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## PROCESS OF IMPROVING ADHERENCE OF HYDROPHILIC LAYER TO HYDROPHOBIC FILM SUPPORT

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9 Claims

### ABSTRACT OF THE DISCLOSURE

In film recording materials, the adherence of a hydrophilic external layer such as a silver halide emulsion or a photoconductive layer to a hydrophobic film support is improved by first applying to the hydrophobic film support a layer of a copolymer formed of from 45-99.5% by weight of at least one chlorine-containing monomer of vinylidene chloride and vinyl chloride, from 0.5-10% by weight of an ethylenically unsaturated hydrophilic monomer, and from 0-54.5% by weight of at least one other copolymerizable ethylenically unsaturated monomer and then exposing the surface of the copolymer layer to a high voltage electric corona discharge. A preferred hydrophobic film support is a film of a highly polymeric linear polyester such as polyethylene terephthalate.

This invention relates to improved subbing layers in film recording materials and to film recording materials so obtained.

The present application is a continuation-in-part of the patent application No. 883,242, filed Dec. 9, 1969 and now abandoned.

In the U.S. patent specification 3,649,336 film recording materials are described comprising a hydrophobic film support carrying a layer (A), which is directly adherent to the hydrophobic film support and comprises a copolymer formed from 45 to 99.5% by weight of at least one of the chlorine-containing monomers vinylidene chloride and vinyl chloride, from 0.5 to 10% by weight of an ethylenically unsaturated hydrophilic monomer, and from 0 to 54.5% by weight of at least one other copolymerizable ethylenically unsaturated monomer, and a layer (B) comprising in a ratio of 1:3 to 1:0.5 by weight a mixture of gelatin and a copolymer of 30 to 70% by weight of butadiene with at least one copolymerizable ethylenically unsaturated monomer.

In the above application the term "film recording materials" includes elements and materials for use in a variety of photo-reproduction systems. Examples of such systems include the well-known use of light-sensitive silver halide emulsions, electrographic and electrophotographic systems, and a recently developed photosensitive system wherein the recording is effected by means of photosensitive semi-conductive substances.

It has now been found that when a biaxially oriented polyester film such as a film of polyethylene terephthalate is used as the support, subbed with two subbing layers as described in the above patent application, the second layer composed of a mixture of gelatin and a copolymer of butadiene can be omitted when after the application of the first subbing layer, the surface of this first layer is exposed to a high voltage electric corona discharge.

According to the invention a process is provided for improving in a recording material the adhesion of a hy-

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drophilic layer to a layer of a copolymer comprising at least one of the chlorine-containing monomers vinylidene chloride and vinyl chloride, which copolymer layer has been applied to a biaxially oriented polyester film support, the process comprising exposing to a high voltage electric corona discharge the surface of said copolymer layer before the application thereto of said hydrophilic layer.

To perform the process according to the invention, for instance, the subbed film support is passed between an earthed roller and a corona electrode, the copolymer layer facing the corona electrode. An A.C. high voltage is applied to the corona electrode to produce a high frequency corona discharge.

The corona discharge treatment can occur at any time before the application of further layers to the subbed biaxially oriented polyester film. Very advantageously the treatment occurs immediately before the application of a further layer or layers. A frequency range of from 10 to 100 kc. has proved very suitable for performing the process according to the invention. Suitable current intensities were between  $0.5 \times 10^{-5}$  and  $1.5 \times 10^{-5}$  a./cm., i.e. the current per length unit of the corona electrode.

