June 19, 1956 H. C. STAEHLE 2,751,315

METHOD OF APPLYING A PROTECTIVE COATING OVER A PHOTOGRAPHIC PRINT

Filed Jan. 2, 1953

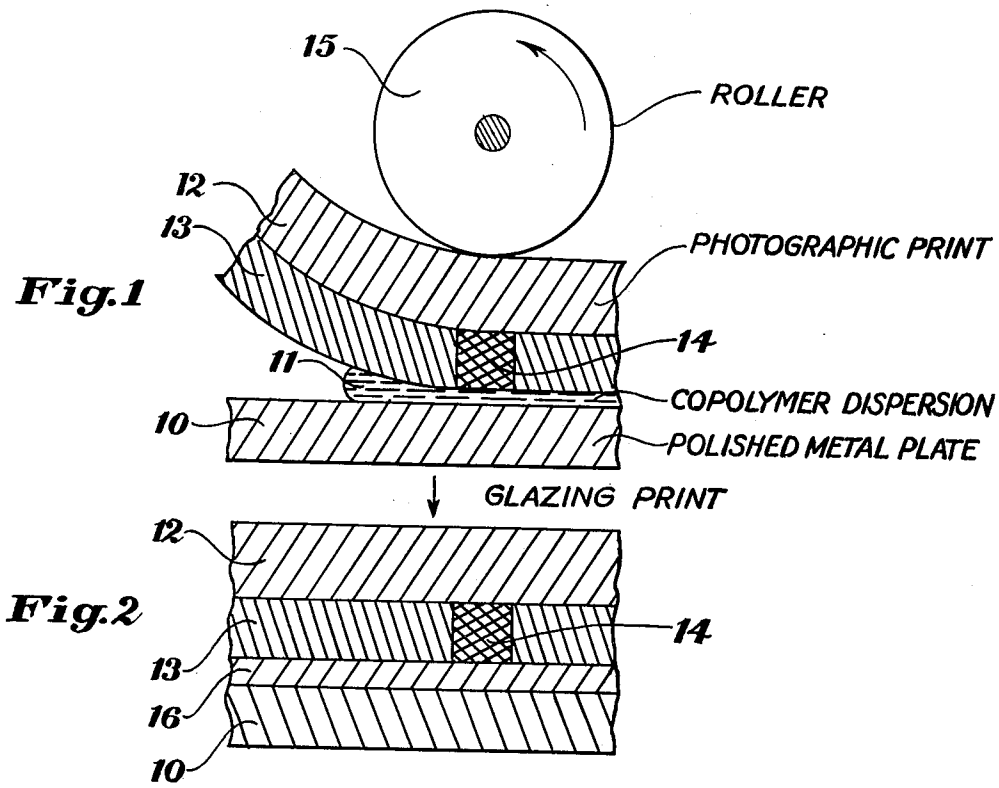


Fig. 1

Fig. 2

DETACHING GLAZED PRINT

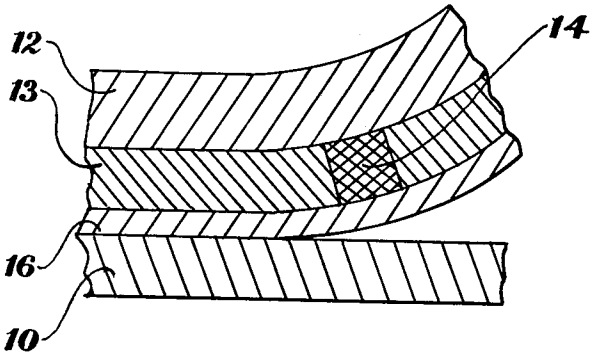


Fig. 3

Henry C. Staehle
INVENTOR.

BY Daniel J. Mayne
W. H. McDowell
ATTORNEY & AGENT

United States Patent Office 2,751,315 Patented June 19, 1956

2,751,315

METHOD OF APPLYING A PROTECTIVE COATING OVER A PHOTOGRAPHIC PRINT

Henry C. Staehle, Rochester, N. Y., assignor to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

Application January 2, 1953, Serial No. 329,227

9 Claims. (Cl. 117—76)

This invention relates to a process for applying synthetic polymer layers to the surface of processed photographic elements.

