(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 035 614
B2

(12) NEW EUROPEAN PATENT SPECIFICATION

(45) Date of publication of the new patent specification: **07.01.88**

(51) Int. Cl.⁴: **G 03 C 1/80**, G 03 C 1/87

(21) Application number: **80300759.0**

(22) Date of filing: **12.03.80**

(54) Improvements in photographic film materials and processes for their production.

(43) Date of publication of application:
16.09.81 Bulletin 81/37

(45) Publication of the grant of the patent:
30.05.84 Bulletin 84/22

(45) Mention of the opposition decision:
07.01.88 Bulletin 88/1

(84) Designated Contracting States:
BE CH DE FR GB IT LU NL

(56) References cited:
DE - A - 1 572 147
DE - A - 1 963 398
DE - A - 2 855 147
DE - B - 2 134 688
GB - A - 1 146 215
GB - A - 1 156 645
GB - A - 1 215 610
GB - A - 1 466 600
GB - A - 2 009 433

(73) Proprietor: **IMPERIAL CHEMICAL INDUSTRIES PLC,**
Imperial Chemical House Millbank, London SW1P 3JF
(GB)

(72) Inventor: **Ealding, Cyril John, 2801 Jolly Lane, Chester,**
Virginia 23831 (US)

(74) Representative: **Arnold, Graham Donald et al, Imperial**
Chemical Industries PLC Legal Department: Patents PO
Box 6, Welwyn Garden City Herts, AL7 1HD (GB)

EP 0 035 614 B2

Description

The present invention relates to a light-sensitive photographic material comprising a light-sensitive photographic emulsion applied to a coated film base and to processes for the production of the light-sensitive photographic material.

It is known in the photographic art that light-sensitive photographic emulsions, such as conventional light-sensitive gelatinous silver halide emulsions, do not adhere readily to the surfaces of supports derived from thermoplastics films, such as films of synthetic linear polyesters. It has therefore become common practice in the art to improve the adhesion between the film support and the photographic emulsions by pretreating the surface of the film support prior to the application of the photographic emulsion, for example, by coating with one or more polymeric adhesion-promoting layers and optionally with a further adhesion-promoting gelatinous layer. Such layers are often termed subbing layers. For example, in DE-A 1 572 147 a polyester film has a subbing-layer of a water-insoluble acrylate or methacrylate copolymer.

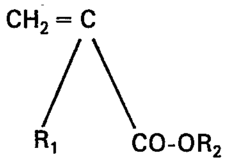
The present invention provides a subbing layer copolymer which is effective in promoting the adhesion of a light-sensitive photographic emulsion to a film support of a synthetic linear polyester.

According to the present invention a photographic material comprises (1) a self-supporting film of a synthetic linear polyester, (2) a continuous subbing layer applied to at least one surface of said self-supporting film and (3) a light-sensitive photographic emulsion layer applied directly or indirectly to the subbing layer, which subbing layer comprises a water-insoluble copolymer comprising (a) a comonomer selected from acrylic acid, methacrylic acid or a derivative of acrylic acid or methacrylic acid characterised in that the subbing layer copolymer further comprises (b) a copolymerisable sulphonated ethylenically unsaturated comonomer selected from vinyl sulphonic acid, allyl sulphonic acid, methallyl sulphonic acid, p-styrene sulphonic acid and the salts of these acids, said comonomers (a) and (b) being present in the respective molar percentages in the ranges (a) 26 to 99% and (b) 1 to 50%.

The invention also provides a process for the production of a light-sensitive photographic material which comprises applying a continuous subbing layer to at least one surface of a self-supporting film of a synthetic linear polyester and applying a light-sensitive photographic emulsion layer directly or indirectly over the subbing layer, wherein the subbing layer is applied from a film-forming composition comprising a water-insoluble copolymer which comprises (a) a comonomer selected from acrylic acid, methacrylic acid or a derivative of acrylic acid or methacrylic acid characterised in that the water insoluble copolymer further comprises (b) a copolymerisable sulphonated ethylenically unsaturated comonomer selected from vinyl sulphonic acid, allyl sulphonic acid, methally sulphonic acid, p-styrene sulphonic acid and the salts of these acids, said comonomers (a) and (b) being present in the respective molar percentages in the ranges (a) 26 to 99%, (b) 1 to 50%.

It has been surprisingly discovered that comonomer (b) is effective in adhering the light-sensitive photographic emulsion to the subbing layer. Comonomer (b) also confers anti-static properties upon the coated film base.

