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PHOTOGRAPHIC IMAGE-RECEIVING ELEMENTS HAVING BEEN TREATED WITH AMMONIA AFTER DRYING

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ABSTRACT OF THE DISCLOSURE

Color transfer image-receiving layers containing polymers of 4-vinylpyridine are treated with ammonia after being dried with heat. The resulting image-receiving elements exhibit improved optical properties, particularly freedom from haze.

This application is a continuation-in-part of Ser. No. 247,865, filed Dec. 28, 1962 (now abandoned).

This application is concerned with photography, and, more particularly, with providing an improvement in the preparation of image-receiving layers for use in diffusion transfer color processes, and to the use in such diffusion transfer processes of the resulting image-receiving layers.

The copending U.S. application of Howard C. Haas, Ser. No. 50,848, filed Aug. 22, 1960 (now U.S. Patent No. 3,148,061 issued Sept. 8, 1964), discloses and claims the use in color diffusion transfer processes of image-receiving layers comprising polymers of 4-vinylpyridine. In particularly useful embodiments thereof, the image-receiving layer comprises the homopolymer of 4-vinylpyridine or mixtures of poly-4-vinylpyridine with alkali-permeable polymers such as gelatin and polyvinyl alcohol, The poly-4-vinylpyridine polymers are customarily dissolved in acidic solutions, particularly low boiling acids such as acetic acid, in order to coat them. It has been found, from time to time, that freshly coated poly-4-vinylpyridine image-receiving layers may exhibit a haziness. This invention is concerned with eliminating such haziness and in otherwise improving the optical properties of such image-receiving layers.

A primary object of this invention, therefore, is to provide image-receiving layers comprising poly-4-vinylpyridine, which layers are clear, glossy and free of haze.

A further object of this invention is to provide a method by which image-receiving layers comprising polymerized 4-vinylpyridine are treated after being coated upon a support, with ammonia, whereby the resulting image-receiving layer is glossy and free of haze.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and order of one or more of such steps with respect to each of the others, and the products possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

As noted above, this invention is concerned with improvements of image-receiving layers for use in color diffusion transfer processes. As noted in the above-mentioned copending U.S. application Ser. No. 50,848, image-receiving layers composed of polymerized 4-vinylpyridine are particularly useful in diffusion transfer processes employing dye developers, i.e., dyes containing a silver halide developing group and capable of developing exposed silver halide, as disclosed and claimed in U.S. Patent No. 2,983,606, issued to Howard G. Rogers on May 9, 1961. In a preferred embodiment of such dye developer diffusion transfer processes, the negative or photosensitive element is an integral multilayer negative having yellow, magenta and cyan dye developers associated, respectively, with blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layers, as disclosed and claimed in the copending U.S. application of Edwin H. Land and Howard G. Rogers, Serial No. 565,135, filed February 13, 1956 (now U.S. Patent No. 3,345,163 issued October 3, 1967). It will be apparent that such color transfer images should be formed of image-receiving layers which are glossy and free of haze.

It has now been discovered that if an image-receiving layer comprising polymerized 4-vinylpyridine is treated with ammonia, the resulting image-receiving layer is glossier and free of haze. Useful results are obtained by treatment with very small quantities of ammonia. While the exact manner in which the ammonia acts to improve the gloss and other optical characteristics of the poly-4-vinylpyridine layers is not understood, it is believed that the ammonia forms a salt with any free acid employed to dissolve the poly-4-vinylpyridine polymers and retained in the coated layer. Thus, where the acidic solvent used in dissolving the poly-4-vinylpyridine polymers is acetic acid, the treatment with ammonia appears to form the ammonium acetate salt. Since an acid like acetic acid is relatively volatile, it would be expected to be removed by drying the coated image-receiving layer with heat. It is possible that some such acid is retained as a salt of the pyridine polymer, and is converted to the corresponding ammonium salt. If such salt is volatile, as is ammonium acetate, drying the thus-treated image-receiving layer with heat may remove it. It is preferable to insure that the amount of ammonia available is sufficient to react with any free acid present. It will be recognized that since only small quantities of acid are present, very little ammonia is needed.

