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METHOD OF MAKING MULTILAYER COATINGS CONTAINING A WATER RESISTANT LAYER

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No Drawing. Continuation-in-part of application Ser. No. 218,145, Aug. 20, 1962. This application May 22, 1967, Ser. No. 640,361
U.S. Cl. 117—34 10 Claims
Int. Cl. G03c 1/74

ABSTRACT OF THE DISCLOSURE

An aqueous organic colloid layer and a water resistant layer are applied simultaneously in liquid form to a web support while maintaining a distinct relationship between the layers. The top or upper layer has a lower surface tension than the under or bottom layer.

This application is a continuation-in-part of our copending application, Ser. No. 218,145 (now abandoned) filed Aug. 20, 1962.

This invention relates to a method of applying a plurality of separate coating materials to a support layer relationship. In a specific aspect this invention relates to a method of coating an aqueous organic colloid layer and a water resistant layer onto a web support. In a more specific aspect this invention relates to a method of coating a photographic emulsion layer containing silver halide and gelatin and a water resistant layer onto a water absorbent web support.

Some supports, especially those of a pervious nature such as thin or light weight papers, upon coating with aqueous solutions deform badly, have low wet strength, tend to tear and are hard to transport through a machine. When photographic materials are applied to such stock, the paper fibers penetrate the layers and the emulsion grains penetrate the paper stock. Exposed and processed samples are unacceptable for many purposes. To prepare acceptable photographic materials using such paper stock, it has been necessary to apply a waterproof or water resistant layer on one or both surfaces of the paper depending upon the requirements of the product. This preliminary treatment of the paper prior to applying the photographic emulsion coating has necessitated coating the stock two or more times in separate operations which added to the cost of preparing the photographic products. In addition, as a rule, the waterproof layers have require some kind of treatment, such as subbing layer, electron bombardment or the like to obtain satisfactory adherence of the photographic emulsion layer thereto. Some film supports, such as cellulose acetate, absorb small amounts of water which decreases dimensional stability and adversely effects their curl properties. In some instances, therefore, it is desirable to coat a water resistant resin layer on a film support, e.g., U.S. Patent 2,698,235. Paper and film supports having low water absorption are particularly useful in photographic materials which are surface processed such as by viscous processing described in Journal of the SMPTE, vol. 70, pp. 875–877, November 1961.

An object of our invention is to provide a method for applying at the same time a plurality of separate coating materials to a support in layer relationship.

Another object of our invention is to provide a method for applying at the same time gelatin photographic emulsions and water resistant layers to papers or film supports to obtain a satisfactory product in one operation.

A further object of our invention is to make possible the use of paper supports for photographic products which

have heretofore been considered unsuitable or poorly suitable for that purpose. Further objects of our invention will appear herein.

We have found that an aqueous organic colloid layer and a water resistant layer can be applied to a web support in liquid form substantially simultaneously while maintaining a distinct relationship between the different layers after they have been cured or dried, if the top layer has a lower surface tension than the under or bottom layer. The details of our invention will be described by applying a silver halide-containing photographic emulsion layer and a water resistant layer to a water absorbent web support, but it will be understood that other types of layers can be similarly applied provided the top layer has a lower surface tension than the latex layer beneath it.

In accordance with our invention a gelatin-silver halide photographic emulsion layer and a water resistant layer can be applied to water absorbent papers or film supports simultaneously or substantially simultaneously to form photographic products of good quality. The composition applied simultaneously or substantially simultaneously with the gelatin-silver halide emulsion layer is a polymeric hydrosol or resin latex preferably having a solids content within the range of 20–50%, and the polymeric hydrosol coalesces on loss of water to form a water resistant layer. In applying the two coatings simultaneously or substantially simultaneously, the surface activity of the top layer should be greater than that of the under layers. This condition can, for instance, be obtained by using lower surfactant concentrations per coating volume in the lower layer or layers than in the top layer. The top layer should have higher surface activity than the intermediate layer or layers.