GB-A 1 215 610 describes a support and an addition polymer layer thereon, the polymer being an interpolymer of (A) from 60% to 90% by weight of a monomer of formula $CH_2 = C(Ro')\text{-}CO\text{-}ORo''$ where Ro′ is H or CH_3 and Ro″ is alkyl; (B) from 3 to 20% by weight of a monomer of formula $CH_2 = C(R_4)\text{-}CO\text{-}O\text{-}R_3\text{-}SO_2\text{-}OM$ wherein R_4 is H or alkyl and R_3 has its indicated valence bonds on different C atoms and is a divalent hydrocarbon radical, or a divalent aliphatic hydrocarbon radical in which a chain of carbon atoms joining the oxygen and sulphur atoms in the above formula is interrupted by at least one oxygen and/or sulphur atom and M is a cationic group; and (C) from 2 to 20% by weight of a monomer of formula:



$$CH_2 = C(R_1)\text{-}CO\text{-}OR_2$$

wherein R_1 is H or alkyl and R_2 is $\text{-}R''\text{-}O\text{-}CO\text{-}CH_2\text{-}X$, R″ being an alkylene group and X being aliphatic acyl or -CN, or R_1 is $\text{-}R'\text{-}O\text{-}CO\text{-}CH_2\text{-}X$, R′ being an alkylene group containing at least two carbon atoms in the alkylene chain and X being as just defined and R_2 is alkyl, cyclo-alkyl or aryl, said interpolymer containing at least 0.1% by weight of active methylene groups as defined.

The formula (B) does not however embrace the sulphonated ethylenically unsaturated comonomers of the present invention nor does the British patent make any reference to the use of the interpolymer as a subbing layer.

GB-A 1 146 215 relates to a coated article comprising a support of a transparent film of a synthetic polymer having on at least one surface a coating which comprises a copolymer of (A) 70–90 percent by weight of an unsaturated ester of a mono carboxylic acid wherein the alcohol component contains no more than four carbon atoms (B) 7–20 percent by weight of an aliphatic poly-functional compound containing at least two sites of carbon to carbon unsaturation, at least one of which is an allyl or vinyl group, or glycidyl acrylate, glycidyl methacrylate, methacrylate esters wherein the alcohol portion of the ester has a free hydroxy group, or fumaric acid, and (C) 3–30 percent by weight of itaconic acid, fumaric acid, acrylic acid or methacrylic acid, with the proviso that when (B) is fumaric acid (C) is itaconic acid, percentages of the constituents of the copolymer being based on the total weight of (A), (B) and (C).

The polyfunctional nature of component (B) indicates that it is intended to act as a copolymerisable cross-linking agent, and by virtue of the requirement that the aliphatic polyfunctional component should include at least two unsaturated functional groups, the definition of component (B) does not embrace the sulphonic acids or salts specified in the present invention.

The subbing copolymer for use in accordance with the present invention may be derived from one or more comonomers falling within the aforementioned definitions of each of the comonomers (a) and (b).

The self supporting film may be produced from any suitable synthetic linear polyester which may be obtained by condensing one or more dicarboxylic acids or their lower alkyl diesters, e.g. terephthalic acid, isophthalic, phthalic, 2,5-, 2,6- and 2,7-naphthalene dicarboxylic acid, succinic acid, sebacic acid, adipic acid, azelaic acid, diphenyl dicarboxylic acid, and hexahydroterephthalic acid or bis-p-carboxyl phenoxy ethane, optionally with a monocarboxylic acid, such as pivalic acid, with one or more glycols, e.g. ethylene glycol, 1,3-propanediol, 1,4-butanediol, neopentyl glycol and 1,4-cyclohexanedimethanol. Polyethylene terephthalate films are particularly preferred especially those films which have been biaxially in sequence in two mutually perpendicular directions typically at temperatures in the range 78 to 125 °C and heat set typically at temperatures in the range 150 to 250 °C, e.g. as described in GB patent specification 838 708.

The copolymers of the subbing composition are essentially water-insoluble. It will be appreciated that water-soluble copolymers would be dissolved by the aqueous solutions which are normally used for photographic processing, e.g. for development and fixing, thereby destroying the adhesion of the superimposed light-sensitive photographic emulsion layer to the underlying polyester film. The subbing compositions including the water-insoluble copolymers may nevertheless be applied to the polyester film as aqueous dispersions or alternatively as solutions in organic solvents.

Comonomer a) for the subbing copolymer is preferably present in an amount 50 to 90 mole % and preferably comprises an ester of acrylic acid or methacrylic acid, especially an alkyl ester wherein the alkyl group contains up to ten carbon atoms such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tertbutyl, hexyl, 2-ethyl, hexyl, heptyl and n-octyl. Copolymers derived from an alkyl acrylate, especially ethyl acrylate, together with an alkyl methacrylate provided particularly effective adhesion between the polyester film and the superimposed light-sensitive photographic emulsion layer. Subbing copolymers comprising an alkyl acrylate, e.g. ethyl acrylate or butyl acrylate, together with an alkyl methacrylate, e.g. methyl methacrylate, desirably in a total molar proportion in the range 55 to 80 mole %, are particularly preferred. The acrylate comonomer of such copolymers is preferably present in a proportion in the range 15 to 45 mole % and the methacrylate comonomer preferably in a proportion exceeding that of the acrylate comonomer generally by an amount in the range 5 to 20 mole %. The methacrylate is preferably present in a proportion in the range 30 to 50 mole %.