The distance between the corona electrode and the layer to be treated depends to a large extent on the corona discharge apparatus used. J. C. von der Heide and H. L. Wilson have described in Modern Plastics, May 1961, pages 199-206 and 344 different methods for improving the printability of polyethylene film surfaces by a corona discharge treatment. In one of these methods the vinyl-covered electrodes were actually in contact with the treated film surface. When, however, a bar knife-edge electrode was used, the latter was spaced from 0.03 to 0.09 in. (0.76 to 2.28 mm.) from the treater roll, whereas for a shoe-type electrode, the gap between electrodes and treated roll was from 0.06 to 0.12 in. (1.5 to 3 mm.). Accordingly, the optimal gap between electrodes and treated layer depends on the form of the electrodes, their number, and the generator used, since there is a relationship between the peak corona discharge voltage and current for various gap sizes. In our case we found that the best results with the above indicated frequency range and current intensities were obtained with distances between the electrodes and the layer to be treated comprised between about 1 and 3 mm.

The same authors also studied the variation of the level of treatment required at various film speeds. They studied speeds from 50 ft./min. to 300 ft./min. (about 15 m. to 91 m./min.) and found that a higher level of electrode corona current is required as film speed increases.

In order to increase the chemical influence of the corona discharge treatment it had already been disclosed to effect the treatment in a gaseous atmosphere essentially consisting of the vapors of an inorganic agent, such as chlorine, having an affinity towards electrons. Such a treatment, e.g. with chlorine gas would render the subbed support useless for application in photography. According to the present invention, however, no special atmosphere of an inorganic agent is needed and the corona discharge treatment occurs in ordinary air in the absence of any special oxidizing agent. As a result the treatment and especially the apparatus needed is much simplified.

The polyester films used as supports in the present invention are always films that have been biaxially stretched to improve their strength and dimensional stability. They include films of highly polymeric linear polyesters such as e.g. polyethylene terephthalate. Such film supports are coated with the vinylidene chloride and/or vinyl chloride copolymer layer. The application of the vinylidene chloride and/or vinyl chloride copolymer layer

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to the polyester film support, may take place after biaxial stretching of the polyester film, or after the longitudinal stretching but before the transverse stretching.

After application of the copolymer layer, the surface thereof is exposed to a corona discharge treatment to provide a layer system, which may be used for a variety of purposes.

A hydrophilic layer may be applied to the electrically treated subbing layer of the sheet material according to the invention, which hydrophilic layer may be either transferred from another material or produced thereon from a liquid system. The hydrophilic layer may contain one or more of the following substances:

- (a) semi-conductive substance(s) in a suitable binding agent;
- (b) electro-conductive agent(s) in a suitable binding agent;
- (c) pigment(s) in a photo-hardenable or photosolubilizable binder;
- (d) matting agent(s) or opaque white pigment(s) in a suitable binder;
- (e) light-sensitive substance(s) including light-sensitive silver halide, photoconductive substances, and other light-sensitive compounds, e.g. diazonium salts and diazo-sulphonates;
- (f) dissolved dye(s) e.g. a dye that is bleachable;
- (g) colour coupler(s) e.g. a colour coupler that is used in silver halide colour photography;
- (h) development nuclei suited in the production of silver images according to the silver halide complex diffusion transfer reversal process.

In recording or reproduction systems for forming a hydrophilic relief pattern a hydrophilic layer can be transferred by stripping off from a temporary support to a permanent support, which has been subbed according to the present invention.

According to a particular embodiment the hydrophilic layer contains photosensitive semi-conductor compounds, compositions or materials, which are reversibly activated by patterns of radiations to create a latent image, which is developed by an aqueous developing solution (see "Unconventional Photographic Systems," Second Symposium, Oct. 26-28, 1967, Washington, D.C., pages 116-117).

The sheet material according to the invention may be used as a wrapping material, particularly when it carries layers specially adapted to accept printing thereon. Alternatively, the sheet material may be used as drafting film.

Particularly useful recording materials are provided by sheet materials according to the invention, which carry hydrophilic pigment coatings, e.g. pigmented gelatin coatings suited for production of relief images that are produced by means of a photo-hardening or photo-solubilizing reaction. Such pigment coatings are of practical interest in the graphic art more particularly in the field known as "colour proofing." Colour proofing materials serve to form a showing proof for submission for approval, by which an example is given of the multicolour halftone reproduction, that will be produced eventually by the successive printing in register with separate standard inks yellow, magenta, cyan and black, as described in the U.S. patent specification 3,642,474 and in Example 16 of the Canadian patent specification 893,631.

