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DEACETYLATED CHITIN MORDANT

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1 Claim. (Cl. 101—149.1)

The invention relates primarily to organic mordanted imbibition blanks used in the making of color pictures by the dye transfer process, particularly with acid dyes.

In the making of color pictures by the above-mentioned process, it is necessary to use a specially prepared dye-receptive material which will carry the final color image. This dye-receptive material is a hydrophilic colloid, usually gelatin, coated on a film or paper support and is often referred to as a "blank." This hydrophilic colloid must be prepared or treated so that it will not be physically damaged during the transfer process, which result is usually obtained by incorporating a hardener at the time of the coating or by treating the coated blank in a hardener solution.

In addition to this resistance to physical damage the imbibition blank must yield transferred images having good density, contrast, and also high definition. This latter condition is obtained by retarding the bleeding or diffusion of the dyes in the colloid after transfer from the matrix by means of a mordant distributed in the colloid. Mordants are introduced in the colloid by mixing them into the coating dope or colloid prior to the coating of the blank or they may be introduced after manufacture of the blank and prior to the dye transfer operation by impregnation of the blank with a mordant solution.

The prior art discloses numerous blanks manufactured by introducing inorganic salts into the gelatin prior to coating. For instances, gelatin containing bichromates of alkali metals have been proposed; see Friedman, "History of Color Photography" page 483. Furthermore basic organic polymers such as polymerized quaternized vinyl-substituted azine compounds have been disclosed for use as mordants in gelatin; see U. S. Patents 2,548,575.

In the case of a blank containing a bichromate it is known that it must be submitted to certain after-treatments to reduce the bichromate in order to obtain the hardening effect of chrome salts. These treatments are expensive and call for numerous and accurate controls.

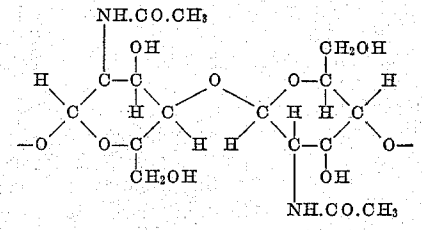
In the case of organic mordants it is known that the type of organic basic polymers disclosed in the prior art are not completely compatible with gelatin and therefore the maximum quantity which can be incorporated in the gelatin is very limited. If it is attempted to increase the concentration of these organic basic resins in the gelatin, the physical properties of the emulsion are considerably changed; for instance, the gelling properties are decreased, its hardening properties are considerably changed and its rate of swelling during the transfer process is decreased. This results in a blank which has an easily damaged emulsion and which will give dye transfer prints with defects known as separation, air and low shoulder density.

Therefore, one of the objects of this invention is to produce pre-mordanted imbibition blank that does not require expensive after-treatments. Another object of the invention is to provide a pre-mordanted imbibition blank containing an organic mordant which is compatible in all

proportions with the hydrophilic colloid coating, exhibits superior transfer behavior, and gives images of high definition. Still another object of the invention is to produce a mordanted blank which is able to absorb the dyes from the matrix with unexpected speed and completeness as compared with those of the prior art. A further object is to produce a dye transfer printing process which is more rapid than those heretofore used. Further objects and advantages will be apparent from the following description of the invention.

In one aspect the present invention involves a pre-mordanted dye imbibition blank comprising a support coated with a hydrophilic colloid containing an organic mordant such as deacetylated chitin or some of its derivatives. Also included within the scope of the present invention is the process of producing said blank, which process involves the addition of amounts of deacetylated chitin and/or some of its derivatives to the hydrophilic colloid, such as gelatin, prior to coating the support. Another feature of the present invention includes an improved process for obtaining deacetylated chitin the essence of which is an alkaline hydrolysis under pressure. In a further aspect the invention involves an improved dye-transfer printing process which requires a transfer time 25 to 40% less than conventional transfer processes as a result of the use of deacetylated chitin and/or certain of its derivatives in a pre-mordanted blank.

The question of the structure of a natural product such as chitin is always a controversial one and, depending upon the author and the method used to determine the structure of the natural product, different concepts of the structural composition will be reported. However, chitin is usually agreed to be a nitrogen-containing polysaccharide having the following structural formula:



Chitin is the main constitutent of shells of various insects and crustaceans such as shrimp, lobster or crab shells and may be readily obtained by following the preparation given in United States Patents 2,040,879 and 2,122,418.