The treatment with ammonia may be effected by exposing the image-receiving layer to ammonia fumes or to a solution of ammonium hydroxide. This treatment is most effective if performed upon the image-receiving layer after it has been dried with heat.

The following examples of the preparation of image-receiving elements in accordance with this invention are given for purposes of illustration only.

EXAMPLE I

A sheet of cellulose nitrate subcoated baryta paper was coated with an aqueous solution containing acetic acid and a 1:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine to provide an image-receiving layer approximately 0.35 mil thick. The thus-coated image-receiving layer was dried at a temperature between 200 and 210° F., and the dried sheet then passed between a pair of squeeze rolls at the nip of which was maintained a quantity of approximately 5% ammonium hydroxide solution prepared by diluting concentrated ammonium hydroxide (28.7% NH_3). After drying at the same temperature, the image-receiving layer was free of haze and glossier than a control image-receiving layer prepared in the same manner but without the ammonia aftertreatment.

EXAMPLE II

300 g. of high viscosity poly-(ethylene/maleic anhydride) [commercially available from Monsanto Chemical Company, St. Louis, Mo., under the trade name DX-840-31 Resin] was dissolved in 1500 cc. of acetone. 150

g. of n-butyl alcohol and 1 cc. of 85% phosphoric acid were added and the mixture was refluxed for 14 hours. The resulting solution, comprising the partial half-butyl ester of poly-(ethylene/maleic anhydride) was allowed to cool and then coated on a cellulose acetate subcoated baryta paper to give a layer about 0.8 mil thick. Over this polymeric acid layer was then applied a polyvinyl alcohol layer approximately 0.5 mil thick. An image-receiving layer approximately 0.4 mil thick of a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine then was applied in a manner similar to that used in Example I employing a coating solution containing acetic acid, and dried at 200–210° F. The image-receiving layer of the resulting image-receiving element was then treated with dilute ammonium hydroxide as it was passed between a pair of squeeze rolls as in Example I and dried at 200–210° F. The resulting image-receiving layer was free of haze and exhibited increased gloss as compared with a control image-receiving sheet which was not so treated with ammonium hydroxide.

EXAMPLE III

The procedure described in Example II was repeated except that the freshly coated, dried image-receiving element was exposed to ammonia fumes. The so-treated image-receiving element was free of haze and showed increased glossiness as compared with an untreated control.

Image-receiving elements prepared as in the above examples were employed in multicolor diffusion transfer processes employing dye developers as disclosed in the previously mentioned U.S. Patent No. 2,983,606 and copending U.S. application Ser. No. 565,135. The resulting multicolor images were glossy and exhibited no reduction in density or light stability as compared with similar image-receiving elements which had not been treated with ammonia. The resulting multicolor dye developer transfer images exhibited high gloss and excellent optical clarity, and those images formed on the image-receiving elements of Examples II and III showed high luminosity. In accelerated fading tests of multicolor dye developer transfer images formed on the image-receiving elements of Examples II and III, wherein the transfer images were exposed to a xenon arc over saturated NaCl, the images showed significant improvements in light stability, as compared with similar images on image-receiving sheets not treated in accordance with this invention. While the precise reasons for the beneficial effects of the ammonia treatment are not known, it appears to swell the heat dried receiving layer and reduce the strains formed therein during coating. The same result is not attained by treating the heat dried sheet with plain water or with water and a wetting agent.

Image-receiving elements containing a layer of a nondiffusible acid reacting reagent, e.g., a polymeric acid, as illustrated in Examples II and III, are disclosed and claimed in the copending U.S. application of Edwin H. Land, Ser. No. 234,864, filed Nov. 1, 1962. It has been found that the treatment with ammonia or ammonium hydroxide of image-receiving elements containing polymeric acid layers as in Examples II and III has no adverse effects upon the reduction by said polymeric acid layer of the pH of the image-receiving layer during inbibition and, in fact, appeared to increase the rate of pH reduction. Any ammonia which might remain as a salt of the polymeric acid is displaced during diffusion transfer process by the alkali of the processing solution.