For case of reference, the layer composed of the copolymer of vinylidene chloride and/or vinyl chloride is hereinafter referred to as the "vinylidene chloride copolymer" layer.

The vinylidene chloride copolymer comprises from 0.5 to 10% by weight of ethylenically unsaturated hydrophilic monomeric units. These units may be derived from ethylenically unsaturated mono- or dicarboxylic acids such as acrylic acid, methacrylic acid, and itaconic acid. Other hydrophilic units, e.g. those derived from N-vinylpyrrolidone, may be present.

The vinylidene chloride copolymer may be formed from

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vinylidene chloride and/or vinyl chloride and hydrophilic monomeric units alone in the ratio indicated above. Preferably up to 54.5% by weight of other recurring units, e.g. acrylamides, methacrylamides, acrylic acid esters, methacrylic acid esters, maleic esters, N-alkyl-maleimides and/or butadiene may also be present.

Suitable vinylidene chloride copolymers are e.g.:

the copolymer of vinylidene chloride, N-tert.-butylacrylamide, n-butyl acrylate, and N-vinylpyrrolidone (70:23:3:4)

the copolymer of vinylidene chloride, N-tert.-butylacrylamide, n-butyl acrylate, and itaconic acid (70:21:5:4), the copolymer of vinylidene chloride, N-tert.-butylacrylamide, and itaconic acid (88:10:2),

the copolymer of vinylidene chloride, N-tert.-butylacrylamide, n-butyl acrylate, and methacrylic acid (65:15:3:17)

the copolymer of vinylidene chloride, n-butylmaleimide, and itaconic acid (90:8:2),

the copolymer of vinylidene chloride, N-tert.-butylacrylamide, butadiene, and itaconic acid (70:18:10:2), the copolymer of vinyl chloride, vinylidene chloride, and methacrylic acid (65:30:5),

the copolymer of vinylidene chloride, vinyl chloride, and itaconic acid (70:26:4),

the copolymer of vinyl chloride, n-butyl acrylate, and itaconic acid (66:30:4),

the copolymer of vinylidene chloride, n-butyl acrylate, and itaconic acid (80:18:2),

the copolymer of vinylidene chloride, methyl acrylate, and itaconic acid (90:8:2),

the copolymer of vinyl chloride, vinylidene chloride, N-tert.-butylacrylamide, and itaconic acid (50:30:18:2),

the copolymer of vinyl chloride, vinylidene chloride, n-butyl acrylate, and itaconic acid (63:30:5:2).

All the ratios given between brackets in the above-mentioned copolymers are ratios by weight.

The above copolymers are only examples of the combinations that can be made with the different monomers, and the invention is not limited at all to the copolymers enumerated.

The different monomers indicated above may be copolymerized according to various methods. For example, the copolymerization can be conducted in an aqueous dispersion containing a catalyst and an activator. Alternatively, polymerization of the monomeric components may occur in bulk without added diluent or the monomers are allowed to react in appropriate organic solvent reaction media.

The vinylidene chloride copolymers may be coated on the polyester film base according to any suitable technique, e.g., by immersion of the surfaces of the film into a solution of the coating material. They may also be applied by spray, brush, roller, doctor blade, air brush, or wiping techniques. The thickness of the dried layer preferably varies between 0.3 and 3  $\mu$ .

Various wetting or dispersing agents may be used when the vinylidene chloride copolymer layer is applied from an aqueous dispersion. This dispersion is obtained directly when the copolymer has been made by an emulsion polymerization process. When coating aqueous dispersions of vinylidene chloride copolymer on a polyethylene terephthalate film support, a very strong adherence to the support is obtained when said dispersion is applied before or during stretching of the polyethylene terephthalate film. The aqueous dispersion may be applied to at least one side of the non-stretched film, but may also be applied to polyethylene terephthalate film, which has been oriented biaxially. The vinylidene chloride copolymer layer may also be coated on at least one side of a polyester film, which has been stretched in only one direction, e.g. longitudinally, whereafter the subbed polyester film is stretched in a direction perpendicular thereto, in this case transversally.