In the resin latex composition employed for the undercoat titanium dioxide or other pigment can comprise up to 40% of the total solids in the latex. The remainder of the solids content is substantially entirely polymer having an average particle size not more than 1 micron in diameter and preferably less than 0.5 micron.

Various types of latexes which coalesce on drying to form water resistant layers can be used. Typical examples are polymeric hydrosols prepared from acrylics as polyethyl acrylate; polyvinyl esters, such as polyvinyl acetate; copolymers, e.g., polyvinyl acetate-isobutyrate or polyvinyl acetate-methyl methacrylate and terpolymers, e.g., poly-n-butylacrylate-styrene-methacrylamide.

The coatings are applied to a moisture-absorbent paper either unsized or insufficiently sized to be resistant to penetration by moisture or to a moisture absorbent film support such as cellulose acetate coated with gelatin or polyvinyl alcohol. The layers are applied by a bead method such as one in which both the undercoating and the emulsion coating are laid down simultaneously onto the paper. The method described in Russell U.S. Patent No. 2,761,791, particularly that described in connection with FIG. 9 of the drawings thereof is especially suitable for applying coatings to paper in accordance with the invention. Other substantially simultaneous methods, however, can be used such as that described in Wynn U.S. Patent No. 2,941,898.

Surfactants or wetting agents useful for the preparation of synethetic resin latices generally may be employed in preparing the undercoating composition.

In the coating operation, the multiple coatings upon application are set by chilling as described in Patent No. 2,761,791 which coating technique results in the formation of a barrier by the latex coat to the penetration of the liquid photographic emulsion composition into the paper. According to our method, satisfactory coatings are obtained having good adhesion to the support without any auxiliary treatment of the barrier or under-layer being

necessary. Diminished temperatures such as on the order of 5–15° C. are conveniently used for chilling the coatings immediately following their simultaneous application to the paper as described.

In some cases it is preferred to coat the water resistant layer over the silver halide emulsion layer where it is advantageous to keep moisture away from the surface of the emulsion. Materials of this type are those processed by heating only such as described in Belgian Patent 593,937 and those having water impervious layers over the silver halide emulsion layer are described in Stewart U.S. application Ser. No. 174,472 filed Feb. 20, 1962 and print-out materials such as those described in U.S. Patents 3,033,678 and 3,033,682; and in Kitze U.S. application Ser. No. 128,378.

The following examples illustrate the application of gelatin-silver halide photographic emulsion layers and latex layers to various supports in accordance with our invention:

Example 1

Two compositions were prepared as follows: (1) To 1300 grams of an emulsion of the type described in U.S. Patent No. 2,716,059, column 3, lines 1–14 containing approximately 0.33 mole of silver halide was added 100 ml. of a 7% aqueous solution of p-tert.-octyl-phenoxy ethoxy ethyl sodium sulfonate and 134 ml. of distilled water; (2) Vinyl acetate was polymerized by an emulsion polymerization procedure to obtain a latex 25% of which was vinylacetate polymer together with the following constituents: 0.23% p-tert.-octyl-phenoxy ethoxy ethyl sodium sulfonate, 0.46% $K_2S_2O_8$ and 0.25% hydroxy ethyl cellulose, these percentages being based on total polymer. The composition was pigmented with titanium dioxide giving a mixture containing in addition the following ingredients: 0.12% $Na_2P_4O_7$, 40% TiO_2 (based on total polymer solids in the dispersion). The pigmented latex diluted to approximately 20% polymer solids, had a pH of 7.2 and a viscosity of about 3.5 cps. These layers were simultaneously applied to absorbent unsized paper, the latex layer being the underlayer, by the procedure described in connection with FIG. 9 of U.S. Patent No. 2,761,791 which coating was immediately set by chilling. The coatings exhibited good adherence to the paper and were free of problems such as deformation of paper, low wet strength, tendency to tear and the like such as would be encountered in coating the paper directly with the silver halide gelatin photographic emulsion.