The image-receiving layer preferably is composed of poly-4-vinylpyridine or mixtures of poly-4-vinylpyridine with polyvinyl alcohol or gelatin in ratios, by weight, between about 1:1 and about 1:3, inclusive. The dye developers preferably are azo and anthraquinone dye developers; numerous examples of suitable dye developers are disclosed in the aforementioned copending U.S. applications and U.S. Patent No. 2,983,606.

Suitable hardening agents may be employed in the image-receiving layer coating solution. Particularly useful hardening agents are acrolein condensates, such as that sold by Shell Development Corporation under the trade name Aldocryl Resin X–12, and disclosed in the copending U.S. application of Lloyd D. Taylor, Ser. No. 229,194, filed Oct. 8, 1962.

The image-receiving elements of this invention are especially useful in composite film units intended for use in a Polaroid Land Camera, made by Polaroid Corporation, Cambridge, Mass. 02139, or a similar camera structure such, for example, as the camera forming the subject matter of U.S. Patent No. 2,435,717, issued to Edwin H. Land on Feb. 10, 1948. In general, such composite film units comprise a photosensitive element, an image-receiving element and a rupturable pod containing an aqueous alkaline processing solution. The elements and pod are so associated with each other that, upon processing, the photosensitive element may be superposed on the image-receiving element and the pod may be ruptured to spread the aqueous alkaline processing solution between the superposed elements. The nature and construction of the pods used in such rolls are well known to the art. See, for example, U.S. Patents Nos. 2,543,181 and 2,634,886, issued to Edwin H. Land.

It will be apparent that by selecting the image-receiving element support from among suitable opaque and transparent materials, one may obtain image-receiving elements suitable for preparing transfer images which are either reflection prints or transparencies.

It will be noted that other materials useful in the diffusion transfer processes may be incorporated into the image-receiving layer or one of the other layers of the image-receiving element. As an example of such a material, mention may be made of development restrainers such as 1-phenyl-5-mercaptotetrazole.

Since certain changes may be made in the above products and processes without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. An image-receiving element for use in color diffusion transfer processes, comprising a support carrying an image-receiving layer comprising a poly-4-vinylpyridine polymer selected from the group consisting of poly-4-vinylpyridine and polymers comprising a major portion of 4-vinylpyridine segments, said image-receiving layer having been treated with ammonia after being dried with heat, whereby said image-receiving layer exhibits increased gloss and freedom from haze.

2. An image-receiving element as defined in claim **1**, wherein said image-receiving layer comprises a mixture of poly-4-vinylpyridine and polyvinyl alcohol.

3. An image-receiving element as defined in claim **1**, including a layer of a polymeric acid positioned between said support and said image-receiving layer.

4. The method of preparing an image-receiving element for use in color diffusion transfer processes comprising forming an acidic aqueous solution of a polymerized 4-vinylpyridine, applying said solution to a support to provide an image-receiving layer composed of said polymerized 4-vinylpyridine, drying said image-receiving layer with heat, and thereafter treating said image-receiving layer with ammonia, whereby said image-receiving layer exhibits increased gloss and freedom from haze.

5. The method as defined in claim **4**, wherein said acidic aqueous solution comprises acetic acid, poly-4-vinylpyridine, and polyvinyl alcohol.

6. The method as defined in claim **4**, wherein said treatment with ammonia is effected by exposing said image-receiving layer to ammonia fumes.

7. The method as defined in claim **4**, wherein said treatment with ammonia is effected by contacting said image-receiving layer with a solution of ammonium hydroxide.

8. In a process for forming a color image by diffusion transfer, wherein an exposed photosensitive element comprising a silver halide emulsion and a dye developer is developed to provide an imagewise distribution of diffusible dye developer which is transferred by diffusion to a superposed image-receiving layer to impart to said image-receiving layer a positive color image, the step of transferring said imagewise distribution of dye developer to an image-receiving element as defined in claim **1**.

References Cited

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