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㉔ Applicant: **AGFA-GEVAERT naamloze vennootschap,**
Septestraat 27, B-2510 Mortsel (BE)

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㉖ Inventor: **Van Paesschen, August Jean, St.**
Vincentiusstraat 6, B-2000 Antwerpen (BE)
Inventor: **Van Gossum, Lucien Janbaptist,**
Verbrandehoevestraat 4, B-2550 Kontich (BE)

㉗ **Film or sheet material coated with a layer promoting the adherence thereto of a hydrophilic colloid layer.**

㉘ A plate, sheet or film material having a hydrophobic resin or glass surface coated with a subbing layer promoting the adherence thereto of a layer containing a hydrophilic colloid, characterized in that said subbing layer is essentially free from synthetic organic polymer and comprises:

- (1) from 35 to 75% by weight of colloidal silica,
- (2) from 25 to 65% by weight of an aromatic hydroxy compound that can be applied from an aqueous medium in dissolved form, and
- (3) from 0 to 15% by weight of a proteinaceous hydrophilic colloid.

Film or sheet material coated with a layer promoting the adherence thereto of a hydrophilic colloid layer.

The present invention relates to a film or sheet material coated with a layer promoting the adherence thereto of a hydrophilic colloid layer in dry and wet state.

It is known that hydrophobic film supports suited for use in the production of photographic materials including a hydrophilic colloid layer, e.g. photographic gelatin-silver halide emulsion layer, have to be coated with one or more layers, called subbing layers, for promoting the adherence thereto of the hydrophilic colloid layer(s).

Subbing basically consists in coating onto the film base of a layer or a series of layers, less than a micron thick when dry, of a material which has physico-chemical affinity (wetting and adhering character) for both the film base and the hydrophilic colloid coating applied thereto. The wet conditions of processing of photographic silver halide emulsion materials require that the adhesion withstands an aqueous alkaline treatment.

In many photographic applications the well-known cellulose acetate film base has been replaced by a film base made of polyethylene terephthalate. Other less commonly used film bases are made of polystyrene, polyvinyl chloride, polycarbonates and homo- or copolymers of acrylic esters. Polymethyl methacrylate can be used as a substitute for glass supports in the production of photographic plates.

Photographic silver halide materials having a glass plate base are known for use in microphotography, astrophotography, holography and applications in the production of micro-electronic integrated circuits (ref. GB-P 1 286 467) and laser beam recording (ref. e.g. US-P 4 363 870).

It is a preferred practice to apply subbing layers from aqueous compositions that exclude the use of expensive, inflammable, explosive and often toxic solvents.

Aqueous subbing compositions are known, e.g. from GB-P 1 589 926, US-P 4 328 283 and 4 394 442 and published EP-A 0 029 620. These subbing compositions are usually applied to film supports, e.g. a polyethylene terephthalate film support, during manufacture thereof between longitudinal and transversal stretching.

According to said EP-A document a subbing layer is applied onto a polyester support from an aqueous dispersion of particular sulphonated
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copolyesters optionally in the presence of resorcinol and colloidal silica as adhesion-improving agents. Resorcinol and other analogous aromatic hydroxy compounds are swelling agents for polyester film (ref. GB-P 1 589 926).

The use of resorcinol in admixture with silica and major amounts of chloral hydrate for application to a biaxially stretched subbing of polyethylene terephthalate film has been described in GB-P 1 371 095, Example 4.

It is an object of the present invention to provide a plate, film or sheet material comprising a hydrophobic base coated with a subbing layer that has been applied from an aqueous medium free from organic synthetic polymer and that allows a hydrophilic colloid layer, e.g. a hydrophilic colloid layer containing gelatin as binder to be bond firmly thereto in dry as well as in wet state .

It is a further object of the present invention to provide a said subbed sheet or film material wherein the subbing layer has been coated on glass or a hydrophobic resin support in the post-stretch stage of the manufacturing of said support or on hydrophobic film supports or sheets that have not been stretched, e.g. on polymethyl methacrylate plates.

It is more particularly an object of the present invention to provide a photographic silver halide emulsion material containing a said subbed sheet or film material as support.

According to the present invention a plate, sheet or film material having a hydrophobic resin or glass surface coated with a subbing layer promoting the adherence thereto of a layer containing a hydrophilic colloid is provided, characterized in that said subbing layer is essentially free from synthetic organic polymer and comprises :

- (1) from 35 to 75 % by weight of colloidal silica,
- (2) from 25 to 65 % by weight of an aromatic hydroxy compound that can be applied from an aqueous medium in dissolved form, and
- (3) from 0 to 15 % by weight of a proteinaceous hydrophilic colloid.

