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(54) Improved inbibition dye printing blank.

(57) An imbibition dye printing blank is disclosed which comprises a polymeric layer which prevents diffusion of soluble mordant components' from the dye printing blank to a matrix element thereby avoiding matrix poisoning.

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IMPROVED IMBIBITION DYE PRINTING BLANK

This invention relates to an improved photographic imbibition dye printing material. In particular, it relates to an improved imbibition dye printing blank.

In the imbibition dye printing process a tanned colloid relief image is formed by exposure of a photosensitive layer on a support followed by differential hardening of the colloid layer with removal of colloid from the support in regions not exposed to light. The resultant colloid relief image is then dyed. The dyed element is referred to as a "matrix". The dye image of the matrix can then be transferred to a "blank" by imbibition. The blank comprises a support having a colloid coating containing a mordant. In this manner, dye images may be obtained which faithfully reproduce a colored subject.

When using blanks containing diffusible basic mordants, there is a tendency for the mordant, or constituents thereof, to diffuse out of the blank into the matrix. The result is that as repeated dye transfers are made from a given matrix, more and more mordant diffuses from the blank into the matrix and combines with dye contained therein. The matrix then takes up more dye than would normally be expected when it is re-dyed. When a transfer is made from the re-dyed matrix excess dye is imbibed onto the blank and the color balance of a print is seriously altered. After a number of transfers, the matrix becomes clogged which results in a drop in higher densities upon repeated transfers. This problem is referred to as matrix poisoning.

A further problem is that since the diffusible constituents of the blank appear also to diffuse into those areas of the matrix support which represent the highlight areas of the print, the final print contains undesirable dye density in highlight region.

Earlier attempts to solve this problem were described in U.S. Patents 3,340,806 and 3,435,761. In U.S. Patent 3,340,806 sulfated or sulfonated derivatives of monomeric esters or carboxylic acid amides were added to an outer colloid layer of a dye printing blank in order to inhibit or to prevent diffusion of a mordant out of the blank and into a colloid matrix. U.S. Patent 3,435,761 describes use of water soluble acid salts, including alkali metal and ammonium sulfates, sulfonates and oarboxylates, of alkyl or aryl substituted polyalkoxy ethers for the same purpose.

Both U.S. Patent 3,340,806 and U.S. Patent 3,435,761 recognized earlier suggestions for applying acidic polymers over the surfaces of mordanted blanks to avoid the problems noted above. However, these patents also recognize the fact that acidic polymers caused other problems, such as sticking or slipping between the blank and the matrix, which prevented obtaining consistently acceptable image quality in relief printing processes.

Accordingly, the problem of avoiding mordant diffusion from a dye printing blank to a matrix element in a non-imagewise manner is still a troublesome matter which causes matrix poisoning.

The object of the present invention is to provide an improved imbibition dye printing blank which comprises a support having coated thereon a hydrophilic colloid layer containing a basic polymeric mordant and also comprising a coating over the mordant which is capable of preventing matrix poisoning.

The object of the present invention is achieved with a coating over the basic polymeric mordant of a polystyrene sulfonic acid compound in a quantity sufficient to prevent diffusion of mordant out of the colloid layer.

The polystyrene sulfonic acid compound can comprise a molecular weight of from 20,000 to 500,000 and can be used as the acid or as a water soluble salt thereof. As used herein, the term "polystyrene sulfonic acid" is intended to mean poly(styrene sulfonic acid) and water soluble salts thereof such as for example the alkali metal and ammonium salts.

The following table describes various polystyrene sulfonic acid compounds which are commercially available and which can be used in this invention.

Table 1

Molecular Weight		Form	Tradename
20,000		Na^+	VERSA-TL-3
70,000		Na^+	VERSA-TL-70
70,000	(18% solids)	H^+	VERSA-TL-72
70,000	(30% solids)	Li^+	VERSA-TL-72
120,000	(30% solids)	NH_4 +	VERSA-TL-125
500,000	(25% solids)	Na^+	VERSA-TL-501
500,000		Na^+	VERSA-TL-502

Information regarding physical and chemical properties of these polystyrene sulfonic acid compounds is available from the publication SPECIALTY POLYMERS published by National Starch and Chemical Corporation, the disclosure of which is hereby incorporated by reference.

The polystyrene sulfonic acid compound can be used in an amount which is effective in preventing or retarding mordant diffusion. Good results are obtained using concentrations of from 1 to 200 mg/m^2 of colloid layer. Where the polystyrene sulfonic acid compound is coated in amounts above 200 mg/m^2 it has been found that the toe portion of the transferred image may not be faithfully reproduced.

A preferred concentration of polystyrenesulfonic acid is from 5 to 25 mg/m^2 of colloid layer.