Example 2

The coating procedure in accordance with the invention can be used to coat three layers particularly where an increased percentage of latex surfactant is encountered. The three layers were applied simultaneously to paper in a manner similar to that in the proceding example but using a three-slot technique. These layers were composed of: (1) a latex or dispersion of polyvinyl-acetate resin of 45% solids concentration which also contained approximately 1.25% of surfactant which layer was applied at the rate of 4.5 grams per square foot of paper, (2) a photographic emulsion applied upon the polyvinylacetate layer at the rate of 108 mg. of silver and 216 mg. of gelatin per square foot, (3) a thin gelatin overcoat on the silver halide emulsion layer from a 7% solution of gelatin containing sufficient surfactant to impart a higher surface activity than in the under layers at the rate of 140 mg. of gelatin per square foot. The product obtained showed good adherence between the respective layers.

Example 3

Two compositions were prepared for a multiple coating application to absorbent paper. The lower coating composition was a polyvinylacetate resin latex adjusted to a solids content of 45% and added thereto was a small amount of a 15% water solution of saponin at the rate of 10 cc. of saponin solution per liter of latex. The uppercoat composition was a silver chloride emulsion containing 450 grams of gelatin per mole of silver. The emulsion was heated to 40° C. and 90 cc. of a 15% water solution of saponin and 270 cc. of a 6⅔% water solution of p-tert.-octyl-phenoxy ethoxy ethyl sodium sulfonate was added per mole of silver. Various paper stocks were coated in the manner described and it was found that the emulsion did not wet through to the paper during processing. Immediately after the coatings were applied, they were chilled causing rapid setting. They were then subjected to a current of warm dry air whereby a photosensitive paper was obtained in which the emulsion layer firmly adheres to the paper support.

Example 4

Two compositions were prepared for multiple coating application to paper as follows: (1) A polyvinyl acetate latex was prepared containing 30% solids, 40% of which solids was TiO_2, substantially the remainder being polyvinyl acetate. The latex had a low surfactant content, (2) a cellulose ester solution as follows:

Hydroylzed cellulose acetate propionate as described in U.S. Patent 2,448,534	grams	88
Distilled water	cc	770
Ethyl alcohol	do	160
Cellosolve	do	160
Acetone	do	40

The mass was stirred at 120° F. until clear and was then diluted further to obtain good coating viscosity. Saponin was added at the rate of 10 cc. of 15% saponin solution per 500 cc. of cellulose ester solution.

The compositions were applied to an absorbent paper simultaneously, the cellulose ester solution being the top layer by the method described in connection with the coating hopper illustrated in U.S. Patent No. 2,761,791. The latex layer was coated at a coverage of 9.5 gm. per square foot and the cellulose ester layer at a coverage of 6.3 gm. per square foot. Upon drying the latex coalesced to form a water resistant coating between the paper and the cellulose ester layer. Similarly coatings may be applied when the cellulose ester composition contains silver halide in dispersion therein as described in U.S. Patent No. 2,448,534.

Example 5

Three coating compositions were prepared as follows: (1) A silver chloride gelatin emulsion of the type described in U.S. Patent 2,716,059, column 3, lines 1–14. This emulsion contained approximately 1 mole of silver halide per 4,000 cc. of emulsion, (2) A latex copolymer of vinyl acetate and vinyl isobutyrate in which the monomers were in 50:50 molecular ratio and the latex contained about 40% solids. The following ingredients were added to the latex, the percentages indicated being based on the polymer solids present in the latex:

	Percent
Tamol 731 (a sodium salt of carboxylated polyelectrolyte marketed by Rohm and Haas)	1
Titanium dioxide	20
Carbitol	1.2
Propylene glycol oleate	0.22
Triton X 200E (p-tert.-octyl-phenoxy ethoxy ethyl sodium sulfonate)	2.1

(3) A 5% gelatin solution containing a small amount of Triton X 200 but in greater proportion than that in either of compositions 1 or 2.

A simultaneous three layer coating was applied to a paper support using a three-slot multiple hopper of the type described in U.S. Patent 2,761,791. The photographic emulsion was coated over the latex layer and the gelatin layer over the photographic emulsion layer. The latex layer was coated at a coverage of 2 grams per square foot,

the silver halide emulsion layer at 4 grams per square foot and the gelatin layer at 1 gram per square foot. Upon drying the latex coalesced to form a water resistant layer between the paper support and the silver halide emulsion layer.

