PROCESS FOR THE PRODUCTION OF PHOTOGRAPHIC MATERIALS

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3,590,107 6/1971 Smith et al.......................... 117/47 A
3,607,473 9/1971 Grunwald et al........................ 117/47 A
3,697,305 10/1972 Tatsuta et al........................ 117/47 A

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ABSTRACT
A polyolefin-laminated paper support for photographic materials, especially suited for use as a support for a color photographic light-sensitive emulsion, having improved image-resolving power and high strength of adhesion to a photographic emulsion layer coated thereon, is obtained by the combination, in sequence, of a preliminary roughening treatment of the polyolefin surface in a conventional manner and subsequent surface activation treatment of the resultant roughened surface any conventional procedure such as corona discharge, flame treatment, ozone oxidation and the like.

14 Claims, No Drawings
PROCESS FOR THE PRODUCTION OF PHOTOGRAPHIC MATERIALS

BACKGROUND OF THE INVENTION

1. Field of the Invention
The present invention relates to a process for the surface treatment of a support used for a photographic material, and has as its object improving the adhesion between a photographic support and a photographic emulsion layer coated thereon, and providing a photographic material having high image-resolving power.

2. Description of the Prior Art
Heretofore, baryta paper has been commonly used as a support for photographic printing papers. Baryta paper is usually prepared by coating a paper with a kneaded mixture of barium sulfate and gelatin.

Recently, a paper surface laminated with polyethylene, i.e., "water-proof paper," has been widely used, with increasing demand for rapid developing procedure. However, since polyethylene-laminated paper has a hydrophobic surface of polyethylene it has such a poor adhesion to a hydrophilic photographic emulsion containing gelatin as a binder that the photographic emulsion has to be coated onto the support after rendering the surface of polyethylene hydrophilic by various surface-activation treatments, for example, a corona discharge treatment.

In a corona discharge treatment, however, there is the drawback that though good adhesion is obtained when the photographic emulsion is coated thereon immediately after the corona discharge, the effect of improved adhesion gradually decreases with time and finally disappears.

Another significant problem is that polyethylene-laminated paper has an extremely poor image-resolving power for a printed picture image as compared to baryta paper. This is due to the fact that polyethylene-laminated paper has a transparent or translucent polyethylene film layer provided on a paper sheet, which itself is a very reflective substance, so that light transmitted through the photographic emulsion layer which is formed on the paper, i.e., the light which passes through the picture image portion, undergoes random reflection at all points, for instance, at the surface and interior of the polyethylene and at the interface between the polyethylene and the paper.

This problem becomes very serious in the case of a color photographic paper since the light-sensitive layer is in a multilayer comprising, successively from the support, a blue sensitive emulsion containing a yellow coupler, a gelatin-containing intermediate layer, a green sensitive emulsion containing a magenta coupler, another gelatin-containing intermediate layer, a red sensitive emulsion containing a cyan coupler and a protective coating of gelatin, which is inherently inferior in image-resolving power to a black-and-white photographic paper having a single photosensitive layer.

A more serious problem is the fact that a polyethylene laminate has an 8–10μ thick polyethylene layer on an opaque paper support (in addition to the above color light sensitive layer) which itself has a multilayered structure, so that it is much more difficult to obtain an improved image-resolving power with such a polyolefin-coated paper used as the support for a color photographic emulsion.

SUMMARY OF THE INVENTION
We the inventors have studied means for overcoming the above drawbacks and have now developed a novel and effective surface treatment process for polyolefin-laminated paper whereby the above-mentioned two drawbacks are eliminated.

More particularly, the process for the preparation of a photographic material according to the present invention comprises preliminarily roughening the surface of the polyolefin and then activating the roughened surface, e.g., by an electric discharge, a flame-treatment or an ozone-oxidation, to thereby render the surface hydrophilic, and thereafter providing onto the resultant activated layer a photographic emulsion layer or an image-receiving layer for a diffusion transfer photographic process.

DETAILED DESCRIPTION OF THE INVENTION
The term "polyolefin" used throughout the specification and claims includes a homopolymer or copolymer which is composed of at least one monomer selected from the group consisting of ethylene, propylene, butylene, and pentene in an amount of at least about 70 mole percent, and the component other than the olefin monomer in the resultant copolymer which may be polymerized with the olefin monomer in an amount of less than about 30 mole percent to modify its properties includes vinyl compounds such as vinyl acetate, styrene, acrylate, methacrylate, acrylonitrile, and the like.

