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SUB COATINGS FOR BONDING PHOTOGRAPHIC EMULSIONS TO RESINOUS SUPPORTS

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This invention concerns a process for subbing hydrophobic surfaces, more particularly subbing surfaces to provide adhesion for photographic emulsions.

Waterproof coatings of paper, fabrics and other absorbent materials are well known. Various waxes have been used to impart water resistance by heating the wax treated material so that the wax permeates the interstices of the material. In addition, various synthetic resins have been used commercially especially to treat fabrics in the clothing and weaving industries. Photographic paper has often been made water resistant by coating with a cellulose lacquer, but this process is unsuitable in certain instances for general paper mill use due to the volatile solvents used and resultant hazards.

The above methods have been found generally unsatisfactory in making a water-resistant paper which may be used photographically, and which is compatible with photographic emulsions, dyes and processing chemicals. For instance, the use of a wax treatment may cause a gelatin emulsion to peel from the paper. Other treatments such as resin coatings from solvent solutions or hot melts permit absorption of dyes into the paper coating resulting in staining and other objectionable after effects. It has also been found that some of the water-resistant surfaces permit retention of processing chemicals in the paper which later affect the photographic images.

Accordingly, it is desirable to have a photographic paper base which is either completely or partially resistant to water and particularly to the processing solutions in which the paper is immersed. Such paper could be rapidly processed without retention of the chemicals in the base and could be squeegeed dry for immediate use. For instance, partially resistant stock might be sufficiently temporarily resistant to water or photographic processing solutions to permit contact with a sheet wet with water or chemicals for a few seconds without sufficient wetting of the stock to cause cockle and mottle or similar defects and yet have a water resistance balanced in such a manner as to be receptive to the transfer of a gelatin image.

Because of the more or less hydrophobic nature of these materials, it is usually necessary to overcoat them with subbing layers which will satisfactorily bond the hydrophilic photographic gelatin emulsion to the base.

The degree of emulsion adhesion necessary is fairly high considering the methods used in processing photographic materials. For instance, these materials are subjected to alkaline developing baths, acid fixing solution, and washing. Under certain conditions, mechanical processes subject the paper to unusually severe conditions of temperature, pH and friction which require a high degree of adhesion to prevent the emulsion layer from picking, stripping or peeling from the base.

I have found a subbing composition which is unique in providing excellent emulsion adhesion to certain thermoplastic resinous coatings applied from dispersions on paper supports.

One object of this invention is to provide a subbing composition for causing photographic emulsions to adhere to certain thermoplastic resinous coatings. Another object is to provide a photographic element consisting of a waterproof paper, a subbing composition, and a photographic emulsion. A further object is to provide a unique subbing composition. Other objects will be apparent from the following description of my invention.

I have discovered that a subbing composition composed basically of casein, polystyrene latex, and gelatin has the property of providing good adhesion for a photographic emulsion on thermoplastic resinous bases such as those provided from styrene-butadiene copolymers, acrylic resins, polystyrene-styrene:butadiene latex coatings, polystyrene coatings, treated polyethylene coatings, and the like. This material may also be used on supports which are not normally considered as hydrophobic such as those listed above including paper, cellulose acetate, and the like. The optimum solids ratio layer is 60:20:20 of latex, casein and gelatin but these proportions can be varied within 5% without sacrificing adhesion. However, the degree of adhesion obtained through the use of any two of these constituents or of proportions outside the 5% limits is decidedly inferior to the combination of all three in the above proportions.

The casein is alkaline-solubilized prior to addition with an alkali, preferably about 6–8% ammonium hydroxide. The amount of ammonium hydroxide or other alkali is only important with respect to the final pH and its effect on coating viscosity, gloss, and the like.

The preferred grades of gelatin are those most efficiently cross-linked with formaldehyde or other hardeners, although other grades may be used.

Sub coverages of from 0.5–3.0 g./m.^{2} may be used. Coatings may be applied by hopper, air knife, spray or any other technique by which the subbing dispersion can be evenly spread over the resinous base.

Various wetting agents may be used such as those sold under the names Triton X100 (alkyl aryl polyether alcohol), Duponol ME (sodium lauryl sulfate) and the like. Other compositions may be added which are helpful in obtaining a good final product but which are not necessary for the operation of our invention. For instance, chelating agents such as the sodium salt of ethylene diamine tetraacetate (Versene regular, Sequestrene NA 4, Nullapon BF–78), and the like may be added to deionize the water. Sodium meta-borate may be added in an amount from 2–6% to improve the gloss under certain conditions.