Plate, sheet or film materials with hydrophobic resin surface consist e.g. of self-supporting polymethyl methacrylate, polyethylene, polypropylene, polystyrene or polyvinyl chloride materials or include these resins as a supported surface layer. Examples thereof are paper or resin supports coated with a water-impermeable layer of polyethylene.

The colloidal silica has preferably a particle size in the range of GV.1307

10 to 120 nm and is commercially available e.g. as "LUDOX" (trade name of E.I. du Pont de Nemours, Wilmington, Del. U.S.A., "SYTON" (trade name of Monsanto Chemical Corporation, Boston, Mass. U.S.A. and "KIESELSOLE" (trade name of Farbenfabriken Bayer, Leverkusen, West-Germany.

The aromatic hydroxy compound is preferably a swelling agent for the resin wherefrom said support is made, e.g. is a polyhydroxy compound such as resorcinol or a chlorinated derivative thereof such as 4-chlororesorcinol.

The optionally present proteinaceous colloid is preferably gelatin. It mainly serves as a thickening agent increasing the viscosity of the coating composition.

The present subbing layer is particularly suited for promoting the adherence thereto of a photographic gelatin-silver halide emulsion layer and likewise other gelatin-containing layers used in photography, e.g. anti-reflection layers or anti-halation layers, filter layers, anti-static layers and layers applied in a photographic diffusion-transfer-reversal material such as image receiving layers containing development nuclei for complexed silver halide or containing mordanting agents for dyes.

The coating of the subbing layer composition may proceed at one or both sides of the support e.g. at a dry coating coverage of 0.5 to 2 g per m².

Although coating proceeds preferably from water, mixtures of water with water-miscible solvents, e.g. methanol, ethanol or acetone may be used likewise with good result.

The coating is dried, e.g. at 30 to 40° C, no higher drying temperature being required.

If desired other useful ingredients may be incorporated in the subbing composition, e.g. surface-active coating agents and embossing agents i.e. particles for creating microscopic protrusions of less than 3 μ m for obtaining a thin air space between the subbed material and a material touching it, e.g. during transport or rolling up of the subbed film. Such embossing agents can be known matting agents, e.g. those described in the published EP-Application 0 003627.

After the coating and drying of the present subbing layer an interlayer or a second subbing layer mainly containing gelatin and plasticizer(s) may be applied thereto.

Useful plasticizers are, e.g. aliphatic polyhydroxy compounds such as glycerol, sorbitol, mannitol, tri(β -hydroxy-ethyl)-glycerol, 1,1,1-tri(hydroxymethyl)-propane, 2-nitro-2-ethyl-1,3-propanediol, 1,3-dichloro-2-propanol, 1,2,4-butanetriol, 1,2,6-hexanetriol, 3-hydroxymethyl-2,4-dihydroxypentane, 2-hydroxymethyl-4-hydroxyamyl alcohol, glycerol-aldehyde, and glycerol dichlorohydrin.

Equally suitable compounds are caprolactam, N,N'-dimethylurea, resorcinol, pyrocatechol, and dichlorodiethyl ether. Other suitable plasticizers are aliphatic carboxylic or sulphonic acids such as malonic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, mono- and di-chloro-acetic acid, 1,2,3-propene-tricarboxylic acid, trimellitic acid, acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, and 2-sulpho-ethyl methacrylate ; further aromatic acids such as phthalic acid, o-sulphobenzoic acid, o-nitrobenzoic acid, o-aminobenzoic acid, p-hydroxybenzoic acid, and salicylic acid.

Moreover, polymeric plasticizers can be added to said gelatin coating composition, e.g. latices of copolymers of butadiene and a lower alkyl ester of acrylic or methacrylic acid e.g. a copolymer of butadiene and methyl methacrylate containing 20-80 % by weight of methyl methacrylate. These latices have been described in the United Kingdom Patent Specification 1,053,043.