It is well known that photographic elements such as prints, negatives, positive transparencies, etc., both black-and-white and colored, and especially those containing gelatin emulsion layers, are readily soiled in handling, particularly through finger-prints which are not readily removable. Such elements are also quite susceptible to abrasion, dust contamination, fungus, and other biological attack, and may undergo undesirable decomposition under adverse conditions of temperature and humidity. A limited amount of success has resulted from coating the viewing surfaces of such elements with protective layers from which the undesirable markings are more readily removable and which protect the elements from atmospheric effects.

Also, it is a common practice in photography to provide paper prints with various surfaces or textures such as glossy, semi-matte, matte, etc. In the latter two cases, the most common procedure is to provide the baryta coating for the photographic element with the desired surface characteristics which are manifest in the final print upon air drying. Surfaces of highest gloss are obtained primarily by ferrotyping the print, generally by drying the print with the emulsion surface in contact with a polished metal surface.

One object of my invention is to provide a method of coating photographic images with protective layers and simultaneously to impart the desired surface characteristics to the elements.

In general, the objects of my invention are accomplished by squeegeeing the emulsion layer of a processed photographic emulsion onto a moisture-repellent surface which may have been waxed, with a thin film or layer of an aqueous colloidal dispersion of certain polymers between the moisture-repellent surface and the emulsion layer. Thereafter, the emulsion layer and polymer are detached from the moisture-repellent surface with the result that a transparent layer of the polymer remains on the emulsion surface. When it is desired to obtain a glossy surface layer in this manner, the moisture-repellent surface used can be that of a highly polished metal plate or other material substantially impermeable to moisture. When surfaces having other light reflection properties are desired, one selects for the surfacing element a suitably textured surface such as an embossed metal plate. In this manner the prints can have a variety of surfaces such as tapestry, silk, matte, semi-matte, etc. One advantage of the latter procedure is that it is not necessary to depend upon a subcoating for the emulsion layer, such as a baryta coating, for obtaining the desired emulsion surface characteristics. Accordingly, more uniformity of product is obtainable by my process.

The aqueous colloidal dispersions of polymeric materials suitable for applying the surface layers to processed photographic elements are somewhat limited. As is well known, many monomeric materials can be polymerized in aqueous medium to obtain colloidal dispersions in water. Not all of such colloidal dispersions are useful in my invention. For example, dispersions of only poly-n-butyl acrylate, polyethyl acrylate, copolymers of methyl acrylate and ethyl acrylate (50/50), butadiene-styrene (75/25), butadiene-styrene (45/55), when used in the manner of my invention, yield elements of the surfaces of which are too sticky to be of any practical value. Other dispersions such as of the ethyl acrylate-acrylonitrile copolymer (50/50) yield powdery coatings rather than continuous adherent coatings on emulsion layers when employed in the manner of my invention. Similarly, dispersions of polyvinyl ethers and polyacrylic acid methyl ester either yield sticky or powdery coatings.

The aqueous polymer dispersions useful in my invention are those of copolymers of methyl, ethyl, propyl and butyl acrylates such as n-butyl acrylate and isopropyl acrylate, with at least one monomer of the group: styrene, acrylonitrile, methacrylamide, N-methyl methacrylamide, N-ethyl methacrylamide, and N-isopropyl acrylamide.

