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Van Paesschen et al.

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[54] SHEET MATERIAL

- [75] Inventors: August Jean Van Paesschen, Antwerpen; Lucien Janbaptist Van Gossom, Kontich; Jan Jozef Priem, Mortsel, all of Belgium
- [73] Assignee: Agfa-Gevaert, N.V., Mortsel, Belgium
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Related U.S. Application Data

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- [58] Field of Search 117/218, 76 F, 83; 96/1.5,
96/87 R

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Primary Examiner—Ralph Husack
Attorney, Agent, or Firm—William J. Daniel

[57] ABSTRACT

Improved adherence is obtained for sheet material having a hydrophobic film support or base, such as a hydrophobic cellulose ester or poly ester, by the combination of a vinyl polymer subbing layer arranged directly on the hydrophobic support, the subbing layer being formed of a copolymer containing at least 45 percent by weight of vinylidene chloride and/or vinyl chloride monomer along with a minor amount of a hydrophilic vinyl monomer with the balance being constituted by any other vinyl monomer, and superimposed upon the vinyl subbing layer a layer containing a mixture of gelatin with a copolymer of butadiene and a vinyl monomer containing 30–70 percent by weight of butadiene, the ratio of the gelatin to the butadiene copolymer being in the range of 1:3 to 2:1 by weight. An additional layer can be applied over the gelatin/copolymer layer and constituted by such ingredients as are desirable for the particular utility of the resultant sheet material, such as electrophotographic layers containing finely divided photoconductive material such as zinc oxide or some other photosensitive semi-conductive material, mat layers containing pigment, diffusion transfer layers containing development nuclei and so on. Alternatively, the ingredients appropriate to some particular ultimate utility can be incorporated into the gelatin/butadiene copolymer layer directly.

1 Claim, No Drawings

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SHEET MATERIAL

This is a division of Ser. No. 165,312, filed July 23, 1971 now U.S. Pat. No. 3,788,856, which Ser. No. 763,382 filed Sept. 27, 1968, now U.S. Pat. No. 3,649,336.

This invention relates to sheet material which comprises a hydrophobic support film and a layer system which is capable, if so desired, of providing a bond between a hydrophilic layer and the said hydrophobic support film, or which may itself provide a vehicle for light-sensitive material as hereinafter described, and particularly relates to film recording materials, films and foils consisting of or comprising said sheet material.

In the following description and claims the terms "photographic film elements" and "film recording materials" include 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.

In the said recently developed photosensitive systems, images are produced by the action of electromagnetic radiation on photosensitive semi-conductor compounds, compositions or materials, which are reversibly activated by patterns of radiations to create a latent image of corresponding activated patterns. The latent image is capable of producing a chemical reaction with a dissolved reactant by an oxidation-reduction chemical process to form a visible image (see "Unconventional Photographic Systems," Second Symposium, Oct. 26-28, 1967, Washington D.C., pages 116-117).

In electrographic systems, electrostatic charges are applied information-wise to an insulating surface. In such process an electrostatic charge pattern is built up on an insulating layer e.g., by means of a modulated electron beam while a conductive element e.g., a conductive support or layer stands in electrical contact with the back side of said insulating layer, to which a voltage is applied. After the pattern-wise charging of the insulating layer, the electrostatic charge pattern is developed, for instance by the application of a powder. Before powder development, the conductive backing element may be removed if desired. An alternative development technique is to bring about an image-wise deformation (ripple image) of the insulating layer as hereinafter described.

In electrophotographic systems, the recording of images is based on a differentiation in electrostatic charge condition, chargeability or electrical conductivity, of a recording layer containing a photoconductive substance, the said layer initially being electrically insulating in the absence of light, but becoming electrically conductive on exposure to light, and being in electrical contact with an electroconductive support or layer. By image-wise exposing the recording layer to image-wise modulated activating electromagnetic radiation, a pattern of the said differential charge condition is obtained. The electrostatic charge images may be developed by an electrostatically attractive marking material, or the conductivity images by electrolysis.

A particular technique of developing the latent image on a recording layer from either an electrographic or an electrophotographic process involves the deforma-

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tion of the exposed areas to produce a so-called "ripple image," by image-wise distortion of the surface under the influence of a differential electrical potential between the recording element and the backing element, and reference may be made to United Kingdom Pat. specification No. 964,881 to "Photographic Science and Engineering," Vol. 7, No. 1 (1963) pages 12-13; to RCA Review, Dec. 1964, pages 692-709, and to United Kingdom Pat. application No. 5307/66, now British Pat. No. 1,445,153.

In the manufacture of photographic film elements for use in silver halide emulsion layer systems, it is common practice to apply to the film support before the light-sensitive silver halide emulsion layer or other colloid layers are applied, a thin subbing layer consisting mainly of gelatin. If such a subbing layer is omitted, the photographic emulsion layer or the other colloid layers will not adhere sufficiently to the base.

