorohexanol, methyl diglycol, methyl glycol, pentasol, n-propanol, iso-propanol, propylene glycol, turpentine (natural), and liquid hydrocarbons of from 5–10 carbon atoms. In this case, the practical effects of contacting thereof may usually be secured by means of dipping the film in said organic solvent, applying said organic solvent to the film by a roller applicator and a brush, or spraying said organic solvent onto the film by a sprayer. The preparation of a film with a whiteness and an opacity suitable for purposes herein, can be easily achieved according to the selection of the solvent to be used and variation of time in contacting the film with the solvent. The effective roughening treatment thereof other than the contacting process with organic solvent, is also obtained without impairing the goals of the present invention. For example, a process of roughening by mechanical abrasion, a process of roughening accompanied by whitening of the whole film incorporated with a foaming agent being capable of generating a gas depending upon the decomposition on heating thereof, or a process of roughening by molding a film together with

[1] It is difficult to distinguish "dissolving" from "swelling." However, it may be said that "dissolving" means that the molecules of polystyrene layer melt into the solvent, while "swelling" means that the solvent is kept in the molecules of the polystyrene.

a compound different from the mother body and then eluting said compound selectively.

The polystyrene resin may contain white pigments, selected from the group consisting of titanium dioxide, barium sulfate, calcium sulfate, barium carbonate, lithopone, alumina white, silica white and the like, of 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 so treated resin.

The polystyrene resin is generally excellent in exhibiting water-resistance, dimensional stability, stiffness and the other properties. Since the film thus treated is excellent in the whiteness and the opacity, it may be very desirable to employ said film as a support for a photographic element. However, a polystyrene resin presents a problem in that it is difficult to firmly bond the coating to the polystyrene support on application of a hydrophilic gelatin-containing emulsion to its surface. This is due to the hydrophobic and chemically inactive properties of polystyrene.

The present invention overcomes the foregoing complications by contacting the roughened polystyrene film with an ozone atmosphere to ozone-oxidize it and thereafter applying the photo-sensitive emulsion containing gelatin, as the binder or a coating composition for an image-accepted layer. In addition to gelatin, other binders may be employed. Illustrative of these are cellulose acetate maleate, copolymers of vinyl compounds and maleic anhydride, copolymers of acrylamide and methacrylic acid polyvinyl pyrrolidone, polyacrylic acid, copolymers of styrene and acrylates, copolymers of styrene and maleic anhydride, and terpolymers of styrene, acrylates and maleic anhydride. This layer is used in the silver salt diffusion transfer process. After oxidizing said film with ozone, a gelatin layer may be applied onto the so treated surface and a photosensitive emulsion may be applied, containing gelatin as the binder or a coating composition for image-accepting layer which is used in the silver salt diffusion transfer process. In accordance with reliable studies, applicants have found that roughened polystyrene film, without being oxidized with ozone, has a contact angle of 80° to 90° when measured with water. On the other hand, upon oxidation with ozone, that value decreases to 10° to 70°, whereby the surface becomes hydrophilic. Naturally, when an unroughened transparent polystyrene film is oxidized with ozone, the contact angle to water decreases to 10° to 70°, thus providing a hydrophilic surface.

Although in the case of a biaxially stretched polystyrene film which has not been roughened, the contact angle is remarkably lowered by the oxidation with ozone, there is still difficulty in effecting firm adhesion between the film and the film coating of emulsion or suspension consisting mainly of gelatin. When, however, the so roughened, biaxially stretched polystyrene film is exposed only in an air atmosphere containing ozone at a concentration of from 1–10 g./500 liter of air for 5 seconds to 30 minutes, the adhesion strength between the so treated support and the photographic emulsion containing gelatin, as well as the image-accepting layer, increases markedly. This is true for both the dry and wet state during development.

Thus, for example, even if the peeling at the interface of these two phases is attempted in a dry state, their adhesions are so strong that cohesive failure is easily caused at the internal support without release of said coating of the photographic emulsion and/or said image-accepting layer from said support. In this case, the cohesive failure strength is sufficient for providing the good adhesion strength required between the photographic emulsion layer or the image-accepting layer and the support to the photographic paper. In addition, it is also possible, if necessary, to apply a gelatin layer as the undercoat to the surface oxidized with ozone.

Accordingly, the adhesion strength between the so treated support and the photographic emulsion layer containing gelatin or the image-accepting layer will not be deteriorated even after storing for long periods of time.

In the foregoing oxidation with ozone, various kinds of ozone-generating apparatus may be employed. As mentioned above, the present invention is characterized by treating the roughened polystyrene support with ozone.