In some cases, adhesion can be further improved through addition to the sub of certain water miscible solvents which act as softening, swelling, tackifying or partial solubilizing agents for the resinous material of the layer being subbed and/or the sub dispersion. Many such solvents are available and include dimethyl formamide, tetrahydrofuran, methylethyl ketone, cyclohexanone, propylene carbonate, Cellosolve acetate, n-methyl pyrollidone and others. One requirement of this technique is that the solvent used be able to be volatilized at the temperature used in drying so that the finished coating is not sticky or tacky.

The following general ranges are my preferred concentrations of the additional components that have worked satisfactorily:

Chelating agent	0.2–0.5% on total weight.
Surfactant	0.05–0.5% on total weight.
Electrolyte	2.0–6.0% on solids.
Hardener	0.1–1.0% on gel and casein solids.
Solvent	3.0–10% on total weight.

A heat treatment may be used at a temperature of 240°–280° F. for 10–20 seconds, but is not necessary.

The following examples are intended to illustrate our invention but not to limit it in any way.

Example 1

A sample of photographic baryta coated paper stock was coated on both sides with a 15 g./m.^{2} coating of 50:50 solids blend of polystyrene latex and styrene:butadiene (60:40) latex. This coated paper was very hydro-

phobic to water and showed a moisture pickup (Cobb test) of approximately 0.02 g./100 cm.^{2} after 8 minutes' exposure to water at 70° F. A 1.0 g./m.^{2} sub coating of the following composition was then coated over the face side resinous layer.

Material:	Weight, gms.
Water	907.9
Chelating agent	2.5
Wetting agent	1.5
Sodium meta-borate	2.0
Casein	7.6
Polystyrene latex (32.5% solids)	70.0
Gelatin	7.6
40% formaldehyde	0.9
	1000.0

The sub coating was dried by passing the paper first through an air drier at 160–180° F. for 10–15 sec. and then in front of a bank of infrared heaters at 240–280° F. for 10–20 sec. The paper was then coated on the face side with a suitable photographic gelatin-based emulsion, and dried. When processed, no evidence of emulsion frill was noted. The same paper without the sub layer showed a complete sloughing off of the emulsion during processing.

When the same latex coated base was subbed with a 1.0 g./m.^{2} sub coating composed of equal parts (by solids weight) of a resin latex mixture of polystyrene resin latex-styrene-butadiene resin latex combination (45:55 by solids weight) and gelatin, adhesion was not considered passable—an objectionable amount of emulsion coating could be rubbed away.

Example 2

A sample of baryta coated photographic paper was coated as described in Example 1 except that the water-proof resinous support layer was made of a blend of polyacrylic resin latexes. This layer was more hydrophobic than the polystyrene-styrene butadiene latex coating but when subbed, sensitized, and processed, showed the same excellent emulsion adhesion.

Example 3

A sample of baryta coated photographic paper was coated on the face side with a 2.0 g./m.^{2} coating of a blend of two styrene:butadiene latexes with casein to provide a water resistant base (Cobb moisture pickup was 0.04 g./100 cm.^{2} in one minute). A 1.0 g./m.^{2} layer of the composition described in Example 1 was applied over this resin layer, dried as previously described, and coated with a suitable photographic gelatin emulsion. When tray processed by hand and also when mechanically processed under extreme temperature, pH and friction conditions, emulsion adhesion was excellent. Without the subbing layer, this same paper showed a complete stripping of the photographic emulsion from the base.

Example 4

A sample of baryta coated photographic paper was coated on the face side with a 2.0 g./m.^{2} coating of a blend of polystyrene latex and casein. A 1.0 g./m.^{2} layer of the sub described in Example 1 was applied over this water-resistant layer, dried, and coated with a suitable gelatino silver halide emulsion. Emulsion adhesion was excellent. An unsubbed sample having the same water-resistant coating showed very poor adhesion.

Example 5

A sample of photographic paper stock was coated with a polyacrylic latex. This was then tub sized with the sub composition described in Example 1 and emulsion coated. Normal processing showed good emulsion adhesion for the subbed base and poor adhesion for a similar sample when unsubbed.

Example 6

A baryta coated photographic paper stock was coated on the face side with 2.0 g./m.^{2} of a blend of two styrene:butadiene latexes with casein to provide a water resistant base (Cobb moisture pickup=0.04 g./100 cm.^{2}/1 min. using water at 70° F.). A 1.0 g./m.^{2} sub coating of the following composition was applied over this resin layer:

	G.
Water	931.4
Tetrasodium salt of ethylene-diamine tetra-acetic acid	2.5
Sodium alkyl polyether	0.75
Anionic alkyl aryl polyether sulfonate surfactant	0.75
Na_3PO_4	2.0
Casein	9.5
Unplasticized polystyrene latex (49%) solids	46.5
Gelatin	5.7
40% formaldehyde	0.9
	[1] 1000.0

[1] 4% solids.