The invention consists of a hydrophobic support film carrying superposed thereon in succession, a layer (A) which is directly adherent to the said hydrophobic support film and comprises a copolymer formed from 45 to 99.5 percent by weight of at least one of the chlorine-containing monomers vinylidene chloride and vinyl chloride, from 0.5 to 10 percent by weight of an ethylenically unsaturated hydrophilic monomer, and from 0 to 54.5 percent by weight of at least one other copolymerisable ethylenically unsaturated monomer; and a layer (B) comprising in a ratio of 1:3 to 1.0.5 by weight of a mixture of gelatin and a copolymer of 30 to 70 percent by weight of butadiene with at least one copolymerisable ethylenically unsaturated monomer.

Hydrophobic support films suitable for use in the sheet material according to the invention, include for example a hydrophobic cellulose ester, e.g. cellulose acetate, cellulose aceto-butyrate and cellulose nitrate; or a highly polymeric linear polyester such as for example polyethylene terephthalate, polystyrene or polymethacrylic acid esters. Such hydrophobic support films are coated with successive layers (A) and (B) according to the invention to provide a layer system which may be used for a variety of purposes. Thus the sheet material may be used for the transference thereto of a hydrophilic layer. Thus in recording or reproduction systems such a hydrophilic layer may be a stripped-off hydrophilic layer carrying a relief pattern. The sheet material according to the invention may be wetted with a liquid system capable of providing a hydrophilic film thereon. Thus the sheet material according to the invention may contain in the said layer (B) photosensitive semiconductor compounds, compositions or materials which are reversibly activated by patterns of radiations to create a latent image, and the said liquid system may then be an aqueous developing solution for the development of such a latent image.

As described a hydrophilic layer may be applied to layer (B) of the sheet material according to the invention which hydrophilic layer may be for example either transferred from another material or produced thereon from a liquid system. Both layer (B) and the hydrophilic layer when present, may contain one or more other substances, e.g. as follows:

- semi-conductive substance(s) in a suitable binding agent
- electro-conductive agent(s) in a suitable binding agent

c. pigment(s) in a photohardenable 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. developing nuclei suited in the production of silver images according to the silver halide complex diffusion transfer process.

The sheet material according to the invention may be used as a wrapping material, particularly when having layers thereon particularly adapted to accept printing thereon, or the sheet material may be used as tracing film.

Particularly useful recording materials are provided by sheet material according to the invention, having hydrophilic pigment coatings thereon, e.g. pigmented gelatin coatings suited for the production of relief images, which 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, whereby an idea may be obtained of the multicolour halftone reproduction which will finally be produced by the successive printing in register with separate standard inks yellow, magenta, cyan and black.

For ease of reference, the layer formed from the copolymer of vinylidene chloride and/or vinyl chloride is hereinafter referred to as the "vinylidene chloride copolymer" layer, and the layer formed with the mixture of gelatin and butadiene copolymer is hereinafter referred to as the "butadiene copolymer" layer.

The vinylidene chloride copolymer comprises from 0.5 to 10 percent 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-vinyl pyrrolidone, may be present.

The vinylidene chloride copolymer may be formed from vinylidene chloride and/or vinyl chloride and hydrophilic monomeric units alone in the ratio indicated above. Preferably up to 54.5 percent by weight of other recurring units, for instance acrylamides, methacrylamides, acrylic acid esters, methacrylic acid esters, maleic esters and/or N-alkylmaleimides, may also be present.

Suitable vinylidene chloride copolymers are e.g.:

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

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

the copolymer of vinylidene chloride, N-tert.-butylacrylamide, and itaconic acid (88:10:2),

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

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),

5 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),

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

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

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

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

25 The vinylidene chloride copolymers may be coated on the hydrophobic 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 may vary between 0.3 and 3 μ preferably.

30 Various wetting or dispersing agents may be used when the vinylidene chloride copolymer layer is applied from an aqueous dispersion. These dispersions are obtained directly when the copolymer has been

35 made by an emulsion polymerisation 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 dispersions are 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.

40 Finally, the biaxially oriented coated polyester film is provided with the second subbing layer of the mixture of gelatin and butadiene copolymer latex.

45 The butadiene copolymer comprises 30 to 70 percent by weight of monomeric butadiene units. The balance is formed by units deriving from other ethylenically unsaturated hydrophobic monomers, such as acrylonitrile, styrene, acrylic acid esters, methacrylic acid esters, and acroleine.

50 The butadiene copolymer is formed by emulsion polymerisation and the primary latex obtained is directly mixed with the aqueous gelatin solutions in such a way that the ratio of gelatin to butadiene copolymer

in the dried layer varies between 1.3 parts and 1:0.5, all parts being by weight. To the mixture known plasticizers for gelatin such as polyethylene oxides and glycerol may also be added.

The mixture of aqueous gelatin solution and of butadiene copolymer latex is coated onto the vinylidene chloride copolymer layer by known means. The thickness of the dried layer generally varies between 0.10 and 20 μ .