Other comonomers falling within the definition of comonomer a) which are suitable for use in the preparation of the subbing copolymer which may be used instead of but are preferably copolymerised as optional additional comonomers together with acrylic acid or methacrylic acid or esters of the acids include acrylonitrile, methacrylonitrile, halo-substituted acrylonitrile, halo-substituted methacrylonitrile, acrylamide, methacrylamide, N-methylol acrylamide, N-ethanol acrylamide, N-propanol acrylamide, N-methylol methacrylamide, N-ethanol methacrylamide, N-methyl acrylamide, N-tertiary butyl acrylamide, hydroxyethyl methacrylate, glycidyl acrylate, glycidyl methacrylate, dimethylamino ethyl methacrylate, itaconic acid, itaconic anhydride and half esters of itaconic acid.

Comonomer b) which provides anti-static protection for the subbing layer and has also surprisingly been found to be effective in promoting the adhesion of the photographic emulsion layer preferably comprises a salt and most preferably an alkali metal salt, e.g. a sodium salt. Vinyl sulphonic acid and its salts are especially effective adhesion-promoting comonomers.

Comonomers which function to modify the properties of the subbing layer may optionally be included in the production of the subbing copolymer, such as comonomers which promote the adhesion of the subbing layer in the wet and dry state to the polyester film and/or to superimposed light-sensitive photographic emulsion layers especially those comprising gelatin.

Itaconic acid and itaconic anhydride are particularly effective comonomers in promoting tenacious adhesion to superimposed gelatin-containing layers and are a preferred comonomer according to this invention. Itaconic acid may be copolymerised in an amount comprising up to 20 mole % of the total comonomeric formulation and preferably in the range 2 to 10 mole %.

The adhesion of the subbing layer to the polyester film may be modified by including one or more comonomers having cross-linkable functional groups in the comonomeric recipe for the formation of the subbing copolymer. Epoxy group-containing comonomers, such as glycidyl acrylate and glycidyl methacrylate, are particularly effective in providing internal cross-linking within the subbing layer and possibly also cross-linking to the polyester film. A comonomeric amount of 5 to 25 mole %, preferably 15 to 25 mole %, of glycidyl acrylate or glycidyl methacrylate is effective in providing the desired adhesion properties.

Other optional comonomers include vinyl esters such as vinyl acetate, vinyl chloracetate and vinyl benzoate; vinyl pyridine; vinyl chloride; vinylidene chloride; maleic acid; maleic anhydride;

butadiene; styrene and derivatives of styrene such as chloro styrene, hydroxy styrene and alkylated styrenes.

When styrene and/or a styrene derivative are employed as a comonomer they must be present only as a minor monomeric constituent, i.e. the molar proportion of the comonomer a) and b) defined above must exceed the molar proportion of the styrene and/or styrene derivative. Thus, the molar proportion of styrene and/or the styrene derivative must be less than 33.3 mole %.

Particularly preferred subbing copolymers for use according to the invention include copolymers comprising 15 to 45 mole % of an alkyl acrylate, e.g. ethyl acrylate, 30 to 50 mole % of an alkyl methacrylate, e.g. methyl methacrylate, 10 to 20 mole % of a sulphonated comonomer, e.g. sodium vinyl sulphonate and 7 to 20 mole % of itaconic acid optionally with other comonomers such as glycidyl acrylate or methacrylate in a proportion generally in the range 10 to 20 mole %. Especially effective subbing copolymers are 40/35/10/15 mole % ethyl acrylate/methyl methacrylate/itaconic acid/sodium vinyl sulphonate; 30/45/10/15 mole % butyl acrylate/methyl methacrylate/itaconic acid/sodium vinyl sulphonate; 25/35/10/15/15 mole % ethyl acrylate/methyl methacrylate/itaconic acid/glycidyl methacrylate/sodium vinyl sulphonate; and 20/40/15/10/15 mole % butyl acrylate/methyl methacrylate/glycidyl methacrylate/monomethyl itaconate/sodium vinyl sulphonate.

Conventional additives may be included in the subbing layer, e.g. adhesion promoters, such as a partially hydrolysed vinyl acetate/vinyl chloride copolymer optionally admixed with a chlorinated phenol, and particulate fillers for providing slip properties.