Example 6

Two compositions were prepared as follows: (1) a polyvinyl acetate latex was prepared containing approximately 20% solids. This latex also contained the following ingredients in the percentages indicated based on the polymer solids:

	Percent
TiO_2	40
Triton X 200E	0.26
Hydroxyethyl cellulose	3.5

400 cc. of a non-ionic dispersion of polyethylene containing approximately 40% solids was added to 600 cc. of this latex. (2) A silver halide emulsion of the type described in U.S. Patent 2,716,059, column 3, lines 1–14 was prepared. The emulsion contained approximately 1 mole of silver halide per 4.2 liters of emulsion. Sufficient saponin was added to this emulsion to produce a higher surface activity than in the coating from the latex composition. These two compositions were simultaneously applied to paper using a multiple hopper of the type described in U.S. Patent 2,761,791, the silver halide emulsion layer being over the latex-polyethylene dispersion layer. The latex layer was coated at a coverage of 3 grams per square foot and the silver halide emulsion layer at a coverage of 4.24 grams per square foot. Upon drying the latex-polyethylene dispersion coalesced to form a water resistant layer between the silver halide emulsion layer and the paper support.

Example 7

Two compositions were prepared as follows: (1) a latex was prepared of a butylacrylate-styrene-methacrylamide terpolymer which latex contained 20% solids of the polymer. Also contained therein were the following materials in the indicated percentages based on the polymer solids present in the latex:

	Percent
TiO_2	40
Tamol 731	1.2
Hydroxyethyl cellulose	1.0
Triton X 200E	0.26

(2) a silver halide emulsion of the type described in U.S. Patent 2,716,059, column 3, lines 1–14 was prepared and sufficient Triton X 200E was added thereto to assure a higher surface activity than that of the latex in layer form. These two compositions were multiple coated by simultaneous application procedure as described in the preceding examples, the silver halide emulsion layer being coated over the latex layer. The emulsion layer was coated at a coverage of 4.25 grams per square foot and the latex layer at a coverage of 3.0 grams per square foot. Upon drying the latex coalesced to form a water resistant layer between the emulsion layer and the paper support.

Example 8

This example relates to the simultaneous coating of a latex water resistant layer and an emulsion layer on a film support which had previously been coated with a gelatin layer.

A polyvinyl acetate latex was prepared containing approximately 20% of solids and 40% of TiO_2, based on the polymer solids. Also prepared was a silver halide emulsion of the type described in U.S. Patent 2,716,059, column 3, lines 1–14. To 3000 grams of this emulsion containing approximately 0.74 mole of silver halide, 56 ml. of a 15% saponin solution was added to serve as a coating aid.

The silver halide emulsion layer was coated over the polyvinyl acetate latex layer by a simultaneous application procedure as described herein in which procedure a multiple hopper of the type described in U.S. Patent 2,761,791 was used which coaitng was over a cellulose acetate film support which had been previously coated with approximately 800 mg. of gelatin per square foot. The latex layer was coated at a wet coverage of 3.0 grams per square foot and the silver halide emulsion layer was coated at a wet coverage of 4.0 grams per square foot. Upon drying the latex coalesced to form a water resistant layer between the cellulose acetate support and the silver halide emulsion layer. The latex layer was characterized in having a higher surface tension than the emulsion layer which had been applied.

Our invention can also be used to coat simultaneously onto a web support an aqueous organic colloid layer other than those containing silver halide and a water resistant layer containing a polymeric hydrosol. For example, the aqueous colloid layer can contain developer nuclei as shown by the following specific example:

Example 9

A disperson of colloidal silver sulfide in gelatin was prepared by adding silver nitrate solution to a solution of sodium sulfide and gelatin. A small amount of sodium alkyl naphthalene sulfonate coating aid was added.