When chitin which has been purified, as for instance by the process of the above-mentioned patents, is submitted to hydrolysis, different products are obtained depending upon the manner in which this reaction is carried out. In the case of an acid catalyzed hydrolysis, if the reaction is carried out at a high temperature, the principal reaction is a breakdown of the polysaccharide chain, and as a secondary reaction the acetyl radical is removed from the acetylamino group. The final product, which is not a polymer, is called glucosamine which is also known as 2-desoxy-2-amino-D-glucose.

If chitin is hydrolyzed in the presence of an alkaline catalyst and at high temperature the primary reaction which now takes place is the removal of the acetyl group from the acetylamino group. This results in deacetylated chitin which is essentially an amino polysaccharide and is the product utilized in the present invention.

Deacetylated chitin is not soluble in water or common organic solvents; however it will dissolve in dilute aqueous acid solutions. This is probably because of the fact that the primary amino group forms the corresponding salt

with the acid involved. For instance, in the case of acetic acid an acetate will be formed by salt formation between the acetic acid and the primary amino radical which serves as a base.

We have found that it is advantageous, though not necessarily a limitation upon the scope of the invention, to carry out the alkaline hydrolysis under pressure as opposed to deacetylation in an open vessel. One of the disadvantages of carrying out a deacetylation in an open vessel is that the alkali employed, for example sodium hydroxide, is in constant contact with the atmosphere which normally contains a certain amount of carbon dioxide. This carbon dioxide reacts with the sodium hydroxide to form sodium carbonate which is not effective as a catalyst for deacetylation. Therefore, the pressure vessel reaction allows the reaction to take place in the presence of sodium hydroxide which will not become carbonated in the course of the reaction and permits of a higher reaction temperature.

Various derivatives of deacetylated chitin which are also useful as mordants are obtained by reacting ethylene oxide, ethylene carbonate, or ethylene chlorohydrin with dispersed chitin to form a reaction product called chitin glycol. These reactions have been described in a paper by C. J. P. Thor and W. F. Henderson, "The preparation and properties of alkali chitin" found in The American Dyestuff Reporter, vol. 29, page 461, of September 16, 1940. According to this paper alkali chitin is prepared by seeping chitin in a concentrated sodium hydroxide solution at low temperature for from 2 to 10 hours. The alkali chitin thus prepared is then dispersed in ice and a stoichiometric amount of ethylene oxide was added. After standing the reaction mixture in the refrigerator, with occasional stirring for 3 hours, a definite increase in viscosity is evident. The reaction mixture is then held at room temperature and sodium hydroxide is added until its concentration is about 45%. The suspension is then transferred to a stainless steel vessel, either open or a pressure cooker, and the temperature increased to carry out the deacetylation. The resulting product is deacetylated chitin glycol. The same procedure applies and the same material results if ethylene oxide is replaced by ethylene chlorohydrin.

In using ethylene carbonate, which may be considered the addition product of ethylene oxide and carbon dioxide, in producing deacetylated chitin glycol, the dispersed alkali chitin is reacted with this product at temperatures near the boiling point of the mixture so as to drive off the carbon dioxide formed, thus avoiding the formation of sodium carbonate which is not a suitable catalyst for deacetylation.

Deacetylated chitin or deacetylated chitin glycol, obtained as described, is a long chain polymer which, when dissolved in dilute acetic acid solution, forms a 5% to 6% solution with a very high viscosity which is difficult to filter. It has been found that this polymeric material can be partially degraded without losing its mordanting properties and without obtaining low molecular weight fractions which might diffuse out of the blank and cause matrix poisoning. This molecular breakdown may be obtained by the controlled and careful addition of hydrogen peroxide solution to the acetic acid solution of the deacetylated chitin as more fully set out hereinafter in Example II.

To more clearly set forth the present invention the following examples are given by way of illustration.

Example I.—A solution containing 10 g. of deacetylated chitin, the result of open vessel alkaline hydrolysis of pure chitin, is placed in 200 ml. of a 3% acetic acid solution and filtered. The filtrate is added to 220 mls. of a 15% gelatin solution and 130 mls. of water is added to the mixture to bring the gelatin concentration to 6%. This mixture is coated on a suitable support, dried and hardened by processing for about 2 minutes in the following alkaline formaldehyde hardening solution:

Formalin	mls	27
Sodium sulfate	g	150
Sodium carbonate	g	10
Water up to 1000 mls.		

The coated blank is rinsed in water for about 3 minutes, dried and it is then ready for the dye transfer process. Transfer dye images made on this new type of blank are very sharp and of normal density and contrast. However, if it is desired to obtain transferred dye images of still higher definition or sharpness, the blank prepared and hardened as described above can be processed in the following solution for approximately 3 minutes:

Sodium sulfate	g	150
Formalin	mls	50
Hydrochloric acid	mls	3
Water up to 1000 mls.		