Aqueous dispersions of copolymers of the following components are particularly useful in my invention:

1. 4% ammonium acrylate
   67% n-butyl acrylate
   29% styrene
2. 4% ammonium acrylate
   67% n-butyl acrylate
   29% acrylonitrile
3. 23% N-isopropyl acrylamide
   63% n-butyl acrylate
   14% acrylonitrile
4. 16% N-methyl methacrylamide
   59% n-butyl acrylate
   25% styrene
5. 50% n-butyl acrylate
   50% acrylonitrile
6. 59% isobutyl acrylate
   16% methacrylamide
   25% styrene
7. 84% n-butyl acrylate
   16% methacrylamide
8. 59% n-butyl acrylate
   16% methacrylamide
   25% styrene
9. 4% N-methyl methacrylamide
   48% n-butyl acrylate
   48% acrylonitrile
10. 8% N-methyl methacrylamide
    46% n-butyl acrylate
    46% acrylonitrile
11. 8% N-methyl methacrylamide
    36.8 n-butyl acrylate
    55.2% acrylonitrile
12. 12% N-methyl methacrylamide
    44% n-butyl acrylate
    44% acrylonitrile

The dispersions of copolymers such as dispersions 1, 2, 4 and 6 to 12 can be obtained as described in the Fowler U. S. Patent application Serial No. 272,709, filed February 20, 1952, and may contain solid concentrations of the order of 20 percent or more as desired.

Dispersions such as 3 and 5 above which yield substantially hydrophobic coatings when applied to photographic elements in the manner described, are prepared in similar fashion by polymerization of the monomeric materials in water in the presence of a catalyst such as potassium persulfate and a dispersing agent such as N-stearamidopropyl - N,N - dimethyl - N - β - hydroxylethyl ammonium chloride, sodium lauryl sulfonate, di-2-ethyl-

hexyl sodium sulfosuccinate etc. Dispersions such as 6 to 8 are less moisture-repellent due to their methacrylamide content but this does not detract from their usefulness.

Copolymers 9–12 above are representative of a group of copolymers forming a preferred embodiment of my invention. This group of copolymers contain from about 1 to 25% by weight of the combined monomers, N-methyl methacrylamide or N-ethyl methacrylamide, from about 25–74% by weight of a combined lower alkyl acrylate such as n-butyl acrylate, and from about 25 to 74% by weight of combined acrylonitrile. When these copolymers are used in the process of my invention for coating processed gelatin emulsion layers, the resultant coatings have the combination of desired properties: good adherence to the emulsion, low water-permeability, good flexibility, and relatively high melting point. The latter characteristic is of particular importance when the coated prints are to be subjected to elevated temperatures in contact with each other or an absorptive surface as in a dry mounting press, and when it is thus desirable to prevent the emulsion overcoating from melting and adhering to such surfaces.

As is apparent from the above, the acrylamide component of the copolymers can be varied to control the hardness and adhesion of the polymer coatings to the emulsion surface; the alkyl acrylate component controls flexibility and moisture permeability as does the acrylonitrile component.

The method I use for applying the polymeric compositions to the processed photographic elements is illustrated in the accompanying drawings wherein Fig. 1 shows in greatly enlarged cross-sectional view the procedure of squeegeeing a print to a surface element, with a bead of the copolymer dispersion between the two elements. Fig. 2 shows the laminated assembly after squeegeeing and Fig. 3 the detachment of the glazed print from the glazing or surfacing element.

My process will now be described with particular reference to the accompanying drawings. As shown in Fig. 1 of the drawings, a plate **10** such as polished or textured aluminum, chromium, or synthetic resin is provided. This plate may be waxed, for example, with an extremely thin coating of carnauba wax, beeswax, or paraffin, etc., and polished if desired. In some cases it will be found that litle or no wax is required particularly when using metal plates. A pool or bead of the aqueous colloidal dispersion of copolymer **11** is then applied at one edge of the plate **10** and the processed photographic element such as a paper print which has been developed and fixed as usual, including a support **12** and gelatin emulsion layer **13** containing the image **14** is then squeegeed on to the plate by means of rollers **15**. Fig. 2 shows the appearance of the laminated element after this procedure according to which the copolymer layer **16** is shown as having lost most of its moisture content due to the absorption of the water of the dispersion by the adjacent gelatin emulsion layer **13**.