With respect to the test of the adhesion between the photographic emulsion layer (hereinafter referred to as "emulsion layer") or the image-accepting layer and the support in following examples, it is carried out as follows:

(1) Method of testing the adhesion in dry state.—A cellulose triacetate film having 0.14 mm. in thickness was adhered to the surface of an emulsion layer on a support or to the surface of an image-accepting layer using an epoxy type adhesive. It was allowed to stand at 23° C., and 65% RH (relative humidity) and then cut into a long strip having a 1 cm. width and a length of 15 cm. Thereafter, said cellulose triacetate film was peeled at a drawing velocity of 7.38 cm./min. At that time, the peeling strength was measured by means of strain gauge. In following examples the term "good adhesion" is intended to cover a peeling strength of over 8 g./min., which is practically sufficient in the adhesion strength between the emulsion layer or the image-accepting layer on the photographic film and the support.

(2) Method of testing the adhesion in wetting state.—The same specimen as employed above was bonded using a cyanoacrylate type adhesive and the releasing strength was measured in the wet state after developing, fixed and washing with water, respectively, according to the same manner indicated above.

In this case, "good adhesion" is intended to show a releasing strength of over 2 g./mm.

A better understanding of the present invention will be attained from the following examples which are merely intended to be illustrative and not limitative of the present invention.

EXAMPLE 1

A biaxially stretched polystyrene support having 0.1 mm. thickness was dipped into a solution consisting of 7 parts ethyl acetate and 1 part ethanol for 3 seconds and then in methanol for 30 seconds to whiten and opalize the support.

The so roughened polystyrene support was divided into three sections, each of them being subjected to ozone-oxidation under the following conditions, respectively, by means of an ozone-generating apparatus (0–10–2 type manufactured by Nippon Ozone Co., Ltd.).

Ozone concentration (g./500 liter air)	Treating time (min.)	Treating temperature (° C.)
1.0	3.0	20
3.0	0.5	20
5.0	0.2	20

Thereafter, each surface on the so ozone-oxidized, roughened polystyrene support was contacted with a gelatin silver halide photographic emulsion having the following composition:

	G.
Silver chlorobromide	3.5
Gelatin	13.0
Formalin (hardener)	0.1
Saponins	0.03

Each film coated with said emulsion was confirmed to be large enough in the adhesion strength between the emulsion layer and the film support as a photographic element according to the test results previously discussed. That is, under every condition, the peeling strength was over 10 g./mm. in dry state and over 2 g./mm. in wet state. The adhesion strength was never deteriorated, even after storing for long periods of time.

On the other hand, in the case where a roughened polystyrene support was employed which had not been oxidized with ozone, but which was coated with the emulsion as above, the adhesion was exceedingly inferior in both dry and wet states. That is, it was below 2 g./mm. in dry state and nearly 0 g./mm. in wet state.

A transparent polystyrene film, treated with ozone but not roughened, was applied with the same emulsion as the above. The results in the peeling test were inferior in both dry and wet states. The adhesion strength was 0 g./mm. in both tests.

EXAMPLE 2

A biaxially stretched polystyrene support having a thickness of 0.1 mm. was dipped in a solution consisting of 1 part acetone and 1 part methyl ethyl ketone for 3 seconds and then in methanol for 30 seconds to obtain a whitened, opalized support with a micro porous layer on the surface. The so roughened polystyrene support was divided and subjected to ozone-oxidation under the same conditions as in Example 1, and thereafter the following aqueous gelatin solution was applied in the following proportions per 1 m.^{2} of said film:

Gelatin ________________g__	10
Formalin (20% aqueous solution) ________cc__	4
Water ________________g__	190

The gelatin-silver halide photographic emulsion as mentioned in Example 1, was applied to said gelatin layers.

Each specimen treated under said conditions exhibited a good adhesion of over 15 g./mm. in dry state and over 4 g./mm. in wet state. On the other hand, one obtained by applying the foregoing gelatin solution to the roughened film, without ozone-oxidation, was inferior in adhesion strength at the interface between said gelatin coating and said support.

EXAMPLE 3

A biaxially stretched polyethylene support having 0.2 mm. thickness was dipped into a solution consisting of 1 part benzene and 1 part acetone for 2 seconds and in methanol for 30 seconds to obtain a whitened, opalized film support with a mirco porous layer on the surface. Said roughened polystyrene support was divided and subjected to ozone-oxidation under the same conditions as in Example 1 and thereafter a coating solution for an image accepting layer, which was used in a silver salt diffusion transfer process, having the following composition was applied thereto in the following proportions per 1 m.^{2} of said film:

	G.
Gelatin ________________	3
Ag_2S colloid ________________	0.001
Phenylmercaptotetrazole ________________	0.01
Saponins ________________	0.02

The peeling test of said image-accepting elements was carried out and the adhesion strength was confirmed to be sufficient for the purpose of using it as an image-accepting layer for a silver salt diffusion transfer process in both dry and wet states.

On the other hand, when said coating solution for the image-accepting layer was applied to said film support, roughened but not subjected to ozone-oxidation, the adhesion was extremely inferior.