Specific examples of the polymer or copolymer employed in this invention are polyethylene, polypropylene, polybutene, polypentene, ethylene-propylene copolymers, ethylene-vinyl acetate copolymers, ethylene acrylate copolymers, ethylene-methacrylate copolymers, etc.

Phrased somewhat differently, the term "polyolefin" includes not only polyolefin homopolymers but also copolymers, so long as the classic properties attributable to the polyolefins are not lost. Thus the 30/70 molar proportions set out and the comonomers set out are not per se absolute recitations, but serve as a guideline to one skilled in the art as to generally useful olefin proportions and the most representative modifying comonomers.

The phrase "having a surface of polyolefin" includes not only films constructed solely of polyolefin(s) but also papers or other substrates which are laminated with a layer of a polyolefin. In any event, any article having at least a surface of a polyolefin is included within the present invention.

While the thickness of the surface of the polyolefin is not overly critical, best results are obtained when the polyolefin surface presented is from about 20 to about 60 microns thick. The use of lesser thicknesses requires undue process control during surface roughening, and no substantial benefits are obtained by using a greater thickness, though if desired such may be used.

The polyolefin may further contain pigments, dyes, optical whitening agents, antistatic agents and the like additives, each of which imparts a certain effect to the polyolefin without impairing the advantageous effect of the present invention.

The polyolefin surface roughening treatment according to the present invention can be carried out in a variety of ways, e.g., by a solvent roughening method characterized by contacting the surface of the polyolefin
with a solvent at an elevated temperature which is capable of dissolving or swelling the polyolefin such as, for example, xylene, toluene, benzene etc., and then contacting the resultant surface with a liquid incapable of dissolving the polyolefin, such as methanol, ethanol, acetone etc.; roughening effected by tightly pressing the surface of the polyolefin onto a body having a rough surface to thereby transcribe the pattern of the roughened surface of the body onto the polyolefin surface; roughening by mechanically grinding or abrading the polyolefin surface; roughening by causing expansion or foaming of the polyolefin layer with a gas generated at elevated temperature from an expanding or foaming agent incorporated into the polyolefin at the time of film forming; roughening by selective dissolution of a foreign soluble substance (preliminarily admixed in the resin) after the resin is formed into a film.

Any of these surface roughening treatments may be employed in the practice of the present invention without causing a substantial difference in the results achieved with the present invention, since the only essential criterion required of the first step is that the polyolefin surface be provided with minute and fine protrusions or a minute porous layer.

For example, appropriate solvent roughening processes are described in U.S. Pat. No. 3,515,567, appropriate foaming or expansion roughening processes in Japanese Patent Publications 44-21,674 and 43-23,038 and appropriate selective dissolution of a foreign substance roughening processes are disclosed in British Pat. No. 1,127,503.

The polyolefin surface provided with fine and minute protrusions or pores is next subjected to a surface activation treatment by a conventional method known per se, including, for example, corona discharge, ozone oxidation, chromic acid treatment or a flame treatment, whereby the surface of the polyolefin is rendered hydrophilic or made to have an increased affinity or reactivity to water. As a result, the polyolefin surface is now ready to be bonded to a hydrophilic photographic emulsion containing gelatin as a binder.

For example, appropriate corona discharge treatments are disclosed in British Pat. Nos. 971,058; 1,005,631; 1,060,526; 1,019,664; 1,043,703; 1,134,211; 1,136,902; 870,224; 771,234; 715,914; 989,377; USP 3,411,908; 3,253,922; 3,549,406; 3,520,242; 3,076,720; etc; appropriate ozone oxidation/chromic acid treatments in Japanese Patent Publication No. 38-22,148, flame treatments in British Pat. No. 1,011,149 and U.S. Pat. Nos. 2,795,820; 3,072,483; 3,153,683; 3,255,034; 3,375,126; 3,431,135; 3,590,107; etc.

The improved adhesion of the polyolefin surface will not decrease or disappear even after storage for a long time after the surface activation treatment before the photographic emulsion is coated thereon, unlike prior polyethylene coated papers having a smooth surface. For instance, a satisfactory adhesion to a photographic emulsion is obtained even when a photographic emulsion is coated after onto the polyethylene surface one half year after roughening by the use of solvent followed by a corona discharge treatment.