If desired, the subbing composition may also contain a cross-linking agent which functions to cross-link the subbing copolymer thereby improving adhesion to the polyester film. Additionally, the cross-linking agent should preferably be capable of internal cross-linking in order to provide protection against solvent penetration. Suitable cross-linking agents may comprise epoxy resins, alkyd resins, amine derivatives such as hexamethoxymethyl melamine, and/or condensation products of an amine, e.g. melamine, diazine, urea, cyclic ethylene urea, cyclic propylene urea, thiourea, cyclic ethylene thiourea, alkyl melamines, aryl melamines, benzo guanamines, guanamines, alkyl guanamines and aryl guanamines, with an aldehyde, e.g. formaldehyde. A useful condensation product is that of melamine with formaldehyde. The condensation product may optionally be alkoxylated. The cross-linking agent may be used in amounts of up to 25% by weight based on the weight of the copolymer in the subbing composition. A catalyst is also preferably employed to facilitate cross-linking action of the cross-linking agent. Preferred catalysts for cross-linking melamine formaldehyde include ammonium chloride, ammonium nitrate, ammonium thiocyanate, ammonium dihydrogen phosphate, ammonium sulphate, diammonium hydrogen phosphate, para toluene sulphonic acid, maleic acid stabilised by reaction with a base, and morpholinium para toluene sulphonate.

The subbing composition may be applied to the polyester film as an aqueous dispersion or a solution in an organic solvent by any suitable conventional coating technique such as dip coating, bead coating, reverse roller coating or slot coating.

The subbing composition may be applied to the polyester film during or after the completion of the process by which the polyester film is produced.

If the subbing composition is applied to the film after the production of the film has been completed, the film may be pretreated or coated in such a way to improve the adhesion of the subbing layer to the film surface. Conventional chemical or physical pretreatments such as coating the film surface with a solution having a swelling, solvent or oxidising action on the film, corona discharge treatment, flame treatment, or ultra-violet light treatment may be used. Alternatively, the plastics film may carry on adhesion-promoting polymeric layer to which the subbing layer according to the invention may be applied.

It has been found however that the subbing compositions bond with acceptable adhesion to the polyester film surface when applied to the film during the process for its manufacture. Satisfactory adhesion is obtainable by direct application of the subbing composition to the polyester film surface without any pretreatment or interposition of an adhesion-promoting layer.

Polyester films are normally manufactured by a process wherein the films are molecularly oriented by stretching in two mutually perpendicular directions. The process is conventionally accomplished by sequentially stretching a flat amorphous polyester film first in one direction and then in another mutually perpendicular direction. Generally, it is preferred to stretch the film firstly in the longitudinal direction, i.e. the direction of passage through the stretching machine, and then in the transverse direction. The stretched films may also be dimensionally stabilised by heat-setting under dimensional restraint. Stretching and heat setting is conventionally carried out by heating the film above ambient temperature. The preferred polyester films for use according to the invention may be made according to such a process. Polyethylene terephthalates are preferably produced by sequential biaxial orientation and heat setting, e.g. as described in GB patent specification 838 708.

Polyester films oriented by sequential stretching may be coated with the subbing composition either before stretching in the first direction of stretching or at a stage intermediate the stretching in the first direction and stretching in the second direction. It is preferred according to this invention that the subbing composition should be applied to the film between the two stretching operations, e.g. by firstly stretching the film in the longitudinal direction over a series of rotating rollers, coating with the subbing composition and then stretching transversely in a stenter oven followed by heat-setting.

Subbing compositions applied to the polyester film surface are preferably applied as aqueous dispersions. The temperatures applied to the coated film during the subsequent stretching and/or heat setting are effective in drying the aqueous medium, or the solvent in the case of solvent-applied compositions, and also in coalescing and forming the coating into a continuous and uniform subbing layer. The cross-linking of cross-linkable subbing compositions is also achieved at such stretching and/or heat-setting temperatures.

The subbing layer is preferably applied to the polyester film at a coat weight within the rang 0.1 to 10 mg/dm^2, especially 1.0 to 3.0 mg/dm^2. For films coated on both surfaces with a subbing layer, each layer preferably has a coat weight within the preferred range.

According to one aspect of this invention, a light-sensitive photographic emulsion layer, e.g. a conventional X-ray or graphic arts gelatinous silver halide emulsion, may be adhered directly or indirectly to the subbing layer. Indirect adhesion may be accomplished by interposing a conventional gelatinous subbing layer between the copolymeric subbing layer and the light-sensitive photographic emulsion layer. However, it has been discovered that adequate wet and dry adhesion can be obtained in the absence of a gelatinous subbing layer and by adhering the light-sensitive photographic emulsion layer directly to the copolymeric subbing layer.

Modification of the surface of the copolymeric subbing layer, e.g. by flame treatment, ion bombardment, electron beam treatment, ultra-violet light treatment or preferably by corona-discharge, may improve the adhesion of a light-sensitive photographic emulsion layer applied directly to the copolymeric subbing layer but may not be essential to the provision of satisfactory adhesion.

The preferred treatment by corona discharge may be effected in air at atmospheric pressure with conventional equipment using a high frequency, high voltage generator, preferably having a power output of from 1 to 20 kw at a potential of 1 to 100 kv. Discharge is conveniently accomplished by passing the film over a dielectric support roller at the discharge station at a linear speed preferably of 1.0 to 500 m per minute. The discharge electrodes may be positioned 0.1 to 10.0 mm from the moving film surface.