When an imbibition dye printing blank of the invention is substituted for an untreated blank, the defects attributed to mordant diffusion are avoided. The blank is conveniently prepared by coating on a support a colloid layer comprising a basic mordant. The mordant can be dispersed in a colloid, such as gelatin, with a hardener compound, and coated on the support. The polystyrene sulfonic acid compound may then be coated over the colloid surface from a solution which may, in addition, contain a vehicle such as gelatin. This treatment of the blank provides a layer containing the polymeric compound as a coating over the mordant containing layer. This coating effectively prevents any basic, diffusible, quaternized components contained in the mordant compound from diffusing into and poisoning the matrix. When such blanks are used for receiving transfers from dyed relief images, photographic quality is improved. Dye molecules present in the matrix are able to transfer undisturbed to the blanks and are fixed on mordant particles contained therein to provide the desired high quality images.

Mordanted blanks treated in accordance with this invention are useful for receiving acid dyes from hydrophilic colloid relief images according to prior art techniques. Any suitable acid dyestuff may be transferred to the treated blanks of the invention, such as Anthracene Yellow GR (400% pure Shultz No. 177), Fast Red S Conc. (Colour Index 176), Pontacyl Green SN Ex. (Colour Index 737), Acid Blue Black (Colour Index 246), Acid Magenta O (Colour Index 692), Naphthol Green B Conc. (Colour Index 5), Brilliant Paper Yellow Ex. Conc. 125% (Colour Index 364), Tartrazine (Colour Index 640), Metanil Yellow Conc. (Colur Index 138), Pontacyl Carmine 6B Ex. Conc. (Colur Index 57), Pontacyl Scarlet R Conc. (Colour Index 487) and Pontacyl Rubine R Ex. Conc. (Colur Index 179).

Although gelatin is preferred, other hydrophilic colloids can be employed in the blanks of this invention. These include both naturally occurring substances and synthetic materials, such as proteins, protein derivatives, cellulose derivatives such as cellulose esters, polysaccharides such as dextran, gum arabic, zein, casein, pectin, collagen derivatives, collodian, agar-agar, arrowroot, albumin and modified gelatins such as alkali-treated or acid treated gelatin and gelatin derivatives such as acetylated gelatin and phthalated gelatin.

This invention is further illustrated by the following examples.

Example 1

A dye imbibition blank was prepared by soaking 454 g of gelatin in 5360 cc of distilled water until swollen. The mixture was then heated to 40° C, to dissolve the gelatin. Saponin solution was then added as a coating aid along with 65 cc of 50% aqueous glycerine and 100 g of a 10% solution of the mordant poly-[styrene-co-1-vinylimidazole-co-3(2-hydroxyethyl)-1-vinylimidazolium chloride] (weight ratio 50:40:10) in dilute acetic acid. The pH of the mixture was adjusted to 4.2 and 27 cc of 10% formaldehyde solution was added. The resulting solution was coated onto a cellulose acetate film support at the rate of 1454 mg/m^2 of gelatin (dry weight) per square meter. The blank thus obtained was then coated with an aqueous solution of VERSA-TL-502 and gelatin (dry weight) to provide a layer comprising 11 mg of VERSA-TL-502 and 646 mg

of gelatin per square meter.

A series of six transfers were made to the resulting blank using a gelatin relief matrix containing an acid yellow dye (e.g., Anthracene Yellow GR, Schultz No. 177). The yellow dye stain in the minimum density areas of the matrix after the six transfers was only 0.03, measured through an appropriate blue filter. There was no loss of dye transfer density and the image definition was better than transfers made with a control. In the control experiment, a similar imbibition blank was employed but the process was altered by omitting the polystyrene sulfonic acid/gelatin layer. The yellow dye stain in minimum density areas of the matrix of the control was 0.15 measured through the same blue filter.

Example 2

The procedure of Example 1 was repeated except that the mordant poly(styrene-co-1-vinylimidazole-co-3-benzyl-1-vinylimidazolium chloride) (weight ratio 50:40:10) was used in the blank and a magenta dye (acid Magenta O, C1 692) was used in the matrix. The blank was coated with an aqueous solution of VERSA-TL and gelatin as described in Example 1.

The matrix stain measured with a green filter after six transfers showed a density of 0.01. In a control experiment which excluded the polystyrene sulfonic and/gelatin layer, the matrix showed a stain of 0.18 in the minimum density areas.

"VERSA-TL", referred to above, is a trade mark.

Claims

1. An imbibition dye printing blank comprising a support having coated thereon a hydrophilic colloid layer comprising a basic quaternized polymeric mordant and, coated over said colloid layer, a coating capable of preventing matrix poisoning characterized in that said coating comprises a polystyrene sulfonic acid compound in a quantity sufficient to prevent diffusion of mordant components out of the colloid layer.

2. The printing blank of claim 1 characterized in that the polystyrene sulfonic acid compound is contained in a colloid layer over the mordant containing layer.

3. The printing blank of claim 1 or 2 characterized in that the polystyrene sulfonic acid compound comprises a molecular weight of from 20,000 to 500,000.

4. The printing blank of claim 3 characterized in that the polystyrene sulfonic acid compound has a molecular weight of 500,000.

5. The printing blank of any one of claims 1 to 4 characterized in that the polystyrene sulfonic acid compound is present in an amount of from 1 to 200 mg/m^2 of colloid layer.

6. The printing blank of claim 5 characterized in that the polystyrene sulfonic acid compound is present in an amount of from 5 to 25 mg/m^2 of colloid layer.