Furthermore, a support treated in accordance with the process of this invention possesses a more excellent image-resolving power than that attained by the use of a conventional polyethylene-coated paper. This is attributable to the fact that light which has passed through the photographic emulsion layer (or image-forming part) is stopped at the minute protrusions of the polyethylene surface and does not further penetrate into the interior of the polyethylene layer, and thereby cause reflection only at the interface between the photographic emulsion layer and the polyolefin.

On the other hand, it has hitherto been proposed to improve the image-resolving power by increasing the concentration of white pigment contained in the polyethylene layer to thereby increase the opacity of the polyethylene layer. However, this method is unsuccessful because the strength of the polyethylene film itself decreases and the dispersion becomes poor whenever the polyethylene film is filled with pigment in an amount sufficient to obtain a desired image-resolving power.

According to the process of this invention, improved image-resolving power is attained in a very simple and efficient manner while simultaneously giving a durable and stable adhesion strength.

The present invention will now be explained in further detail by referring to the following examples:

**EXAMPLE 1**

A polyethylene resin containing 7 percent by weight of powdered titanium dioxide dispersed therein was coated on each side of a 150μ thick paper at a thickness of 20μ. The laminated paper was firstly contacted at one side with toluene heated to 90°C for 2 seconds, and then with methanol heated to 250°C for 30 seconds to thereby effect roughening of the polyethylene surface of the laminated paper.

The surface of the polyethylene thus roughened was subsequently subjected to a corona discharge treatment by the use of a Lepel type corona discharge apparatus at an electric output of 150W and at an electrode passage speed of 2m/min. After allowing the polyethylene coated paper thus obtained to stand in a room over two months, it was then coated with a color photographic silver halide emulsion as described below. The adhesion strength between the emulsion layer so formed and the laminated paper support was so strong that it was impossible to strip or peel off between the emulsion layer and the polyethylene coat at the interface thereof.

On the other hand, another laminated paper prepared in the same manner as above with no preceding surface roughening treatment was readily peeled off at the interface between the polyethylene layer and the emulsion layer, and the strength at peeling was approximately 2g/mm.

A photographic picture was printed onto each of these samples in conventional manner and the image resolving power of each sample was compared. The laminated paper on which the roughening treatment was effected gave an outstandingly sharp image as compared to that without the surface roughening treatment.

**Preparation of Color Photographic Emulsion**

0.2 g of magenta coupler, 4-(3,5-dibutoxy carbonylphenyl azo)-5-amino-1-naphthol, was dissolved in 2 ml of tricresylphosphate. The solution was added to a 10 percent by weight aqueous gelatin solution containing 2 ml of a 10 weight percent aqueous sodium alkyl benzene sulfonate solution and then the mixture was subjected to homogeniz-
ing to emulsify. Six g of the resulting emulsion was mixed with 20 g of a silver chlorobromide photographic emulsion containing about 30 g of silver bromide per 1 kg of the emulsion.

**EXAMPLE 2**

A polyethylene sheet of a thickness of 250μ containing 10 percent by weight of fine particles of powdered titanium dioxide dispersed therein was firstly dipped for 2 seconds in xylene at 120°C then immersed in methanol for 30 seconds at 20°C to thereby effect surface roughening. The thus roughened surface of the polyethylene sheet was subsequently subjected to flame treatment using a propane-oxygen flame (flow rate: 100 parts of propane to 1,600 parts of oxygen), allowed to stand in a room for 2 months and then coated with a black-and-white photographic emulsion as described below.

Testing of this sample to determine the adhesion strength between the emulsion layer and support showed a stripping resistance of 30g/m². On the other hand, a stripping test on another polyethylene sheet in which flame treatment under the same conditions was imparted without a previous surface roughening showed poor adhesion between the emulsion layer and the support (2g/mm²).

Upon printing a picture image onto each of the above samples, the former sample, i.e., the one coated with the emulsion after roughening, gave an outstandingly excellent image-resolving power compared to the latter, i.e., the one coated with the emulsion without the surface roughening treatment.

**EXAMPLE 3**

A polyethylene resin containing 7 percent by weight titanium dioxide dispersed therein was extruded from a T-die upon a 50μ thick paper sheet to form a polyethylene coating of a thickness of 30μ, and then immediately cooled by passage over a cold roll having a sand blusted face (240 mesh) to thereby make a laminated paper having a matted polyethylene surface.