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In order to check whether the process of the invention actually provides a recording material in which a strong adhesion is realized between the hydrophobic support and the hydrophilic layer, the recording material can be subjected to some tests. On top of the dry hydrophilic layer an adhesive tape can be applied, which after some pressure can be torn off at once. If by the corona treatment a good adhesion is accomplished between the hydrophilic layer and the adhesive layer, and consequently also with the hydrophobic support, no substance at all may be torn away from the hydrophilic layer by the adhesive tape and stick to the latter. This method was described in Example 1 of the U.S. patent specification 3,271,345.

Also in wet condition e.g. during the treatment of the recording material in the photographic baths, the adhesive power can be tested. Indeed, the sample that has been soaked with photographic baths is scratched by means of a pin. These scratches in the hydrophilic layer even have to reach the polyester support. In case of a favourable adhesion no pieces of the hydrophilic layer from the edges of these scratches may come loose when these scratches are rubbed over with the finger. This method was described in Example 4 of the above mentioned U.S. patent specification.

The following examples illustrate the present invention. The vinylidene chloride copolymers, which are used in these examples are manufactured according to the methods described in the U.S. patent specification 3,649,336.

## EXAMPLE 1

To one side of a biaxially oriented polyethylene terephthalate film having a thickness of  $180\mu$  a layer was applied in a ratio of 1.4 g./sq. m. from the following composition:

Copolymer of vinylidene chloride, n-tert.-butylacrylamide, n-butyl acrylate, and N-vinylpyrrolidone (70:23:3:4) -----g	5
Methylene chloride -----ml	60
1,2-dichloroethane -----ml	35
Methanol -----ml	5

After this layer was dried, the surface thereof was exposed to 4 successive corona discharges from a high frequency power supply, the electrodes being placed at a distance of 1.5 mm. from the surface. This power supply produced a pulsating voltage, the waveform comprising a narrow pulse of a magnitude of 500 kv., followed by a flat portion of 5 kv. The repeat frequency amounted to about 35 kc. The current intensity for each electrode was  $1.5 \times 10^{-5}$  a./cm. and the film speed was 10 m./min.

After the corona discharge treatment the vinylidene chloride copolymer layer was coated in a ratio of approximately 2 g. of zinc oxide per sq. m. with a composition prepared as follows.

80 g. of zinc oxide were dispersed whilst stirring thoroughly in 450 ml. of demineralised water, to which 1.5 g. of sodium hexametaphosphate had been added. A solution of 53 g. of gelatin in 550 ml. of demineralized water, 7 ml. of 12.5% by weight solution of saponine in demineralized water, and 7 ml. of 20% by weight solution of formaldehyde in demineralized water were added at  $40^\circ\text{C}$ . together with 45 ml. of ethylenedichlorohydrin.

The dried light-sensitive material was exposed image-wise through a transparent original and dipped in the following baths:

- 5 seconds in a 5% solution of silver nitrate in demineralized water;
- 5 seconds in a 0.6% solution of p-monomethylaminophenol sulphate in demineralized water;
- 30 seconds in an acid fixing bath containing 200 g. of sodium thiosulphate pentahydrate and 25 g. of potassium metabisulphite per litre.

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Subsequently, the material was rinsed for 5 minutes in running water and then dried. A black negative image of the original was obtained.

The adhesion of the photosensitive layer to the subbed support was very good in dry as well as in wet state. When omitting the corona discharge treatment, the adhesion of the photosensitive layer was rather inferior.