Hardening agents, spreading agents, antistatic or metal-complexing agents can also be added to the aqueous gelatin-containing coating composition. Suitable antistatic or metal complexing agents are the sodium salt of polystyrene sulphonic acid, alkali metal salts of co(styrene/maleic acid), inorganic salts such as sodium chloride, potassium chloride, and sodium orthosilicate, further citric acid, sulphosalicylic acid, 2,5-disulphohydroquinone, the sodium salt of ethylenediamine tetraacetic acid, ethanol-amino-diacetic acid, the sodium salt of N(o-hydroxybenzyl)-amino-diacetic acid, the monosodium salt of vanadic acid, 3,5-disulphopyrocatechol, phosphono-acetic acid, ethylene-1,2-diphosphonic acid, butylene-1,4-disphosphonic acid, and ascorbic acid.

Other possible ingredients for the second subbing layer are, e.g. colloidal silica, and the already mentioned embossing agents.

A photographic material may be formed by applying a hydrophilic light-sensitive layer such as a gelatine silver halide emulsion layer

directly to the present subbing layer or to a said second subbing layer mainly containing gelatin.

The composition of the photographic silver halide emulsion layers may be of any type known to those skilled in the art and for their composition preparation and coating reference is made, e.g. to Research Disclosure 17,643 of December 1978.

According to a preferred embodiment of the present invention the photographic silver halide emulsion layer is a high-resolution Lippmann emulsion that is directly applied to a polymethyl methacrylate plate that has been subbed with a subbing layer as described hereinbefore.

The hydrophilic colloid layer may contain photosensitive substances other than photosensitive silver halide, e.g. photosensitive iron salts or complexes, e.g. iron(III)ammonium oxalate or diazonium compounds.

Layers other than gelatin-containing layers which adhere directly very well to the present subbing layer contain e.g. polymers or copolymers including free carboxylic acid groups.

These polymers and copolymers may be used as polymeric binder material for a dye or pigment applied in alkali-soluble antihalation layers as described e.g. in the United Kingdom Patent Specification 1,380,052 relating to a motion picture film material including a magnetic recording stripe anchored to such antihalation layer by a cross-linking reaction.

Before applying the present subbing layer to hydrophobic resin supports, such supports, e.g. a polyethylene support or polyethylene coated base may be treated with a corona-discharge to improve the adherence of the subbing layer thereto. The technique of corona-discharge treatment has been described e.g. in GB-P 1 286 457.

The application of a subbing layer according to the present invention is illustrated by the following examples. The percentages mentioned therein are by weight.

Example 1

Onto a transparent plate of polymethyl methacrylate being 1.5 mm thick the following composition was doctor-blade coated at a wet coverage of 50 m² per litre :

30 % aqueous dispersion of colloidal silica (having an average particle size of 100 nm)

100 ml

resorcinol

30 g

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10 % aqueous solution of gelatin	80 ml
saponine (10 % in water)	30 ml
methanol	100 ml
water	690 ml

The coated layer was dried for 10 minutes at 40 °C in a ventilated drying stove.

The dried subbing layer was coated with a Lippmann-type gelatin-silver bromide emulsion containing silver bromide grains with an average grain size of 0.07 micron.

The adhesion of the photosensitive layer to the subbed polymethyl methacrylate plate was very good in dry as well as in wet state. The adhesion quality was tested by scratching the silver halide emulsion layer cross-wise by means of a sharp knife, whereupon an adhesive tape was pressed thereon and torn off at once. No pieces were torn off in dry state and no damage was detected in wet state.

Example 2

Example 1 was repeated with the difference, however, that the transparent plate was made of glass. Equally good results in the adherence test were obtained.

Example 3

Onto a corona-discharge treated polypropylene film being 75 μm thick the following composition was reverse-roll coated at a coverage of 40 m^2 per litre :

30 % aqueous dispersion of colloidal silica (having an average particle size of 100 nm)	200 ml
resorcinol	30 g
10 % aqueous solution of gelatin	80 ml
10 % aqueous solution of 7-ethyl-2-methyl-4-undecanol-sulphonic acid sodium salt as wetting agent	40 ml
methanol	100 ml
water	680 ml

The subbed film was conveyed through a ventilated drying stove wherein it was dried at 90 °C for 2 minutes.

The dried subbing layer was coated with a gelatin layer containing colloidal nickel sulphide as development nuclei and serving for the well-known silver complex diffusion transfer reversal process.

The adhesion was tested as described in Example 1 and proved to be

very good in dry as well as in wet state.

Example 4

Example 3 was repeated with the difference that the polypropylene film was replaced by paper being double-side coated with polyethylene.

The adhesion was tested as described in Example 1 and proved to be very good in dry as well as in wet state.