This coating was dried, coated with a suitable photographic emulsion and tray tested as described in Example 1 showing excellent emulsion adhesion. When processed mechanically and continuously under conditions of high temperature (100–120° F.), high pH (10–11), and unusual friction, emulsion adhesion was also excellent. Without the sub layer, this same paper showed a complete stripping of the photographic emulsion from the base.

Example 7

A baryta coated photographic paper stock was coated with 10 g./m.^{2} of a blend of 2-ethylhexyl acrylate:styrene (54:46) latex with straight polystyrene latex in a latex solids ratio of 43:57. This coating was considered extremely hydrophobic showing a Cobb moisture pickup of 0.01 g./100 cm.^{2}/8 min. using water at 70° F. This base was then hopper coated with a 1.0 g./m.^{2} sub of the following composition:

	G.
Water	882.0
Tetrasodium salt of ethylene-diamine tetra-acetic acid	2.5
Sodium alkyl polyether	1.5
$Na_2B_2O_4$–$4H_2O$	1.5
Casein	7.6
Unplasticized polystyrene latex (49%) solids	46.5
Gelatin	7.6
40% formaldehyde	0.8
Dimethyl formamide	50.0
	[1] 1000.0

[1] 4% solids.

This paper was dried, emulsion coated, processed and tested as in Example 1 showing excellent emulsion adhesion. With dimethyl formamide eliminated from the sub formula, adhesion was not passable.

When the same latex coated base was subbed with a 1.0 g./m.^{2} sub coating composed of equal parts (by solids weight) of a resin latex mixture of polystyrene resin latex-styrene-butadiene resin latex combination (45:55 by solids weight) and gelatin, adhesion was not considered passable—an objectionable amount of emulsion coating could be rubbed away.

Example 8

A photographic paper stock was coated on both sides by extrusion with a low-density type of polyethylene, with a resulting water resistance equal to or better than that described in Example 1. The polyethylene surface was treated on the face side by electron bombardment (Tesla coils) to a degree that the surface was readily wettable

with water. This treated surface was then subbed as described in Example 1 except that the coating was air dried at 135–150° F. with no subsequent radiant heat treatment. After photographic emulsion coating, tray processing frill tests showed satisfactory emulsion adhesion using the normal sub formula and excellent adhesion with (1) the addition of 5% of either dimethyl formamide, tetrahydrofuran, or cyclohexanone or (2) substitution for formaldehyde of an equal amount of amine type hardener.

Example 9

A baryta-coated photographic paper stock was coated with 12 g./m.^{2} of a polyvinyl acetate-polyvinyl stearate (85:15) latex and showed waterproofness equivalent to a Cobb test moisture pickup of 0.02 g./100 cm.^{2}/8 min. When subbed, dried, sensitized, processed, and tested as in Example 1, this base showed satisfactory emulsion adhesion.

The preceding examples are intended to show the successful use of my invention in achieving satisfactory adhesion of photographic gelatin-based emulsions to a number of radically different resinous coatings. Many other polystyrene, styrene:butadiene, polyacrylic, polyvinyl chloride and polyvinyl acetate homopolymer and copolymer latexes have been subbed successfully.

This sub is effective for coating over thermoplastic material deposited from solutions or from latexes. It may also be coated over such a resinous surface when the surface has been deposited or coated on various supports such as resinous supports, paper, leather, synthetic fibers, or the like.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as

described hereinabove and as defined in the appended claims.

I claim:

1. A photographic element comprising a thermoplastic resinous film base carrying on the surface a subbing composition comprising 55–65% polystyrene resin latex, 15–25% casein, and 15–25% gelatin, solids basis, and having a light-sensitive gelatino-silver halide emulsion coated over the subbing composition.

2. A photographic element comprising a paper base having thereon a thermoplastic resinous coating, carrying on the surface of the coating a subbing composition comprising 55–65% polystyrene resin, 15–25% casein, and 15-25% gelatin, and having a light-sensitive gelatino-silver halide emulsion over the subbing composition.

3. A photographic element comprising a paper base having thereon a thermoplastic resinous coating, carrying on the surface of the coating a subbing composition comprising 60% polystyrene resin, 20% casein, and 20% gelatin, and having a light-sensitive gelatino-silver halide emulsion over the subbing composition.

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