The addition of a latex of a copolymer of butadiene and a lower alkyl ester of acrylic or methacrylic acid to a gelatin-containing layer of a photographic material has been described already in the United Kingdom Patent Specification No. 1,053,043. According to this Patent Specification the butadiene copolymer latex is added to reduce the brittleness of the gelatin layer, to procure a higher dimensional stability to the photographic material, wherein it is used, and to decrease its curling tendency. However, it cannot be deduced from this Patent Specification that the layer of gelatin and butadiene copolymer latex combined with a vinylidene chloride copolymer layer would procure an adequate subbing combination for any hydrophobic film support, and especially for polyester film supports.

The subbed film support consists of a hydrophobic film support and the combination of the two anchoring subbing layers used according to the invention. As mentioned before the hydrophobic film support may be a film of cellulose triacetate, of polyethylene terephthalate, of polycarbonate, of polystyrene, of polymethacrylic acid ester, etc. The subbed hydrophobic film support may be provided on only one side or on both sides with the combination of subbing layers.

A colloid layer may be deposited on the subbed film support thus obtained. This colloid layer may be a simple gelatin layer, a gelatin silver halide emulsion layer, a gelatin filter layer, a gelatin matting layer containing e.g. finely divided silica, an antistatic layer or an antihalation layer containing a hydrophilic colloid binding agent. If an antistatic layer is deposited on the subbed film support, known antistatic agents, e.g. salts, are dispersed in the colloid binding agent, e.g. gelatin. In the latter case too, these salts may be added already to the aqueous gelatin solution, which is to be mixed with the butadiene copolymer for the formation of the second layer of the subbing layer combination.

In the manufacture of electrophotographic recording materials containing a hydrophobic electrically insulating film support and a photoconductive layer containing a photoconductive substance applied in a binder, normally an electrically insulating binder, it is necessary to apply between the photoconductive recording layer and the said support an electrically conductive interlayer having a conductivity substantially higher than the conductivity in the dark of the photoconductive recording layer. Such an interlayer preferably contains a hydrophilic colloid in combination with antistatic or hygroscopic agents, e.g. those described in the U.S. Pat. No. 3,148,982, conductive pigments e.g. carbon black and/or polyionic polymers e.g. those containing quaternized nitrogen atoms as described in the United Kingdom Patent Specification 950,960. Good results are obtained with CALGON CONDUCTIVE POLYMER 261 manufactured by Calgon Corporation, Calgon Center Box 1346, Pittsburgh, U.S.A. (Calgon is a registered Trade Mark). Such antistatic or electroconductive hydrophilic colloid layers perfectly adhere

to hydrophobic film supports subbed according to the present invention.

In the manufacture of interesting photochemically recording materials e.g. as described in the Belgian Patent Specification No. 655,384 and the published Dutch Patent Application No. 6413011, semiconductive light-sensitive pigments are dispersed in a binder containing a hydrophilic colloid.

In the manufacture of interesting electrostatic recording materials e.g. as described in the United Kingdom Patent Application No. 16,459/66 now British Pat. No. 7,756,822 and the published Dutch Patent Application No. 6,608,815 a n-type photoconductor pigment is dispersed in a binder having a hydrophilic character.

A hydrophobic film support is firmly bonded to such pigment coatings by means of the composite subbing layer according to the present invention.

In all the above described applications of the combination of subbing layers according to the invention, at least one layer is deposited on top of the butadiene copolymer layer. The layer deposited thereon may be a simple hydrophilic colloid layer e.g. a gelatin layer, a hydrophilic colloid layer containing light-sensitive silver halide salts, a hydrophilic polymer or colloid layer containing all kinds of special additives such as antihalation dyestuffs, antistatic agents, electroconductive pigments, photoconductive insulating pigments, photosensitive semiconductive pigments and matting agents. All these additives may also be added already to the coating composition of the butadiene copolymer layer. Thus, there can be incorporated into the butadiene copolymer layer finely divided silicium dioxide, photosensitive titanium dioxide, photoconductive zinc oxide and carbon black. According to a preferred embodiment these additives are dissolved when they are soluble in the coating composition or homogeneously dispersed in the mixture of aqueous gelatin solution and butadiene copolymer latex before casting of the second subbing layer on top of the vinylidene chloride copolymer layer. When the subbed hydrophobic film support is to be used as a tracing film support, there may be added to the butadiene copolymer layer, which already contains a white pigment e.g. titanium dioxide and/or silicium dioxide, also urea-formaldehyde or melamine-formaldehyde resins to render the surface of the layer more resistant to writing and tracing operations.

In a particular embodiment of the invention a n-type photoconductive substance e.g. photoconductive zinc oxide is dispersed in the butadiene copolymer layer and no further radiation sensitive layers are deposited on top of the said layer. In this way a photographic material is produced, which is suited for use according to the process described in the United Kingdom Patent Application No. 16,459/66, now British Pat. No. 7,756,822.