Fig. 3 shows the print being detached from the plate **10**, leaving a substantially dry, uniform coating of the copolymer **16** attached to the emulsion layer **13**. Since this procedure utilized plate **10**, the surface of which is highly polished, water-impermeable and non-adherent to layer **16**, when the print carrying the copolymer coating is viewed, it is found to have a surface as glossy as obtainable by conventional ferrotyping methods.

	Cc.
Polymer latex (40% by weight of copolymer of ethyl acrylate-acrylonitrile 50/50)	250
Polymer latex (20% by weight of copolymer of n-butyl acrylate-methacrylamide-styrene 59/16/25)	80
Butyl alcohol	2
Toluol	14
Butyl acetate	9

The organic solvents are absorbed by the latices by milling the composition overnight.

As mentioned, the ethyl acrylate-acrylonitrile dispersion, if used alone, dries to a fine, white powder. The organic solvents in the above composition, together with the other copolymer, induce the formation of a homogeneous, clear film upon drying. The latter copolymer also improves adhesion of the coatings to the gelatin surfaces of the photographic elements.

It will be apparent that my process is not limited to applying the copolymer coatings to dry photographic elements since it is equally useful with freshly processed elements still damp with processing solutions or wash water. Naturally, excess water should be removed from the photographic element prior to the lamination step to prevent undue dilution of the copolymer dispersions.

My process is especially useful in applying protective coatings to photographic elements containing colored images in gelatin layers. Such elements containing colored images are obtainable by well known methods, such as by color development of gelatino-silver halide emulsion layers in the presence of coupler compounds, or by imbibition dye printing methods in which dye images are imbibed onto gelatin layers, etc. In the manner described above, the color prints or films are squeegeed to the surfacing element, utilizing the copolymer dispersions, and separation of the temporarily laminated element yields a photographic element carrying a coating of copolymer on the colored image, of the desired surface texture. In this connection, the surface coating on colored photographic elements may serve a further purpose if an ultra-violet absorber is incorporated into the copolymer dispersion. The absorber prevents harmful ultra-violet rays from reaching the colored images and thereby increases the stability of the colored images. However, a preferred method includes first applying the ultra-violet absorber to the emulsion surface of the element and then applying the protective coating of polymer in the manner described above. For example, a solution of 1 gram of an absorber such as 2-phenylimino-3-phenyl-4-keto-5-(2′-sulfobenzal)thiazolidine, in 6 cc. of methyl ethyl ketone and 40 cc. of water is prepared. This solution is applied to the surface of a color print, the excess removed and the print dried. Suitable amounts of cyan and magenta dyes can be added to compensate for the slight yellow color of the absorber. The glazing operation described above can then be employed to provide the color print with a protective coating.

My process is especially applicable to protecting photographic elements prone to deterioration in the presence of heat and moisture. For example, silver paper prints and films which have been stabilized so as to obviate the washing step following fixing, for example, as described in the Russell U. S. Patents 2,453,346 and 2,453,347, and Brice U. S. Patent 2,448,857 are coated as described above with layers of the more moisture-repellent copolymer dispersions to obtain moisture-impermeable coatings over the emulsion layer with the result that moisture is materially prevented from deteriorating the silver images. When such stabilized photographic elements also include a moisture-impermeable support, moisture is entirely prevented from reaching the emulsion layer containing the stabilized silver image.

My process is readily adapted to the continuous production of elements carrying a coating of the copolymer compositions. A procedure is now available by which black-and-white or colored motion-picture elements are continuously laminated to the desired surfacing element by means of a bead of copolymer dispersion and continuously stripped from the surfacing element to obtain a layer of the copolymer attached to the emulsion layer containing the photographic image. Similarly, paper, film, and other webs free of photographic images can be quickly coated by my process. I merely apply the co-

polymer dispersions to the web, or to the surfacing element, by the usual coating methods and thereafter laminate the web to the surfacing element by means of rollers and then strip the two elements apart as described above. In such application it is desirable to use an endless belt of suitable material as the surfacing element, as will be readily understood. Obviously, this procedure possesses the advantage that extensive drying methods are obviated inasmuch as a minimum of coplymer dispersion is used.