A polyvinyl acetate latex containing 55% of solids was diluted with water to 45% solids. The colloidal silver sulfide was applied as a layer over the latex onto absorbent paper by simultaneous application technique using a coating hopper as described in U.S. Patent No. 2,761,791. A satisfactory coating was obtained and upon drying the latex layer coalesced to form a water resistant barrier between the paper and the silver sulfide layer.

Also, our invention can be used to coat polyvinyl alcohol or gelatin layers containing mordants as described in U.S. 3,260,597 and U.S. 3,271,471; antihalation or backing layers as described in U.S. 3,282,699; layer containing light sensitive components as described in French Patent 1,453,635, British Patent 920,277 and U.S. 3,152,-903; thermographic layers as described in U.S. 2,899,334; and dye-developer layers as described in U.S. 2,983,606.

It is also possible in practicing our invention to coat additional layers other than the aqueous organic colloid layer and water resistant layer onto the web support. For example, a gel layer can be applied between the colloid layer and the water resistant layer. The gel layer would, of course, be applied from a solution having a lower surface tension than the under layer or water resistant layer.

The surface activity of the respective layers is indicated inversely by the relationship of their surface tensions; those layers having lower surface tensions having higher surface activities than layers exhibiting higher surface tensions.

The invention has been described in considerable detail with particular reference to certain 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 described in the appended claims.

We claim:

1. A method of coating an aqueous organic colloid layer and a water resistant layer onto a web support which comprises applying to one side of the support the aqueous organic colloid layer and a polymeric hydrosol layer in superposed relation while both are in liquid form, substantially simultaneously, the layer on top having a lower surface tension than the under layer and drying the superposed layers.

2. A method in accordance with claim 1 wherein the web support is water absorbent.

3. A method of coating a photographic emulsion layer composed of silver halide dispensed in an aqueous organic colloid and a water resistant layer onto a water absorbent web support which comprises applying to one

side of the support the silver halide layer and a polymetric hydrosol layer in superposed relation, while both are in liquid form, substantially simultaneously, the top layer being characterized by lower surface tension than the under layer and drying the superposed layers.

4. The method defined in claim **3** in which the silver halide emulsion layer is the top layer.

5. The method defined by claim **3** in which the polymeric hydrosol layer is the top layer.

6. The method defined by claim **3** in which the photographic emulsion is a silver halide-gelatin emulsion.

7. The method defined by claim **3** in which the polymeric hydrosol is a polyvinyl ester hydrosol.

8. The method defined by claim **3** in which the polymeric hydrosol contains a pigment therein.

9. A method of preparing a photographically sensitized paper which comprises simultaneously applying to a water absorbent paper a polyvinyl ester hydrosol having a relatively low surfactant concentration, and a gelatin-silver halide photographic emulsion having a relatively high surfactant concentration, in which each coating liquid is fed as a layer into a bead in superposed relation and the surface of the paper is moved continuously in contact with the bead, the hydrosol being the under layer and the photographic emulsion the top layer, the latter being characterized by lower surface tension than the under layer and drying the superposed layers.

10. A method of preparing a photographically sensitized paper which comprises simultaneously applying to a water absorbent paper a polyvinyl ester hydrosol and a gelatin-silver halide photographic emulsion in which each coating liquid is fed as a layer into a bead in superposed relation and the surface of the paper is moved continuously in contact with the bead, the hydrosol being the under layer and the photographic emulsion the top layer, the latter being characterized by lower surface tension than the under layer and drying the supersod layers.

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117—73, 76, 83; 96—85, 87

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,425,857 February 4, 1969

Robert E. Bacon et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 26, after "support" insert -- in --; line 50, "require" should read -- required --. Column 3, line 54, "proceding" should read -- preceding --. Column 6, line 2, "coaitng" should read -- coating --; line 37, "layer" should read -- layers --; line 73, "dispensed" should read -- dispersed --. Column 7, line 2, "metric" should read -- meric --; line 10, "^{6}" should read -- 6 --. Column 8, line 12, "supersod" should read -- superposed --.

Signed and sealed this 24th day of March 1970.

(SEAL)
Attest:

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Commissioner of Patents