The thus matted laminated paper was subjected to corona discharge treatment under the same conditions as were used in Example 1 and then allowed to stand in a room over two months. An image-receiving layer for use in a diffusion transfer photographic process as described below was coated on this paper. The adhesion strength between the image receiving paper and the support was 25 g/mm², whereas the adhesion strength was so small that natural peeling off occurred when the same polyethylene-laminated paper was treated by corona discharge under the same conditions without a previous roughening treatment and then coated with an image-receiving layer after being allowed to stand in a room for two months.

**Preparation of an Image Receiving Material**

**Composition of Black & White Photographic Emulsion**

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver chlorobromide containing 50 mole % of silver bromide (particle size: 0.6 micron)</td>
<td>28 g</td>
</tr>
<tr>
<td>Gelatin</td>
<td>120 g</td>
</tr>
<tr>
<td>6 wt. % aqueous saponin solution</td>
<td>2.5 cc</td>
</tr>
<tr>
<td>5 wt. % aqueous chromium alum solution</td>
<td>5 cc</td>
</tr>
<tr>
<td>6 wt. % aqueous formaldehyde solution</td>
<td>10 cc</td>
</tr>
<tr>
<td>Water</td>
<td>to 1000 cc</td>
</tr>
</tbody>
</table>

**EXAMPLE 4**

250 cc of a 5 percent by weight aqueous silica aerogel dispersion (pH 3.8) was prepared and its pH was adjusted to approximately 10 by adding a 1N aqueous solution of caustic soda. Then the following aqueous solutions were added in the recited order to the dispersion to prepare the coating solution.

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% by weight aqueous solution of lead acetate (3 hydrate)</td>
<td>1.5 cc</td>
</tr>
<tr>
<td>3% by weight aqueous solution of cadmium acetate (2 hydrate)</td>
<td>2.3 cc</td>
</tr>
<tr>
<td>5% by weight aqueous solution of zinc nitrate (5 hydrate)</td>
<td>5.0 cc</td>
</tr>
<tr>
<td>3% by weight aqueous solution of sodium sulfide (9 hydrate)</td>
<td>1.0 cc</td>
</tr>
</tbody>
</table>

Into 100 cc of the coating solution thus prepared was added 2 cc of a 6 weight percent aqueous saponin solution as a coating aid. The resultant coating solution was applied to the support at a ratio of 20 cc/m² and dried, thereby forming an image receiving material for a diffusion transfer photographic process. While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. A process for the production of a photographic material comprising a photographic layer coated on a polyolefin resin layer, which process comprises firstly roughening the surface of the polyolefin resin and then subjecting the thus roughened surface to a surface activation treatment to thereby render the surface of the polyolefin resin hydrophilic, thereafter coating the thus activated surface with a photographic layer comprising gelatin.

2. The process of claim 1 wherein the polyolefin resin layer is at least 20 microns thick.

3. The process of claim 2 wherein the polyolefin resin layer is from about 20 to about 60 microns thick.

4. The process of claim 1 wherein the polyolefin resin layer is laminated to a non-polyolefin substrate.

5. The process of claim 4 wherein said non-polyolefin substrate is paper.

6. The process of claim 1 wherein the polyolefin is a polyolefin homopolymer or a copolymer of ethylene, propylene, butylene or pentene, the olefin comprising at least about 70 mole percent of the copolymer.

7. The process of claim 6 where the olefin is copolymerized with vinyl acetate, styrene, acrylate, methacrylate or acrylonitrile.

8. The process of claim 1 wherein the roughening is accomplished by contacting the surface of the polyolefin layer with a solvent capable of dissolving or swelling the polyolefin, contacting being at an elevated temperature, and then contacting the resultant surface with a liquid incapable of dissolving the polyolefin.

9. The process of claim 1 wherein the roughening is accomplished by foaming or expanding the surface of the polyolefin layer.

10. The process of claim 1 wherein the roughening is accomplished by incorporating a non-polyolefin substance in the surface of the polyolefin layer and thereafter dissolving the substance.

11. The process of claim 1 wherein the surface activation is a corona discharge.
12. The process of claim 1 wherein the surface activation is accomplished by oxidizing the surface of the roughened polyolefin layer by contacting the surface with ozone.

13. The process of claim 1 wherein the surface activation is accomplished by contacting the surface of the roughened polyolefin layer with chromic acid.

14. The process of claim 1 wherein the surface activation is accomplished by contacting the surface of the polyolefin layer with an oxidizing gas flame.