## EXAMPLE 2

To one side of a non-stretched polyethylene terephthalate film a subbing layer was applied from an aqueous suspension of a copolymer of vinyl chloride, vinylidene chloride, n-butyl acrylate and itaconic acid (63:30:5:2) whereafter the polyethylene terephthalate film was oriented. The layer of vinylidene chloride copolymer was exposed to 4 successive electric corona discharges as in Example 1, the electrodes being placed at the same distance and the film moving with the same speed. The current intensity, however, has been reduced to  $0.6 \times 10^{-5}$  a./cm.

After corona discharge treatment the vinylidene chloride copolymer layer was coated with a pigment dispersion prepared as follows.

35 g. of titanium dioxide having a particle size of 15 to 35 nm. and a specific surface of approximately 50 sq. m./g. was stirred for 2 minutes with 150 ml. of demineralized water and 0.75 g. of sodium hexametaphosphate by means of an Ultra-Turrax stirrer, so that a homogeneous dispersion was produced. To the resulting mixture a solution at  $35^\circ\text{C}$ . of 35 g. of gelatin in 500 ml. of demineralized water and 100 ml. of ethylenedichlorohydrin in 250 ml. of water at  $35^\circ\text{C}$ . were added successively with stirring. Finally, 5 ml. of a 4% solution of formaldehyde in demineralized water were added.

This pigment dispersion was applied to the vinylidene chloride copolymer layer in such a proportion that 2 g. of titanium dioxide was preest per sq. m. of the layer.

The dried material was then exposed image-wise through a transparent original and dipped successively in the following baths:

- (1) 30 seconds in a 10% by weight solution of silver nitrate in demineralized water;
- (2) 30 seconds in a 3% by weight solution of p-monomethylaminophenol sulphate in demineralized water;
- (3) 60 seconds in an acid fixing bath containing 200 g. of sodium thiosulphate pentahydrate and 25 g. of potassium metabisulphite per litre.

A sharp black negative silver image of the exposed original was obtained upon rinsing and drying.

The titanium dioxide layer adhered very well to the vinylidene chloride copolymer layer. Without corona discharge the titanium dioxide layer is easily separated from the subbed polyester film.

## EXAMPLE 3

The procedure of Example 2 was repeated, but the composition of the vinylidene chloride copolymer layer used therein was replaced by a mixture of 3 parts by weight of a copolymer of vinylidene chloride, N-tert.-butylacrylamide, n-butyl acrylate and methacrylic acid (65:15:3:17), and 2.5 parts by weight of a copolymer of vinylidene chloride, N-tert.-butylacrylamide, n-butyl acrylate and N-vinylpyrrolidone (70:23:3:4) dissolved in 80 parts by weight of methylene chloride and 20 parts by weight of methyl glycol.

4 successive corona discharges were carried out as described in Example 1, the current intensity, however, being reduced to  $1.3 \times 10^{-5}$  a./cm.

Without corona discharge the titanium dioxide layer did not adhere to the vinylidene chloride copolymer layer in the wet state. With corona discharge the adhesion was excellent.

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## EXAMPLE 4

The procedure of Example 1 was repeated, but the composition of the vinylidene chloride copolymer layer was replaced by a 5% by weight solution of a copolymer of vinylidene chloride, N-tert-butylacrylamide, butadiene, and itaconic acid (70:18:10:2) in 60 parts by volume of methylene chloride, 35 parts by volume of 1,2-dichloroethane and 5 parts by volume of methanol.

After a corona discharge as described in Example 3, the adhesion of the pigment layer was very good, whereas without corona discharge the pigment layer did not adhere to the vinylidene chloride layer in wet or in dry state.

## EXAMPLE 5

A non-stretched polyethylene terephthalate film was subbed with an aqueous suspension of a copolymer of vinylidene chloride, methyl acrylate and itaconic acid (88:10:2), whereafter the polyethylene terephthalate film was oriented.