According to a special and very interesting embodiment of the invention a photo-sensitive semiconductor material is dispersed in the butadiene copolymer layer and no further radiation-sensitive layers are deposited on top of the said layer. In this way a photographic recording material is obtained by which visible or latent images can be formed in the absence of an externally applied electric field by means of the image-wise modulated action of electromagnetic radiation reversibly activating the photo-sensitive semiconductor material in such a way that by means of a dissolved reactant, a portion of which may be present in the recording material

before the exposure, images corresponding to the light-activated pattern are produced by an oxidation-reduction reaction, the said photosensitive semiconductor itself being substantially chemically unchanged at the end of the process. So, the recording material according to the present invention is composed of a hydrophobic film support coated with the vinylidene chloride copolymer layer and having thereon the butadiene copolymer layer, in which the photosensitive semiconductor material is dispersed. Photo-sensitive semiconductor compounds suited for use in process for producing visible or latent images by an oxidation-reduction reaction as indicated above are described e.g. in the United Kingdom Patent Specification No. 1,043,250, which pertains to a related process. Titanium dioxide is of special interest as semiconductor material, but other known semiconductors, which become conductive on irradiation, can also be used e.g. zinc oxide, zinc sulphide, lead monoxide, red lead oxide, silicon dioxide, aluminium dioxide, chromium oxide, osmium oxide, and cadmium sulphide.

In the said process the average particle size of the finely divided semiconductors is important. Particle sizes not larger than 250 millimicrons and preferably comprised between 5 and 100 millimicrons are very advantageous.

The finely divided semiconductor is dispersed in the above described binder material consisting of gelatin and butadiene copolymer in such a proportion that in the dried layer the ratio of binding agent to semiconductor varies between 3:1 and 1:10 by weight. The thickness of the radiation-sensitive coating applied on the vinylidene chloride copolymer layer by known means should be generally situated between 0.10 and 20 μ after drying.

Activation of the semiconductor surfaces is effected by exposure to radiation of sufficient energy. Ultraviolet radiation having a wavelength of less than approximately 4,000 Å is very appropriate. However sensitization of the semiconductors e.g. by doping with foreign ions or dye sensitization techniques can be employed to make the semiconductor sensitive to radiation in the visible spectrum.

Exposure to a suitable source of radiation modified by an image pattern establishes gradients of differential chemical reactivity between the exposed and non-exposed portions and establishes an image pattern in the exposed portions of the semiconductor material. Said image pattern is reversible and can be erased therefrom, e.g. by heating. It can also be made permanent by bringing the activated portions in contact with suitable oxidising or reducing agents according to known techniques. This reaction forms a visible image pattern.

The reversible image, which was obtained upon exposure to a source of radiation need not be treated with the oxidising or reducing agents directly after exposure. It can be stored for a certain time and at a later stage it can be erased or developed to produce either positive or negative images corresponding with the image stored in the exposed semiconductor. After development, the semiconductor surface is thoroughly washed to remove any remaining developer, whereupon the semiconductor surface can be reused if new information should be added to the already developed image. For development, numerous developers including silver ions, can be employed.

If the degree of semiconductor activation is high, the quantity of e.g. metallic silver formed by reduction of silver ions by the light-activated photoconductor will be sufficient to form a visible image directly. If not so, a latent developed image is produced in the semiconductor. Such a image is irreversible and can be stored for long periods. It can also be intensified by an image intensification development according to which e.g. solutions containing substances such as univalent silver ions, mercurous ions, and mercuric ions, which are reducible by the light-activated semiconductor to finely divided black-appearing metallic silver or mercury, are used in combination with chemical redox systems, preferably organic redox systems such as those containing hydroquinone or p-monomethylamino-phenol sulphate.

After development the semiconductor surfaces are rendered incapable of further development by thoroughly washing e.g. in water containing a solubilizing or complexing agent to aid removal of residual developer. In an analogous manner as in the fixing solutions employed in silver halide photography, such solutions solubilize the remaining developer e.g. silver ion, and they facilitate the removal thereof by washing.

In contradistinction with the above-described process for forming an irreversible image in a semiconductive layer, it is also possible to soak the semiconductive layer before the exposure with a solution of the developer. In this way there is immediately obtained an irreversible image upon exposure.

When hydrophobic film e.g. polyester film was used as the support for the radiation-sensitive semiconductive coating, at least two subbing layers were needed hitherto, to obtain a sufficient adhesion between the semiconductor coating and the support. The possibility of incorporating the photosensitive semiconductive substances in one of the subbing layers offers the considerable advantage, that but two subbing layers must be applied. With these two subbing layers the adhesion as well as the photographic properties are excellent.

The following examples illustrate the present invention.