Satisfactory adhesion of light-sensitive gelatinous silver halide emulsions, especially conventional X-ray emulsions, applied directly to the surface of some subbing layer can however be achieved without any prior surface modification, e.g. by corona discharge treatment. Examples of subbing copolymers which provide adequate adhesion without corona discharge treatment are 40/35/10/15 mole % ethyl acrylate/methyl methacrylate/itaconic acid/sodium styrene sulphonate and 41/41.5/8.5/9.0 mole % ethyl acrylate/methyl methacrylate/glycidyl methacrylate/sodium styrene sulphonate.

The light-sensitive photographic emulsion may optionally include any of the conventional additives.

Light-sensitive photographic emulsion layers applied directly or indirectly to the subbing layer of the coated film bases according to this invention adhere with excellent dry and wet adhesions. The coated film bases also have excellent antistatic properties such that they pass effectively and without interruption through coating machines, e.g. for the application of light-sensitive photographic emulsions.

The invention is further illustrated by the following examples, in which dry and wet adhesions have the following meanings and were assessed by the following tests.

Dry adhesion refers to the adhesion of a gelatinous silver halide emulsion to the plastics film in the final photographic film, assessed, both before and after processing in standard photographic chemicals, by sticking a self-adhesive tape along the torn edge of the film and rapidly separating the tape from the film.

Wet adhesion refers to the adhesion of a gelatinous silver halide emulsion to the plastics film in the final photographic film, assessed, after processing in the standard photographic chemicals and washing in water for 15 minutes by rubbing with a sponge over a series of lines scored in the still wet emulsion.

Example 1

An aqueous dispersion of an ethyl acrylate/-methyl acrylate/itaconic acid/sodium vinyl sulphonate copolymer of respective proportions 40/35/10/15 mole % was prepared by conventional emulsion polymerisation of the following ingredients:

Ethyl acrylate	286 ml
Methyl methacrylate	319 ml
Itaconic acid	98 g
Sodium vinyl sulphonate	146 g
Sodium salt of a sulphated alkyl phenoxy polyethoxy ethanol	97 ml
Ammonium persulphate	1 g
Sodium metabisulphite	3 g
Distilled water	3000 ml

A subbing composition was produced from the resulting aqueous dispersion as a mixture of the ingredients:

Ethyl arylate/methyl methacrylate/ itaconic acid/sodium vinyl sulphonate copolymer dispersion	10 g
Hexamethoxy methyl melamine (commercially available as "Cymel" 300, trademark	1 g
Distilled water	89 g

A polyethylene terephthalate film was melt extruded, cast onto a coated rotating drum and stretched in the direction of extrusion to about three times its original dimension in that direction by conventional procedure and was coated on both sides with a uniform layer of the aqueous subbing composition. The coated film was passed into a heated stenter oven where the coatings were dried and the film stretched about three times its original dimension in the transverse direction in a conventional manner. The film was then heat set under dimensional restraint at a temperature of about 200°C by conventional procedure. The applied subbing layers were formed into uniform continuous layers each having a dry coat weight of approximately 1.5 mg/dm^2 and the film had an overall thickness of about 100 μm.

The subbing layers were then coated with a conventional silver halide X-ray emulsion which was chilled to gel the coating and dried for 20 minutes at 33°C. The dry and wet adhesions of the silver halide emulsion layers to the polyethylene terephthalate film were determined by the tests noted above and were found to be strong and acceptable for photographic use.

The subbed film was found to have excellent antistatic properties when tested at a temperature of 20°C and a relative humidity of 60% and before the application of the silver halide emulsion layers, i.e. a surface resistivity of 1.6×10^{10} ohms/square.

Examples 2 to 4

Example 1 was repeated using similar aqueous dispersions but containing different subbing copolymers as shown in the following Table, with the exception that the hexamethoxy methyl melamine component was omitted from the composition for Example 3.

Prior to the application of the silver halide X-ray emulsions, the subbing layers were subjected to corona discharge treatment by passing the film at 6.1 metres per minute through a commercially available "Vetaphone" (trademark) 3 kw treater using a power of 2 kw and electrode to film distance of 1 mm.

In each case the dry and wet adhesions of the silver halide emulsion layers to the polyethylene terephthalate film were assessed by the tests noted above and were found to be strong and acceptable for photographic use.

The subbed films were found to have excellent antistatic properties, represented by the surface resistivities noted in the Table when measured at a temperature of 20°C and a relative humidity of 60%.