What I claim is:

1. A method of applying a protective coating over a supported processed gelatin emulsion layer containing a photographic image, which comprises squeegeeing said emulsion layer onto a water-repellent surface with a layer between said emulsion and said surface, of an aqueous colloidal dispersion of a copolymer containing from about 1 to 25% of combined N-methyl methacrylamide, about 25 to 74% of combined n-butyl acrylate, and about 25 to 75% of combined acrylonitrile, thereafter removing said emulsion and copolymer layers together from said surface to obtain a coating of the copolymer on the emulsion surface.

2. A method of applying a protective coating over a supported processed gelatin emulsion layer containing a photographic image, which comprises squeegeeing said emulsion layer onto a water-repellent surface with a layer between said emulsion and said surface, of an aqueous colloidal dispersion of a copolymer containing from about 4 to 12% of combined N-methyl methacrylamide, about 44 to 48% of combined n-butyl acrylate and about 44 to 48% of combined acrylonitrile, thereafter removing said emulsion and copolymer layers together from said surface to obtain a coating of the copolymer on the emulsion surface.

3. A method of applying a protective coating over a supported processed gelatin emulsion layer containing a photographic image, which comprises squeegeeing said emulsion layer onto a water-repellent surface with a layer between said emulsion and said surface, of an aqueous colloidal dispersion of a copolymer containing about 4% combined N-methyl methacrylamide, about 48% combined n-butyl acrylate, and about 48% combined acrylonitrile, thereafter removing said emulsion and copolymer layers together from said surface to obtain a coating of the copolymer on the emulsion surface.

4. A method of applying a protective coating over a supported processed gelatin emulsion layer containing a photographic image, which comprises squeegeeing said emulsion layer onto a water-repellent surface with a layer between said emulsion and said surface, of an aqueous colloidal dispersion of a copolymer containing about 8% combined N-methyl methacrylamide, about 46% combined n-butyl acrylate, and about 46% combined acrylonitrile, thereafter removing said emulsion and copolymer layers together from said surface to obtain a coating of the copolymer on the emulsion surface.

5. A method of applying a protective coating over a supported processed gelatin emulsion layer containing a photographic image, which comprises squeegeeing said emulsion layer onto a water-repellent surface with a layer between said emulsion and said surface, of an aqueous colloidal dispersion of a copolymer containing about 8% combined N-methyl methacrylamide, about 36.8% combined n-butyl acrylate and about 55.2% combined acrylonitrile, thereafter removing said emulsion and copolymer layers together from said surface to obtain a coating of the copolymer on the emulsion surface.

6. A method of applying a protective coating over a supported processed gelatin emulsion layer containing a photographic image, which comprises squeegeeing said emulsion layer onto a water-repellent surface with a layer between said emulsion and said surface, of an aqueous colloidal dispersion of a copolymer containing about 12% combined N-methyl methacrylamide, about 44% combined n-butyl acrylate, and about 44% combined acrylonitrile, thereafter removing said emulsion and copolymer layers together from said surface to obtain a coating of the copolymer on the emulsion surface.

7. The process of claim 1 in which the photographic image is colored.

8. The process of claim 1 in which the photographic image is black-and-white.

9. The process of claim 1 in which the water-repellent surface is embossed.

References Cited in the file of this patent

UNITED STATES PATENTS

31,906	Rawson	Apr. 2, 1861
2,123,599	Fikentscher	July 12, 1938
2,140,048	Fikentscher	Dec. 13, 1938
2,173,480	Jung	Sept. 19, 1939
2,267,470	Kabela	Dec. 23, 1941
2,311,518	Caligari	Feb. 16, 1943
2,550,652	Drechsel	Apr. 24, 1951
2,592,218	Weisgerber	Apr. 8, 1952

OTHER REFERENCES

Ser. No. 397,138, Fikentscher (A. P. C.), published May 11, 1943.