EXAMPLE 1

In a reaction flask equipped with a stirrer, a nitrogen inlet, a dropping funnel, and a condenser were placed 10 litres of water and 2.88 litres of a 10 percent aqueous solution of the sodium salt of sulphonated dodecyl benzene. Then the reaction flask was rinsed with nitrogen and the liquid was heated to 60°C. In another flask were placed successively 800 ccs of isopropanol, 144 g of N-vinyl-pyrrolidone, 108 g of n-butyl acrylate, 830 g of N1tert.-butylacrylamide and 2,520 g of vinylidene chloride. The mixture was stirred and brought to dissolution by gentle heating.

Through the dropping funnel a solution was added of 21.6 g of ammonium persulphate in 400 ccs of water. Immediately pumping of the monomer solution into the reaction flask was started. the rate of pumping was such that after 75 min. all the monomer solution was pumped over. Together with the monomer solution a further amount of ammonium persulphate solution was added dropwise (64.8 g in 1,200 ccs of water). During the whole reaction period the temperature of the mixture was maintained at 60°C while refluxing. After all the monomer had been added, again an amount of 21.6 g of ammonium persulphate dissolved in 400 ccs of

water was added at once. After refluxing, stirring was continued for another 30 min. at 60°C, whereupon the reaction mixture was cooled to room temperature.

In order to precipitate the copolymer of vinylidene chloride, N-tert.-butylacrylamide, n-butyl acrylate, and n-vinylpyrrolidone (70:23:3:4), the latex formed was poured into a mixture of 40 litres of 10 percent aqueous sodium chloride solution and 40 litres of methanol while stirring. The fine grainy precipitate which was obtained was repeatedly washed with water and finally dried.

An amount of 2.5 g of the vinylidene chloride copolymer formed above were dissolved in a mixture of 90 ccs of butanone and 10 ccs of nitroethane. The solution obtained was warmed to 25°C and coated on a plate of polymethyl methacrylate in such a way that 0.75 to 1.0 g of copolymer was present per sq.m. This layer was dried at room temperature.

To the subbing layer obtained a second layer was applied at 35° to 50°C in a ratio of 0.4 to 0.6 g/sq.m from the following composition:

20 % latex of copolymer of butadiene and methyl methacrylate prepared as described hereinafter	10 g	5
gelatin	1 g	
water	55 ccs	
acetone	40 ccs	
methyl glycol	5 ccs	

After drying, a light-sensitive gelatin silver halide emulsion layer as commonly used in the graphic art was applied to this layer. The layers of the photographic material manufactured in this way showed a good adherence before, during as well as after processing in the photographic baths.

The copolymer latex was prepared as follows:

In a 20 litres autoclave were placed successively:

water boiled under nitrogen	10.2 l	30
10 % aqueous solution of oleylmethyltauride	0.6 l	
10 % aqueous solution of the sodium salt of heptadecyl-disulphonobenzimidazole	0.6 l	
azodiisobutyronitrile	6 g	
methyl methacrylate	1500 g	
butadiene	1500 g	

After sealing of the autoclave, the strongly stirred emulsion was polymerised for 6 h at 60°C. This polymerisation was slightly exothermic for a short while. Then the pressure dropped rapidly. The polymerisation was finished under reduced pressure. The latex of the copolymer of butadiene and methyl methacrylate (50:50) was then freed from residual traces of monomer by blowing at 60°C and under a slight vacuum an air current above the latex. Then the latex was cooled and filtered.

EXAMPLE 2

To a cellulose triacetate film a layer was applied at a ratio of 0.75 to 1 g/sq.m from the following composition at 25°C:

copolymer of vinylidene chloride, N-tert.-butyl-acrylamide, n-butyl acrylate, and N-vinyl pyrrolidone of example 1	2 g	55
acetone	50 ccs	
ethyl acetate	10 ccs	
methanol	10 ccs	
ethanol	10 ccs	
butanone	10 ccs	

A second layer was applied to the resulting dried layer in a ratio of 0.4 to 0.6 g/sq.m at 35°-50°C from the following composition:

20 % latex of copolymer of butadiene and methyl methacrylate of example 1	5 g
gelatin	1 g
water	60 ccs
methanol	40 ccs

A light-sensitive gelatin silver halide emulsion layer was coated thereon.

The layers of the photographic material thus obtained possessed an excellent adherence in wet as well as in dry state.

EXAMPLE 3

In an autoclave were placed 1,650 ccs of water and 9.6 g of itaconic acid. After dissolution a solution of 6 g of sodium hydrogen carbonate in 120 ccs of water was added. Subsequently 98 ccs of a 10 percent aqueous solution of the disodium salt of disulphonated dodecyl diphenyl ether and 49 ccs of a 10 percent aqueous solution of the sodium salt of sulphonated dodecyl benzene were added as emulsifying agents. Then 96 g of n-butyl acrylate, 144 g of vinylidene chloride, 9.8 g of ammonium persulphate, and 4.9 g of potassium metabisulphite were added. The autoclave was sealed and stirring started. Under nitrogen pressure 240 g of vinyl chloride were pressed into the autoclave, which was then heated to 50°C, while stirring. When this temperature had been reached, stirring was continued for 15 to 30 min. The temperature of the latex rose to about 65°C. The reaction was continued for about 3 h whereupon the latex was cooled to room temperature. The pH thereof amounted to 2.6 and was brought to 6 by means of 100 ccs of 1N aqueous sodium hydroxide. It was very well filtrable and consisted of the copolymer of vinylidene chloride, vinyl chloride, n-butyl acrylate, and itaconic acid (30:50:18:2) in a concentration of 20 percent.