Table

Example	Comonomers for preparation of subbing copolymer	Respective proportions of comonomers in subbing copolymer mole %	Surface resistivity of subbed film measured at 20°C and 60% relative humidity ohms/square
1	EA/MMA/IA/SVS	40/35/10/15	1.6×10^{10}
2	BA/MMA/IA/SVS	30/45/10/15	2×10^{10}
3	EA/MMA/IA/GMA/SVS	25/35/10/15/15	1×10^{11}
4	BA/MMA/GMA/MMI/SVS	20/40/15/10/15	8×10^{10}

Key:
EA = ethyl acrylate
BA = n-butyl acrylate
MMA = methyl methacrylate
IA = itaconic acid
GMA = glycidyl methacrylate
SVS = sodium vinyl sulphonate
MMI = mono methyl itaconate

Example 5

An aqueous subbing latex was prepared by conventional emulsion polymerisation of the following monomeric mixture:

Ethyl acrylate	41.0 mole %
Methyl methacrylate	41.5 mole %
Glycidyl methacrylate	8.5 mole %
Sodium styrene sulphonate	9.0 mole %

The latex was prepared by adding 306 g of the monomeric mixture together with 18.5 ml of an emulsifier comprising nonyl phenol condensed with 12 moles of ethylene oxide, 22.5 g of sodium dodecyl benzene sulphonate and 2 g of potassium persulphate to one litre of water.

A polyethylene terephthalate film was melt extruded and quenched to the amorphous state on a cooled rotating drum. The resulting film was stretched in the direction of extrusion to about 3.5 times its original length. It was then coated on both sides with the aqueous latex prepared above by a roller coating technique and passed into a stenter oven where the coating was dried. The dried coated film was then stretched sideways about 3.5 times its original width and finally heat set at a temperature of about 210°C. The final thickness of the coating on each side of the biaxially drawn film was about 0.2 micrometer, and the total thickness of the coated film was about 100 micrometers.

The subbed film had a surface resistivity of about 10^{11} ohms/square at 20°C and a relative humidity of 60%. The copolymeric subbing layers were then coated directly with a conventional gelatinous silver halide photographic emulsion without prior treatment by corona discharge and tested for dry and wet adhesion. The adhesions were strong in each case.

Claims

1. A photographic material comprising (1) a self-supporting film of a synthetic linear polyester, (2) a continuous subbing layer applied to at least one surface of said self-supporting film and (3) a light-sensitive photographic emulsion layer applied directly or indirectly to the subbing layer, which subbing layer comprises a water-insoluble copolymer comprising (a) a comonomer selected from acrylic acid, methacrylic acid or a derivative of acrylic acid or methacrylic acid characterised in that the subbing layer copolymer further comprises (b) a copolymerisable sulphonated ethylenically unsaturated comonomer selected from vinyl sulphonic acid, allyl sulphonic acid, methallyl sulphonic acid, p-styrene sulphonic acid and the salts of these acids, said comonomers (a) and (b) being present in the respective molar percentages in the ranges (a) 26 to 99% and (b) 1 to 50%.

2. A photographic material according to claim 1, in which comonomer (a) comprises a mixture of an alkyl acrylate and an alkyl methacrylate in a total molar proportion in the range 55 to 80 mole %.

3. A photographic material according to claim 2, in which comonomer (a) comprises a mixture of 15 to 45 mole % of the alkyl acrylate and 30 to 50 mole % of the alkyl methacrylate.

4. A photographic material according to any preceding claim, in which the subbing copolymer is derived from one or more additional comonomers selected from itaconic acid, itaconic anhydride, half esters of itaconic acid, glycidyl acrylate and glycidyl methacrylate.

5. A photographic material according to claim 3, in which the subbing copolymer comprises 15 to 45 mole % alkyl acrylate/30 to 50 mole % alkyl methacrylate/10 to 20 mole % sulphonated comonomer/7 to 20 mole % itaconic acid.

6. A process for the production of a light-sensitive photographic material which comprises applying a continuous subbing layer to at least one surface of a self-supporting film of a synthetic linear polyester, and applying a light-sensitive photographic emulsion layer directly or indirectly over the subbing layer, wherein the subbing layer is applied from a film-forming composition comprising a waterinsoluble copolymer which comprises (a) a comonomer selected from acrylic acid, methacrylic acid or a derivative of acrylic acid of methacrylic acid characterised in that the water-insoluble copolymer further comprises (b) a copolymerisable sulphonated ethylenically unsaturated comonomer selected from vinyl sulphonic acid, allyl sulphonic acid, methallyl sulphonic acid, p-styrene sulphonic acid and the salts of these acids, said comonomers (a) and (b) being present in the respective molar percentages in the ranges (a) 26 to 99%, (b) 1 to 50%.

7. A process according to claim 6, in which comonomer (a) comprises a mixture of an alkyl acrylate and an alkyl methacrylate in a total molar proportion in the range 55 to 80 mole %.

8. A process according to claim 7 in which comonomer (a) comprises a mixture of 15 to 45 mole % of the alkyl acrylate and 30 to 50 mole % of the alkyl methacrylate.

9. A process according to any one of claims 6 to 8 in which the subbing copolymer is derived from one or more additional comonomers selected from itaconic acid, itaconic anhydride, half esters of itaconic acid, glycidyl acrylate and glycidyl methacrylate.