The layer of vinylidene chloride copolymer was exposed to 4 successive electric corona discharges as in Example 1, the current intensity, however, being reduced to  $1.0 \times 10^{-5}$  a./cm. A pigment layer as described in Example 1 was then applied thereto.

Adhesion in wet and dry state was very good.

## EXAMPLE 6

To one side of a non-stretched polyethylene terephthalate film a subbing layer was applied from a 20% by weight latex of a copolymer of vinyl chloride, vinylidene chloride, n-butyl acrylate and itaconic acid (63:30:5:2), containing 3% by weight of formamide.

The subbed film was biaxially oriented, whereafter the vinylidene chloride copolymer layer was exposed to 4 corona discharges according to the method described in Example 1.

The material was then coated with a gelatine silver halide emulsion layer as commonly used in X-ray materials. The adherence of the emulsion layer to the subbed support was excellent. The fog values and the sensitivity of the photographic emulsion were hardly influenced by the corona discharge.

## EXAMPLE 7

A non-stretched polyethylene terephthalate film was subbed with an aqueous suspension of a copolymer of vinyl chloride, vinylidene chloride, n-butyl acrylate,  $\beta$ -chloroethyl acrylate and itaconic acid (43:30:5:20:2). After the subbed film was biaxially stretched one part of the film was exposed to a corona discharge according to the method described in Example 1, whereas another part of the film remained untreated.

Both film bases were then coated with a gelatin silver halide emulsion layer for lithographic purposes. The adherence of the emulsion layer to the surface of the film treated with the corona discharge was good in dry and wet state, whereas no adherence could be remarked on the non-treated film.

We claim:

1. Process for improving in a recording material the adhesion of a hydrophilic layer to a layer comprising a copolymer formed from 45 to 99.5% by weight of at least one vinylidene chloride or vinyl chloride monomer, from 0.5 to 10% by weight of an ethylenically unsaturated hydrophilic monomer, and from 0 to 54.5% by weight of at least one other copolymerizable ethylenically unsaturated monomer, and which copolymer layer has been ap-

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plied to a biaxially oriented polyester film support, which comprises exposing the surface of said copolymer layer before the application thereto of said hydrophilic layer in ordinary air to a high voltage electric corona discharge equivalent to that produced by passing said film support carrying said copolymer layer at a speed of about 10 m./min. over a grounded electrode at a distance between 1 and 3 mm. of a corona electrode with the copolymer layer facing the latter, a pulsating A.C. voltage having a frequency of 10-100 kc. being imposed on said corona electrode at a current intensity of  $0.5-1.5 \times 10^{-5}$  a./cm. of electrode length.

2. A process according to claim 1, wherein the ethylenically unsaturated hydrophilic monomer is of the group consisting of acrylic acid, methacrylic acid, itaconic acid and N-vinylpyrrolidone.

3. A process according to claim 1, wherein up to 54.5% by weight of at least one of the monomers acrylamide, methacrylamide, acrylic acid esters, methacrylic acid esters, maleic acid esters, N-alkyl-maleimides and butadiene is present.

4. A process according to claim 1, wherein polyethylene terephthalate film has been used for the polyester film support.

5. A process according to claim 1, wherein the copolymer layer has been formed from a latex of a copolymer of vinylidene chloride, vinyl chloride, n-butyl acrylate, and itaconic acid.

6. A process according to claim 1, wherein the copolymer layer has been formed from a solution of a copolymer of vinylidene chloride, N-tert-butylacrylamide, n-butyl acrylate, and N-vinylpyrrolidone.

7. A process according to claim 1, wherein a light-sensitive gelatino-silver halide emulsion layer is applied as a hydrophilic layer to the copolymer layer after said corona discharge treatment.

8. A process according to claim 1, wherein a hydrophilic layer comprising a photosensitive semiconductive substance is applied to the copolymer layer after said corona discharge treatment.

9. A process according to claim 8, wherein the photosensitive semiconductive material is finely divided titanium dioxide or zinc oxide.

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