To an extruded polyethylene terephthalate film, which had been stretched longitudinally up to 3 times its original length, a subbing layer was applied in a ratio of about 2 g/sq.m from an aqueous suspension containing:

20 % latex of copolymer of vinylidene chloride, vinyl chloride, n-butyl acrylate and itaconic acid (30:50:18:2) (manufactured as above)	500 g
finely divided silica	5 g

The film coated in this way was then stretched transversely up to 3 times its original width, whereupon a second subbing layer was applied in a ratio of 0.4 to 0.6 g/sq.m at 35°-50°C from the following composition:

20 % latex of copolymer of butadiene and methyl methacrylate of example 1	7.5 g
gelatin	1 g
water	60 ccs
methanol	40 ccs

55 This subbed film was provided with a light-sensitive gelatin silver halide emulsion layer as commonly used for graphic purposes. The layers of photographic material thus obtained possessed a good adherence before as well as after processing.

EXAMPLE 4

To one side of a biaxially oriented polyethylene terephthalate film of 180 μ thickness a layer was applied at 25°-30°C in a ratio of 1.5 to 1.75 g/sq.m from the following composition:

copolymer of vinylidene chloride, N-tert.-butyl-acrylamide, n-butyl acrylate, and N-vinyl pyrrolidone of example 1	5.5 g
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methylene chloride	65	ccs
dichloroethane	35	ccs

After drying of the first layer, a second layer was applied thereto in a proportion of 0.4 g/sq.m from the following composition:

20 % latex of copolymer of butadiene and methyl methacrylate of example 1	6.25	g
gelatin	1	g
water	43	ccs
silica	0.5	g
polystyrene sulphonic acid	1.8	g
methanol	40	ccs

A gelatin silver halide emulsion layer as used in photographic X-ray material was then coated on this antistatic layer. The layers of the photographic material thus obtained possessed a good adherence in all circumstances.

EXAMPLE 5

To both sides of a biaxially oriented polyethylene terephthalate film of 100 μ thickness a layer was applied from the following composition at 25°–30°C:

copolymer of vinylidene chloride, N-tert.-butylacrylamide, n-butyl acrylate, and itaconic acid (70:21:5:4) prepared analogously to the vinylidene chloride copolymer of example 1	7	g
methylene chloride	65	ccs
dichloroethane	35	ccs

This coating composition was applied in such a way that the dried layer had a thickness of 1.5 to 1.75 μ . To both subbing layers a layer was applied in a proportion of 0.4 to 0.6 g/sq.m from the following composition at 35°–50°C:

20 % latex of copolymer of butadiene and styrene (60:40) prepared analogously to the latex of the copolymer of butadiene of example 1	5	g
gelatin	1	g
water	60	ccs
methanol	40	ccs

A light-sensitive gelatin silver halide emulsion layer as commonly used in the graphic art was applied to one of the coated sides of the resulting dry material. An antihalation layer of gelatin and manganese dioxide was coated on the back-side of the material. The layers of the photographic material thus obtained showed a very good adherence in wet as well as in dry state.

EXAMPLE 6

Example 5 was repeated, with the difference, however, that the coating composition for the second subbing layer was replaced by the following one:

20 % latex of copolymer of butadiene and ethyl acrylate (50/50)	6.25	g
gelatin	1	g
water	60	ccs
ethanol	40	ccs

The adherence of the layers of the material obtained was excellent.

EXAMPLE 7

Example 5 was repeated, with the difference, however, that the coating composition of the second subbing layer was replaced by the following one:

20 % latex of copolymer of butadiene, ethyl acrylate and acrolein (55:40:5)	6	g
gelatin	0.80	g
water	60	ccs
methanol	40	ccs

The adherence of the layers of the material was excellent.

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EXAMPLE 8

Example 5 was repeated, but the coating composition of the second subbing layer was replaced by the following one:

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20 % latex of butadiene and acrylonitrile (60:40)	6	g
gelatin	0.80	g
water	60	ccs
methanol	40	ccs

The adherence of the layers of the material obtained was excellent.

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EXAMPLE 9

Example 5 was repeated, but the coating composition of the second subbing layer was replaced by the following one:

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20 % latex of copolymer of butadiene and ethyl hexyl acrylate (60:40)	6	g
gelatin	0.80	g
water	60	ccs
methanol	40	ccs

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The adherence of the layers of the material obtained was excellent.