EXAMPLE 4

A biaxially stretched polystyrene film support having a thickness of 0.2 mm. was dipped into a solution consisting of 15 parts ethylene dichloride, 15 parts ethanol and 1 part water for 3 seconds and then into methanol for 30 seconds to obtain a whitened and opalized film support with a micro porous layer on the surface. Said roughened polystyrene support was divided and subjected to ozone-oxidation under the same conditions as in Example 1. Subsequently a gelatin-silver halide color photographic emulsion having the following composition was applied in the following proportions per 1 m.^{2} of said film:

Silver chlorobromide ________________g__	3.0
Gelatin ________________g__	3.5
Emulsified dispersion containing 10 g. of benzoyl-aceto-2-chloro-5-dodecyl - oxycarbonyl anilide (as yellow coupler) ________________g__	14.0
Triethylene phosphamide (3% acetone solution) ml__	3.0
Polyvinyl pyrrolidone ________________g__	0.7

The peeling test of the films coated with said color photographic emulsion was carried out, and as a result, the adhesion strength required for the purpose of using them as a color photographic element was confirmed to be sufficient in both dry and wet states.

On the other hand, when said gelatin-silver halide color photographic emulsion was applied to said film support, roughened but not subjected to ozone-oxidation, the adhesion was exceedingly inferior.

Although the present invention has been adequately described in the foregoing specification and examples included therein, it is readily apparent that various modifications and changes may be made without departing from the scope thereof.

What is claimed is:

1. A method for the production of a photographic element which comprises ozone-oxidizing a roughened, biaxially stretched polystyrene film and applying thereon, a suspension containing gelatin as the binder.

2. The method of claim **1** wherein in the ozone-oxidizing step, said polystyrene film is exposed to an air atmosphere containing ozone in a concentration of from 1 to 10 g./500 liters of air for a period of from 5 seconds to 30 minutes.

3. The method of claim **1** wherein said biaxially stretched polystyrene film is prepared by subjecting said film to simultaneous biaxial stretching.

4. The method of claim **1** wherein the gelatin suspension is an emulsion.

5. The method of claim **1** wherein said suspension is a composition for forming an image-receiving layer which comprises a gelatin binding agent and particles of a developing nucleus capable of reducing light-exposed silver halide, dispersed therein.

6. The method of claim **1** wherein the biaxially stretching is carried out in consecutive steps.

7. The method of claim **1** wherein the polystyrene film contains white pigment particles.

8. The method of claim **7** wherein the pigment particles are selected from the group consisting of titanium dioxide, barium sulfate, calcium sulfate, barium carbonate, lithopone, white alumina and white silica.

9. The method of claim **1** wherein the pigment is colored.

10. The method of claim **1** wherein the roughened polystyrene film is prepared by treating the biaxially stretched polystyrene film with an organic solvent capable of dissolving or swelling the surface of said polystyrene film and subsequently contacting the so treated film with a non-solvent for said polystyrene.

11. The method of claim **10** wherein the organic solvent is a member selected from the group consisting of tetrahydrofuran, methyl ethyl ketone, methyl isobutyl ketone, methylene chloride, ethylene chloride, cyclohexane, dimethyl formamide, acetone, acetonyl acetone, amyl acetate, amyl propionate, amyl toluene, benzene, n-butanol, iso-butanol, sec-butanol, n-butyl acetate, n-butyl lactate, iso-butyl acetate, sec-butyl acetate, n-butyl propionate, carbon tetrachloride, chlorobenzene, chloroform, cumene, cyclohexanone, cyclohexyl acetate, cyclopentadiene, cymene, di-iso-butyl ketone, dioxane, ethyl acetate, ethylene dichloride, ethylene glycol diacetate, ethylene glycol monoacetate, ethylene glycol acetate, 2-ethylhexyl acetate, ethyl lactate, hexyl acetate, isophorone, mesityl oxide, 3-methoxy butyl acetate, methyl acetate (80%), methyl amyl acetate, methyl n-butyl ketone, methyl chlorohexane, methyl iso-butyl ketone, methyl chlorohexanone, methylene chloride, methyl cyclohexyl acetate, methyl glycol acetate, methyl n-propyl ketone, pentachloroethane, n-propyl acetate, isopropyl acetate, solvent naphtha (from coal), tetrachlorethane, tetrachlorethylene, tetrahydronaphthalene, toluene, trichlorethane, trichlorethylene, xylene, or mixtures of same.

12. The method of claim **10** wherein the non-solvent is a member selected from the group consisting of amyl alcohol, benzyl alcohol, butylene glycol, butyl glycol, cyclohexanol, diacetone, diethylene glycol, diethyl glycol, diluol-3, dipentene, ethanol, ethyl diglycol, ethylene glycol, ethyl glycol, hexylene glycol, methanol, methyl iso-butyl carbinol, methyl chlorohexanol, methyl diglycol, methyl glycol, pentasol, n-propanol, iso-propanol, propylene glycol, turpentine (natural) and liquid hydrocarbons of from 5–10 carbon atoms.

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RONALD H. SMITH, Primary Examiner

U.S. Cl. X.R.

96—76 R, 84 R, 87 R; 117—34