Example 5

A bi-axially stretched polystyrene film being 100 μm thick was corona-discharge treated and coated with the following subbing composition at a coverage of 40 m^2 per litre :

30 % aqueous dispersion of colloidal silica (having an average particle size of 100 nm)	75 ml
resorcinol	30 g
saponine (10 % aqueous solution)	30 ml
methanol	100 ml
water	745 ml

The subbing layer was dried as described in Example 3 and coated with a gelatin-containing silver halide emulsion layer as used in the manufacture of a photographic material for application in the graphic arts.

The adhesion in dry state was checked before and after processing (development, rinsing, fixing and washing). The gelatin-containing silver halide emulsion layer was scratched cross-wise by means of a sharp knife, whereafter an adhesive tape that had been pressed thereon was torn off at once. The quality of adhesion proved to be particularly good.

The adhesion in wet state was checked by scratching the material superficially and trying to rub off the photographic gelatin containing layer with a finger after each step of the photographic processing (development, rinsing, fixing, rinsing). The processed photographic layer was not rubbed off.

Example 6

Example 5 was repeated with a polyvinyl chloride film support replacing the polystyrene base.

The subbing layer was dried at 50 °C.

The same good adherence results were obtained.

CLAIMS

1. A plate, sheet or film material having a hydrophobic resin or glass surface coated with a subbing layer promoting the adherence thereto of a layer containing a hydrophilic colloid, characterized in that said subbing layer is essentially free from synthetic organic polymer and comprises :

- (1) from 35 to 75 % by weight of colloidal silica,
- (2) from 25 to 65 % by weight of an aromatic hydroxy compound that can be applied from an aqueous medium in dissolved form, and
- (3) from 0 to 15 % by weight of a proteinaceous hydrophilic colloid.

2. A plate, sheet or film material according to claim 1, characterized in that the hydrophobic resin is polymethyl methacrylate, polyethylene, polypropylene, polystyrene or polyvinyl chloride.

3. A plate, sheet or film material according to claim 1 or 2, characterized in that said colloidal silica has a particle size in the range of 10 to 120 nm.

4. A plate, sheet or film material according to any of claims 1 to 3, characterized in that the aromatic hydroxy compound is a polyhydroxy compound being a swelling agent for said hydrophobic resin.

5. A plate, sheet or film material according to any of claims 1 to 4, characterized in that the aromatic hydroxy compound is resorcinol.

6. A plate, sheet or film material according to any of claims 1 to 5, characterized in that the proteinaceous hydrophilic colloid is gelatin.

7. A plate, sheet or film material according to any of claims 1 to 6, characterized in that the subbing layer is present at a dry coating coverage of 0.5 to 2 g per m².

8. A plate, sheet or film material according to any of claims 1 to 7, characterized in that the subbing layer after coating has been dried at a temperature of 30 to 40 °C.

9. A photographic material containing a photosensitive hydrophilic colloid layer and a subbed film, sheet or plate according to any of claims 1 to 8.



European Patent
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EUROPEAN SEARCH REPORT

0157019
Application number

EP 84 20 0414

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	DE-A-2 613 918 (FUJI) * Page 8, lines 11-16; page 2, line 11 - page 6, line 26; page 10, lines 5-13; page 19, line 21 - page 22, line 16; page 23, lines 13-14; example 1; claims * ---	1-9	G 03 C 1/80
X	US-A-2 341 877 (E.B. MIDDLETON) * Page 2, column 2, lines 43-45 * ---	1, 4, 6	
Y	GB-A-1 096 168 (FUJI) * Claims * ---	1, 4-6	
Y	US-A- 873 009 (R.B. CAMPBELL) * Whole document * ---	1-3, 6	
Y	PATENTS ABSTRACTS OF JAPAN, vol. 4, no. 131(P-27)(613), 13th September 1980, page 100P27; & JP - A - 55 83042 (FUJI SHASHIN FILM K.K.) 23-06-1980 ---	1, 3	TECHNICAL FIELDS SEARCHED (Int. Cl.4) G 03 C 1/80 G 03 C 1/76
Y	FR-A-2 257 437 (LA CELLOPHANE) * Claims * ---	1	
Y	FR-A-2 095 773 (AGFA-GEVAERT) * Example 4 * ---	1	
A	US-A-3 864 132 (A.A. RASCH) * Claims * -----	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 21-11-1984	Examiner RASSCHAERT A.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			