EXAMPLE 10

To a biaxially oriented polyethylene terephthalate film of 180 μ thickness a layer was applied at 25° C in a proportion of 2 g/sq.m from the following composition:

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copolymer of vinyl chloride, n-butyl acrylate, and methacrylic acid (70:26:4)	8	g
methylene chloride	80	ccs
dichloroethane	20	ccs

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A second layer was applied thereto at 25° C in a proportion of 0.6 g per sq.m from the following coating composition:

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20 % latex of copolymer of butadiene and ethyl acrylate (50:50)	6.25	g
gelatin	1	g
water	60	ccs
methanol	40	ccs

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The dried combination of subbing layers was coated successively with an antistatic gelatin layer and a light-sensitive gelatin silver halide emulsion layer as commonly used in X-ray photographic material. The layers

of the material thus obtained showed an excellent adherence before, during as well as after processing.

EXAMPLE 11

To a biaxially oriented polyethylene terephthalate film of 180 μ thickness a layer was applied at 25°C in a proportion of 1 g/sq.m from the following coating composition:

copolymer of vinylidene chloride, n-butyl-maleimide, and itaconic acid (90:8:2)	8 g
methylene chloride	80 ccs
dichloroethane	20 ccs

To this layer a second layer was applied at 35°C in a ratio of 0.4 to 0.6 g/sq.m from the following composition:

20 % latex of copolymer of butadiene and n-butyl acrylate (70:30)	6 g	20
gelatin	0.80 g	
water	60 ccs	
methanol	40 ccs	

This layer was coated successively with a known anti-static gelatin layer and a light-sensitive gelatin silver halide emulsion layer as commonly used in X-ray material. The adherence of the layers was excellent.

EXAMPLE 12

To one side of a non-stretched polyethylene terephthalate film of about 1 mm thickness a layer was applied at 25°C in a proportion of about 5 g/sq.m from a latex of a copolymer of vinyl chloride, n-butyl acrylate, and itaconic acid (66:30:4).

This subbed film was simultaneously stretched longitudinally and transversally to about 10 times its original size. Another layer was applied at 40°C to the vinylidene chloride layer in a proportion of 0.4 to 0.6 g/sq.m from the following coating composition:

20 % latex of copolymer of butadiene and ethyl hexyl acrylate (60:40)	6 g
gelatin	0.80 g
water	60 ccs
methanol	40 ccs

The dried material was then coated with a gelatin silver halide emulsion layer as commonly used for graphic purposes.

The graphic material formed possessed an excellent adherence of the layer in dry as well as in wet state.

EXAMPLE 13

A first subbing layer as described in Example 4 and a second subbing layer as described in Example 3 were applied successively to a biaxially stretched polyethylene terephthalate support of 100 μ thickness. The resulting material was then coated with a light-sensitive layer prepared as follows:

120 g of zinc oxide was dispersed whilst stirring thoroughly in 700 ml of demineralised water, to which 2 g of sodium hexametaphosphate had been added. A solution of 80 g of gelatin in 820 g of demineralised water, 10 g of a 12.5 percent solution of saponine in demineralised water, and 10 g of a 20 percent solution of formaldehyde in demineralised water were added at 40°C. The mixture was then coated in a ratio of approximately 2 g of zinc oxide per sq.m.

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

5 seconds in a 5 percent solution of silver nitrate in demineralised water;

5 seconds in a 0.6 percent solution of p-monomethylaminophenol sulphate in demineralised water;

30 seconds in an acid fixing bath containing 200 g of sodium thiosulphate 5 aq. and 25 g of potassium metabisulphite per litre.

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

EXAMPLE 14

A biaxially oriented polyethylene terephthalate support having a thickness of 100 μ was coated with a subbing layer consisting of a solution in dichloroethane of a copolymer of vinylidene chloride, N-tert.-butylacrylamide, n-butyl acrylate, and vinyl pyrrolidone prepared as described in Example 1, in such a way that the resulting dried layer had a thickness of 1 μ .

30 g of titanium dioxide having a particle size of 15 to 40 μ and a specific surface of approximately 50 sq.m/g were stirred for 2 min. with 150 ccs of demineralized water and 0.5 g of sodium hexametaphosphate by means of an Ultra-Turrax stirrer, so that an homogeneous dispersion was produced. To the resulting mixture a solution at 30°C of 12.5 g of gelatin in 412.5 ccs of demineralized water and a 20 percent by weight latex of a copolymer of butadiene and methyl methacrylate prepared as described in Example 1 were added successively while stirring. Finally, 250 ccs of demineralized water at 30°C were added.

The resulting pigment dispersion was applied to the polyester film subbed with vinylidene chloride copolymer in such a proportion that 1.59 of titanium dioxide were present 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 sec. in a 10 percent by weight solution of silver nitrate in demineralized water;

2. 30 sec. in a 3 percent by weight solution of p-monomethylaminophenol sulphate in demineralized water;

3. 60 sec. in an acid fixing bath containing 200 g of sodium thiosulphate 5 aq. and 25 g of potassium metabisulphite per litre.

