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COATING METHOD FOR WASH-OFF SOLVENT TRANSFER

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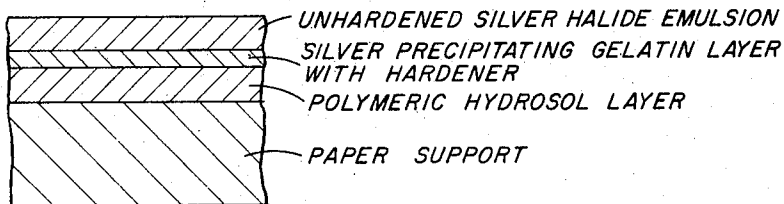


FIG. 1

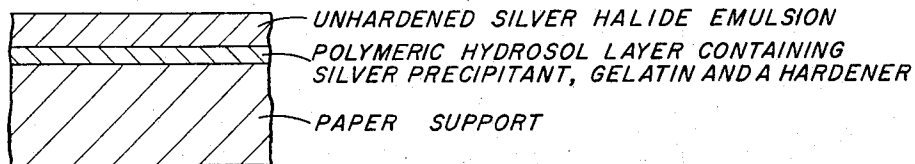


FIG. 2

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3,369,901 COATING METHOD FOR WASH-OFF SOLVENT TRANSFER

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This invention relates to preparing products useful in wash-off solvent transfer systems employing paper supports in which a polymeric water-resistant layer applied from a hydrosol is applied to paper support substantially simultaneously with the silver halide emulsion layer deposited thereon. The invention also relates to the products so prepared.

In the wash-off solvent transfer systems in which a multi-layer element is used the element can carry on the support two gelatin layers of different solubility. For example, the underlayer would contain a silver precipitating agent and would be harder than the outer gelatin layer which is a gelatin emulsion layer containing silver halide. After exposure of the element development is carried out with a developer containing silver halide solvent so as to obtain a silver positive in the hardened gelatin layer having a silver precipitating agent. Following this the emulsion layer containing the negative silver image is washed off leaving the positive-image-containing layer on the support.

In such elements using conventional paper supports the fibrous character of the paper surface sometimes impedes complete removal of the emulsion layer. Another problem (sometimes even more serious) is that the silver halide emulsion may be hardened by certain compounds diffusing from the paper support.

One object of our invention is to provide an element which overcomes the difficulties previously associated with products for use in wash-off solvent transfer systems having a conventional paper support. Another object of our invention is to prepare such elements including a layer which protects the photosensitive layer thereof from hardening action which might be encountered by migration of materials from the paper support on which the necessary layers have been deposited. Other objects of our invention will appear herein.

We have found that the above objects are attained, in the formation of the photographic element composed of an unhardened gelatin-silver halide emulsion layer and a gelatin layer thereunder containing silver precipitating agent, if there is also applied thereunder and upon the paper support a layer from a polymer hydrosol (latex) which coalesces on loss of water to form a water-resistant layer, which is desirably applied by a bead coating method. Also included in this polymeric hydrosol is an inorganic pigment such as titanium dioxide, zinc oxide, or any one of the various pigments which may be incorporated in coating compositions. The accompanying drawing illustrates a sensitive element illustrating our invention. FIG. I shows a three-layer application upon a paper support. Instead of having a three-layer element the water-resistant polymeric hydrosol layer may include the silver precipitating agent so as to combine the bottom two layers shown in FIG. I into a single layer which is illustrated by FIG. II of the accompanying drawing.

The layers to form the sensitive element in accordance with our invention are desirably applied to the paper support substantially simultaneously by the method described and claimed in Bacon and Fogg U.S. application Ser. No. 218,145, filed Aug. 20, 1962. The emulsion is characterized by a lower surface tension than the composition or compositions employed for the underlayers. The latex coating applied to the surface may conveniently be a dis-

persion of titanium dioxide in a polyvinyl acetate polymeric hydrosol. However, various types of latices which coalesce on drying to form water-resistant layers can be used. Typical examples are polymeric hydrosols prepared from acrylics as polyethyl acrylates, polyvinyl esters such as polyvinyl acetate, copolymers such as polyvinyl acetate-isobutyrate or polyvinyl acetate-methyl methacrylate or terpolymers such as poly-n-butylacrylate-styrenemethacrylamide. It is ordinarily desirable to include therein a pigment such as titanium dioxide or other pigment which 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.