10. A process according to claim 9, in which the subbing copolymer comprises 15 to 45 mole % alkyl acrylate/30 to 50 mole % alkyl methacrylate/10 to 20 mole % sulphonated comonomer/7 to 20 mole % itaconic acid.

11. A process according to any one of claims 6 to 10 in which the surface of the subbing layer is subjected to corona discharge treatment prior to the application of the light-sensitive photographic emulsion layer directly thereto.

Patentansprüche

1. Fotografisches Material mit (1) einer selbsttragenden Folie aus einem synthetischen linearen Polyester, (2) einer auf mindestens eine Oberfläche der selbsttragenden Folie aufgebrachten kontinuierlichen Unterschicht und (3) einer lichtempfindlichen Fotoemulsionsschicht, die unmittelbar oder mittelbar auf die Unterschicht aufgebracht ist, wobei diese Unterschicht ein wasserunlösliches Copolymer enthält, das (a) ein aus Acrylsäure, Methacrylsäure oder einem Derivat von Acrylsäure oder Methacrylsäure ausgewähltes Comonomer enthält, dadurch gekennzeichnet, dass das Copolymer der Unterschicht ferner (b) ein aus Vinylsulfonsäure, Allylsulfonsäure, Methallylsulfonsäure, p-Styrolsulfonsäure und den Salzen dieser Säuren ausgewähltes copolymerisierbares sulfoniertes, ethylenisch ungesättigtes Comonomer enthält, wobei die Comonomere (a) und (b) in molaren Anteilen von (a) 26 bis 99% bzw. (b) 1 bis 50% vorliegen.

2. Fotografisches Material nach Anspruch 1, bei dem das Comonomer (a) eine Mischung eines Alkylacrylats und eines Alkylmethacrylats in einem gesamten molaren Anteil von 55 bis 80 Mol-% enthält.

3. Fotografisches Material nach Anspruch 2, bei dem das Comonomer (a) eine Mischung von 15 bis 45 Mol-% des Alkylacrylats und 30 bis 50 Mol-% des Alkylmethacrylats enthält.

4. Fotografisches Material nach einem der vorhergehenden Ansprüche, bei dem das Copolymer der Unterschicht von einem oder mehr als einem zusätzlichen, aus Itaconsäure, Itaconsäureanhydrid, Halbestern der Itaconsäure, Glycidylacrylat und Glycidylmethacrylat ausgewählten Comonomer abgeleitet ist.

5. Fotografisches Material nach Anspruch 3, bei dem das Copolymer der Unterschicht 15 bis 45 Mol-% Alkylacrylat/30 bis 50 Mol-% Alkylmethacrylat/10 bis 20 Mol-% sulfoniertes Comonomer/7 bis 20 Mol-% Itaconsäure enthält.

6. Verfahren zur Herstellung eines lichtempfindlichen fotografischen Materials, bei dem auf mindestens eine Oberfläche einer selbsttragenden Folie aus einem synthetischen linearen Polyester eine kontinuierliche Unterschicht aufgebracht wird und unmittelbar oder mittelbar über der Unterschicht eine lichtempfindliche Fotoemulsionsschicht aufgebracht wird, wobei die Unterschicht aus einer filmbildenden Masse, die ein wasserunlösliches Copolymer enthält, das (a) ein aus Acrylsäure, Methacrylsäure oder einem Derivat von Acrylsäure oder Methacrylsäure ausgewähltes Comonomer enthält, aufgebracht wird, dadurch gekennzeichnet, dass das wasserunlösliche Copolymer ferner (b) ein aus Vinylsulfonsäure, Allylsulfonsäure, Methallylsulfonsäure, p-Styrolsulfonsäure und den Salzen dieser Säuren ausgewähltes copolymerisierbares sulfoniertes, ethylenisch ungesättigtes Comonomer enthält, wobei die Comonomere (a) und (b) in molaren Anteilen von (a) 26 bis 99% bzw. (b) 1 bis 50% vorliegen.

7. Verfahren nach Anspruch 6, bei dem das Comonomer (a) eine Mischung eines Alkylacrylats und eines Alkylmethacrylats in einem gesamten molaren Anteil von 55 bis 80 Mol-% enthält.

8. Verfahren nach Anspruch 7, bei dem das Comonomer (a) eine Mischung von 15 bis 45 Mol-% des Alkylacrylats und 30 bis 50 Mol-% des Alkylmethacrylats enthält.

9. Verfahren nach einem der Ansprüche 6 bis 8, bei dem das Copolymer der Unterschicht von einem oder mehr als einem zusätzlichen, aus Itaconsäure, Itaconsäureanhydrid, Halbestern der Itaconsäure, Glycidylacrylate und Glacidylmethacrylat ausgewählten Comonomer abgeleitet ist.

10. Verfahren nach Anspruch 9, bei dem das Copolymer der Unterschicht 15 bis 45 Mol-% Alkylacrylat/30 bis 50 Mol-% Alkylmethacrylat/10 bis 20 Mol-% sulfoniertes Comonomer/7 bis 20 mol-% Itaconsäure enthält.