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

EXAMPLE 15

One side of a biaxially oriented polyethylene terephthalate film having a thickness of 180 μ was coated with the following composition at 25°-30°C in a ratio of 1.5 to 1.75 g/sq.m:

copolymer of vinylidene chloride, N-tert.-butylacrylamide, n-butyl acrylate, and N-vinyl pyrrolidone prepared as described in example 1	5.5 g
methylene chloride	65 ccs
dichloroethane	35 ccs

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The resulting layer was coated with a mixture of 95 parts by weight of water and 5 parts by weight of ethylenechlorhydrin, which mixture comprises 13.5 percent by weight of titanium dioxide, 1.6 percent by weight of gelatin, and 5 percent by weight of a latex of the copolymer of butadiene and methylmethacrylate (50:50 percent by weight) prepared as described in Example 1. Upon drying the layer formed had a thickness of 4-5 μ . The coating composition was prepared as follows: 2,025 g of titanium dioxide was dispersed in 7,500 ccs of water with 37 ccs of hexametaphosphate as dispersing agent. The dispersion was stirred fastly for 10 min. at 5°-15°C and then heated to 35°C. A 10 percent by weight aqueous solution of gelatin was added thereto while stirring rapidly. The following composition was then added while stirring slowly to avoid scumming:

10 % aqueous solution of gelatin water	2600 ccs	20
20 % by weight latex of the copolymer of butadiene and methyl methacrylate prepared as described in example 1	300 ccs	
10 % by weight aqueous solution of the sodium salt of oleylmethyltauride ethylenechlorhydrin	3750 ccs	
	225 ccs	15
	750 ccs	

Before coating the dispersion having a viscosity at 35°C of 8 cP was filtered.

The butadiene copolymer layer was then covered with a gelatin silver halide emulsion layer as known in the graphic art. The thus formed photographic material can be used whenever a dimensionally stable support is needed and whenever the favourable light reflection characteristics of the titanium dioxide layer are needed.

In certain applications the titanium dioxide can be replaced by other pigments, e.g. silicium dioxide.

EXAMPLE 16

In the same way as in Example 15, a biaxially oriented polyester film is coated with a layer of vinylidene chloride copolymer. The resulting layer was coated with a composition comprising 3 percent by weight of carbon black, 1 percent by weight of gelatin, and 3 percent by weight of the copolymer of butadiene and methyl methacrylate prepared as described in Example 1.

This composition was prepared as follows:

187.5 ccs of a 16 percent by weight aqueous dispersion of carbon black comprising 2 percent by weight of

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poly-N-vinyl pyrrolidone was diluted with 300 ccs of water. 5 ccs of a 40 percent by weight latex of the copolymer of ethyl acrylate and N-vinyl pyrrolidone (90:10 percent by weight) and 100 ccs of a 10 percent by weight aqueous solution of gelatin were added thereto at 35°C. The mixture was stirred rapidly for 5 min. A mixture at 35°C of 150 ccs of a 20 percent by weight latex of the copolymer of butadiene and methyl methacrylate prepared as described in example 1, 15 ccs of a 10 percent by weight aqueous solution of the sodium salt of oleylmethyltauride, 5 ml of a 40 percent by weight latex of the copolymer of ethyl acrylate and N-vinyl pyrrolidone (90:10 percent by weight), and 187.5 ml of water were added thereto while stirring slowly.

Subsequently 50 ml of methanol were added. The mixture was then filtered while warm.

The vinylidene chloride copolymer layer was coated with this composition so that upon drying a layer having a thickness of 4-5 μ was formed.

The latter layer was then coated successively with a gelatin subbing layer and a high-sensitive gelatin silver halide emulsion layer having a soft gradation.

The black-pigmented photographic material could be used for producing images according to a silver complex diffusion transfer process, wherein the sandwich formed by the light-sensitive and the image-receiving layer can be removed from the camera or the cassette during development of the negative image and during the positive image formation by diffusion transfer.

We claim:

1. Sheet material comprising a hydrophobic film support, a first layer directly adherent to said hydrophobic film support and comprising a copolymer formed from 45 to 99.5 percent by weight of at least one vinylidene chloride or vinyl chloride monomer, from 0.5 to 10 percent by weight of an ethylenically unsaturated hydrophilic monomer, and from 0 to 54.5 percent by weight of at least one other copolymerizable ethylenically unsaturated monomer; a second layer adjacent said first layer comprising in a ratio of 1:3 to 1:0.5 percent by weight a mixture of gelatin and a copolymer of 30 to 70 percent by weight of butadiene with at least one copolymerizable ethylenically unsaturated monomer; and in exterior relation to said second layer in successive order a hydrophilic electroconductive layer and electrically insulating layer.

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