The coatings are applied to moisture-absorbent paper either unsized or insufficiently sized to be resistant to penetration by moisture. The layers to form the sensitive element are applied by a bead method as for example that described in Russell U.S. Patent No. 2,761,791 particularly in connection with FIG. 9 of the drawings thereof. Surfactants or wetting agents such as are customarily used in preparing synthetic resin latices may be present in the undercoating composition. In the coating operation diminished temperatures such as on the order of 5–15° C. are conveniently used for chilling the coatings immediately following their application to the paper as described.

The silver precipitating layer comprises gelatin containing a nucleating material such as colloidal heavy metal or a heavy metal sulfide in quite small amount. Suitable silver precipitating agents include sulfides, selenides, polysulfides, polyselenides, thiourea, mercaptans, stannous halides, heavy metals and heavy metal salts, or fogged silver halide. Heavy metal sulfides such as lead, silver, zinc, antimony, cadmium and bismuth sulfides are useful particularly the sulfides of lead or zinc alone or in admixture, or complex salts of these such as with thioacetamide, dithiooxamide or 2,4-dithiobiuret. Useful heavy metals include silver, gold, platinum, palladium and mercury.

Instead of the silver precipitating layer being a layer separate from that of the water-resistant polymeric layer the compositions may be combined so as to form but one layer as the underlayer in the products being prepared.

The gelatin-silver halide emulsion which is applied as the top layer may be an emulsion of the various silver halides which are useful for photographic purposes such as silver bromide, silver chloride, silver bromide or the like. It is often desirable to include a material which will facilitate washing off procedure such as degraded gelatin and possibly some other material such as a semicarbazide or a water soluble salt thereof. The emulsion should be free of hardener whereas in the underlayer it is desirable that some hardening material such as formaldehyde or the like be present whereby the gelatins of the two layers are differentially hardened. Although any material recognized as useful as a hardener for gelatin might be employed in this layer the aldehyde type hardeners have been found to be especially useful.

The following examples illustrate our invention:

Example 1

A sensitive element was prepared by simultaneously coating gelatin sized paper using the coating technique described in U.S. Patent No. 2,761,791 with three layers, the bottom layer being a dispersion of titanium dioxide in a polyvinyl acetate latex. This layer was coated at the rate of 3 grams per square foot. The next adjacent layer resulted from the application of a composition comprising zinc sulfide in suspension in a gelatin solution which solution also contained formaldehyde. The solution contained

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0.00535 percent ZnS in 7.8% gelatin and as the hardener therein 100 cc. of 10% formaldehyde solution per pound of gelatin. This layer was applied at the rate of 2 grams per square foot. The top layer which was coated at the rate of 4 grams per square foot was composed of a mixture of gelatin-silver chlorobromide photographic emulsion 816 grams (1 mole); degraded gelatin, 20% aqueous solution, 466 grams; and poly(vinyl semicarbazide)-HCl, 10 grams. The product thus obtained was processed after exposure in a developer adapted for this purpose. After processing the negative or top layer could be washed off easily. After processing a similar material which did not contain a water-resistant underlayer it was noted that it was very difficult to completely remove the negative or top layer.

Example 2

A sensitive element useful in a wash-off solvent transfer system was prepared in the same manner as in the preceding example except that the latex composition was mixed with the zinc sulfide in gelatin composition in the proportion of 80% of the former and 20% of the latter. This mixture was coated on gelatin sized paper support at the rate of 5.0 grams per square foot simultaneously with the gelatin-silver halide emulsion layer as described in the preceding example. The emulsion was coated at the rate of 4 grams per square foot. This product was exposed and processed in a developer of the type used in wash-off solvent transfer systems. The top layer was washed off carefully and it was found that it could be readily removed leaving a direct positive image.

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 defined in the appended claims.

We claim:

1. A method of preparing a product useful in wash-off solvent transfer systems which comprises simultaneously applying to a paper support a polymeric hydrosol which coalesces on loss of water to form a water-resistant layer, a nucleating material and a hardener free gelatin-silver halide photographic emulsion containing a material which will facilitate its removal by the wash-off solvent in which each of the compositions are fed as layers into a bead in superposed relation and onto the surface of the paper in the order given, the photographic emulsion composition being characterized by a lower surface tension than the compositions employed for the underlayers.

2. A method of preparing a product useful in wash-off solvent transfer systems comprising simultaneously applying to paper a polyvinyl ester hydrosol which coalesces on loss of water to form a water-resistant layer, a composition comprising an aqueous solution of gelatin containing a nucleating material and a gelatin-silver halide photographic emulsion containing degraded gelatin to facilitate its removal by the wash-off solvent in which each of the compositions are fed as a layer into a bead in superposed relation which is then applied to the paper in the order given, the photographic emulsion composition being characterized by a lower surface tension than the compositions employed for the underlayers.