11. Verfahren nach einem der Ansprüche 6 bis 10, bei dem die Oberfläche der Unterschicht einer Koronaentladungsbehandlung unterzogen wird, bevor die lichtempfindliche Fotoemulsionsschicht unmittelbar auf die Unterschicht aufgebracht wird.

Revendications

1. Matériau photographique comprenant (1) un film autoporteur en polyester linéaire synthétique (2) une couche d'ancrage continue appliquée sur au moins une surface de ce film autoporteur et (3) une couche à émulsion photographique photosensible appliquée directement ou indirectement sur la couche d'ancrage, laquelle couche d'ancrage comprend un copolymère insoluble dans l'eau comprenant (a) un comonomère choisi parmi l'acide acrylique, l'acide méthacrylique ou un dérivé d'acide acrylique ou d'acide méthacrylique, caractérisé en ce que le copolymère de la couche d'ancrage comprend de plus (b) un comonomère à insaturation éthylénique sulfoné copolymérisable choisi parmi l'acide vinylsulfonique, l'acide allylsulfonique, l'acide méthallylsulfonique, l'acide p-styrènesulfonique et les sels de ces acides, ces comonomères (a) et (b) étant présents selon des pourcentages molaires respectifs compris dans les gammes (a) de 26 à 99% et (b) de 1 à 50%.

2. Matériau photographique suivant le revendication 1, dans lequel le comonomère (a) comprend un mélange d'acrylate d'alcoyle et de méthacrylate d'alcoyle selon une proportion molaire totale comprise dans une gamme allant de 55 à 80 moles %.

3. Matériau photographique suivant la revendication 2, dans lequel le comonomère (a) comprend un mélange de 15 à 45 moles % de l'acrylate d'alcoyle et de 30 à 50 moles % du méthacrylate d'alcoyle.

4. Matériau photographique suivant l'une quelconque des revendications précédentes, dans lequel le copolymère d'ancrage est dérivé d'un ou plusieurs comonomères additionnels choisi parmi l'acide itaconique, l'anhydride itaconique, les hémi-esters d'acide itaconique, l'acrylate glycidylique et le méthacrylate glycidylique.

5. Matériau photographique suivant la revendication 3, dans lequel le copolymère d'ancrage comprend de 15 à 45 moles % d'acrylate d'alcoyle/30 à 50 moles % de méthacrylate d'alcoyle/10 à 20 moles % de comonomère sulfoné/7 à 20 moles % d'acide itaconique.

6. Procédé pour la production d'un matériau photographique photosensible, consistant à appliquer une couche d'ancrage continue sur au moins une surface d'un film autoporteur en polyester linéaire synthétique et à appliquer une couche d'émulsion photographique photosensible directement ou indirectement sur la couche d'ancrage, selon lequel la couche d'ancrage est appliquée à partir d'une composition filmogène comprenant un copolymère insoluble dans l'eau qui comprend (a) un comonomère choisi parmi l'acide acrylique, l'acide méthacrylique ou un dérivé d'acide acrylique ou d'acide méthacrylique, caractérisé en ce que le copolymère insoluble dans l'eau comprend de plus (b) un comonomère à insaturation éthylénique sulfoné copolymérisable choisi parmi l'acide vinylsulfonique, l'acide allylsulfonique, l'acide méthallylsulfonique, l'acide p-styrènesulfonique, et les sels de ces acides, ces comonomères (a) et (b) étant présents selon les pourcentages molaires respectifs compris dans les gammes (a) de 26 à 99% (b) de 1 à 50%.

7. Procédé suivant la revendication 6, dans lequel le comonomère (a) comprend un mélange d'un acrylate d'alcoyle et d'un méthacrylate d'alcoyle, selon une proportion molaire totale comprise dans une gamme allant de 55 à 80 moles %.

8. Procédé suivant la revendication 7, dans lequel le comonomère (a) comprend un mélange de 15 à 45 moles % de l'acrylate d'alcoyle et de 30 à 50 moles % du méthacrylate d'alcoyle.

9. Procédé suivant l'une quelconque des revendications 6 à 8, dans lequel le copolymère d'ancrage est dérivé d'un ou plusieurs comonomères additionnels choisis parmi l'acide itaconique, l'anhydride itaconique, les hémi-esters d'acide itaconique, l'acrylate glycidylique et le méthacrylate glycidylique.

10. Procédé suivant la revendication 9, dans lequel le copolymère d'ancrage comprend de 15 à 45 moles % d'acrylate d'alcoyle/de 30 à 50 moles % de méthacrylate d'alcoyle/de 10 à 20 moles % de comonomère sulfoné/de 7 à 20 moles % d'acide itaconique.

11. Procédé suivant l'une quelconque des revendications 6 à 10, dans lequel la surface de la couche d'ancrage est soumise à un traitement par effluves avant l'application directe sur celle-ci de la couche d'émulsion photographie photosensible.