3. A method of preparing a product useful in wash-off solvent transfer systems comprising simultaneously applying to paper the following compositions in the order given, a polyvinyl ester hydrosol which coalesces on loss of water to form a water-resistant layer, an aqueous solution of nucleating material selected from the group consisting of the colloidal heavy metals and heavy metal sulfides and a hardener-free gelatin-silver halide photographic emulsion containing degraded gelatin to facilitate its removal by the wash-off solvent, the emulsion composition being characterized by a lower surface tension than that of the other two compositions.

4. A method of preparing a product useful in wash-off

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solvent transfer systems comprising simultaneously applying to paper a polymeric hydrosol which coalesces on loss of water to form a water-resistant layer, a nucleating material and a hardener free-gelatin-silver halide photographic emulsion containing degraded gelatin to facilitate its removal by the wash-off solvent, the emulsion being applied as a separate layer, the coating compositions being fed as a bead onto the surface of the paper, the photographic emulsion being the top layer and being characterized by the lowest surface tension of all.

5. A method of preparing a product useful in wash-off solvent transfer systems which comprises simultaneously applying to paper a polymeric hydrosol which coalesces on loss of water to form a water-resistant layer, a nucleating material and an unhardened gelatin-silver halide photographic emulsion containing degraded gelatin to facilitate its removal by the wash-off solvent, the first two being employed in the form of their mixture, in which each composition is fed as a layer into a bead in superposed relation and is thereupon applied to the paper, the photographic emulsion, the top layer, being characterized by lower surface tension than the mixture of hydrosol and nucleating material.

6. A method of preparing a product useful in wash-off solvent transfer systems comprising simultaneously applying to paper a polyvinyl acetate hydrosol which coalesces on loss of water to form a water-resistant layer containing therein a heavy metal sulfide nucleating material and an unhardened gelatin-silver halide photographic emulsion containing degraded gelatin to facilitate its removal by the wash-off solvent, each of which are fed as a layer into a bead in superposed relation and then to the surface of the paper, the photographic emulsion, the top layer, being characterized by a lower surface tension than the hydrosol composition.

7. A method of preparing a product useful in wash-off solvent transfer systems comprising simultaneously applying to paper a polyvinyl acetate latex which coalesces on loss of water to form a water-resistant layer containing pigment therein, a composition of zinc sulfide in suspension in a gelatin solution containing formaldehyde and an unhardened gelatin-silver halide photographic emulsion containing degraded gelatin to facilitate its removal by the wash-off solvent, each of which are fed as a layer into a bead in superposed relation in the order given and are applied to the surface of the paper, the photographic emulsion being characterized by the lowest surface tension of all.

8. A method of preparing a product useful in wash-off solvent transfer systems which comprises simultaneously applying to paper a polyvinyl acetate latex which coalesces on loss of water to form a water-resistant layer containing titanium dioxide and zinc sulfide in gelatin and an unhardened gelatin-silver halide photographic emulsion containing degraded gelatin to facilitate its removal by the wash-off solvent, each of which are fed as a layer into a bead in superposed relation and then applied to the paper, the photographic emulsion, the top layer, being characterized by lower surface tension than the latex composition.

9. A product useful for wash-off solvent transfer systems comprising a paper support containing thereon a water-resistant polymeric layer, a silver precipitating gelatin layer containing hardener and a layer of unhardened silver halide photographic emulsion containing a material which will facilitate its removal by the wash-off solvent in that order.

10. A product useful in wash-off solvent transfer systems comprising a paper support containing thereon a pigmented water-resistant polyvinyl acetate latex layer, a gelatin layer containing zinc sulfide and gelatin hardener and a layer of unhardened silver halide photographic emulsion containing a material which will facilitate its removal by the wash-off solvent, the layers being present on the paper support in that order.

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11. A product useful in wash-off solvent transfer systems comprising a paper support having thereon a layer of a water-resistant polymeric latex containing a silver precipitant therein and thereover an unhardened silver halide photographic emulsion layer containing a material which will facilitate its removal by the wash-off solvent.

12. A product useful in wash-off solvent transfer systems comprising a paper support having thereon a layer of water-resistant polyvinyl acetate latex, titanium dioxide, zinc sulfide, gelatin and a hardener and having thereover a layer of an unhardened silver halide photo-

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graphic emulsion containing a material which will facilitate its removal by the wash-off solvent.

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