The blank is then rinsed and dried and may then be used for the dye transfer process.

Example II.—In a 4-quart stainless steel pressure cooker, 100 grams of purified chitin obtained from shrimp shells were covered with 2 liters of 40% sodium hydroxide solution. The vessel was closed and was heated until the internal pressure of 15 pounds per square inch was obtained. The heating was regulated to maintain this pressure for approximately 9 hours. This vessel was then cooled, opened and the contents removed and filtered to separate the hydroxide solution from the solid white residue. The residue was washed until free of alkali and dried. The material so obtained weighed 80 grams and was deacetylated chitin.

Deacetylated chitin and 5% acetic acid solution are put in a resin flask provided with a heating mantle. The amount of deacetylated chitin and acetic acid solution are so chosen that a 10% chitin solution will result. The temperature of the mix is brought to approximately 30° C. After a short time the deacetylated chitin swells considerably and forms a very tacky and plastic mass which cannot be stirred conveniently. Hydrogen peroxide solution, such as "Superoxol" which is 30% H_2O_2, is added to the chitin material a few milliliters at a time while the mass is being constantly kneaded. After approximately 5 hours and after adding from 3 to 7 mls. of "Superoxol" per 100 grams of deacetylated chitin, a very definite lowering of the viscosity is observed. Provided deacetylation was carried out properly, 8 to 10% chitin solution is obtained which has a low viscosity and can be filtered through cloth, felted material or fast filter paper. This partially degraded deacetylated chitin polymer has lost none of its mordanting properties and does not contain any low molecular weight fractions which might diffuse out of the blank and cause matrix poisoning.

A solution containing 10 grams of degraded deacetylated chitin in 200 mls. of 3% acetic acid is filtered, and the filtrate is added to 200 mls. of a 15% gelatin solution; 130 mls. of water is added to the mixture to bring the gelatin concentration up to 6%. The mixture is coated on a suitable support, dried, hardened by a solution as in Example I, rinsed, and if desired treated with acid formaldehyde solution to obtain transfer dye images of very high definition.

The amount of mordant used in a coating is not critical but usually at least two parts of deacetylated chitin to ten parts of gelatin are required for satisfactory definition and excellent definition is obtained when the mordant is present in the gelatin in a ratio of three parts of mordant to ten parts of gelatin by weight. While the proportion of chitin may be increased indefinitely without harm, little if any improvement results from an increase beyond three parts chitin to ten parts gelatin. Blanks containing the mordants described in the present

disclosure are free from stain and opalescence. They exhibit superior transfer behavior, give images of high definition, normal shadow quality and normal density and are free from the defect known as matrix poisoning.

Inasmuch as these chitin derivatives are all large polymers they should be incorporated in the gelatin before the gelatin is coated on the film.

While the dye transfer technique is generally the same for blanks made according to the present disclosure as it is with blanks made according to prior art, these special blanks are able to absorb dyes from the matrix much faster and much more completely than blanks of the prior art. Accordingly blanks of the present invention require 25% to 40% less transfer time than those of the prior art and their use results in the following advantages: The definition of the transferred image is increased due to the fact that lateral diffusion in the blank emulsion is greatly diminished in view of the shorter time during which the blank is maintained in a wet condition; and the film output of a given transfer machine can be increased by increasing the film velocity, resulting in a lower contact time between the matrix and the blank. Instead of decreasing the transfer time, the transfer temperature can be lowered.

It is of course obvious from the foregoing that various substitutions in the procedures set forth in the examples are within the scope of the invention. For instance the dewaxing procedure may be adapted to the chitin, chitin glycol, deacetylated chitin or deacetylated chitin glycol, the degrading step of Example II is equally effective with deacetylated chitin and/or chitin glycol whether obtained under pressure or not, and the deactylated chitin and deactylated chitin glycol may be mixed in any desired proportion for use as a mordant.

The relative proportions of the components and temperatures as set forth in the specification are not to be considered critical except where so stated, and this invention includes all modifications and equivalents that come within the scope of the appended claim.

I claim:

As a process for producing a pre-mordanted dye absorptive blank comprising a gelatin coating, the steps of adding an aqueous solution of an acid salt of deacetylated chitin to the gelatin before coating a support therewith, coating the support with the solution of the gelatin and deacetylated chitin, hardening the colloid coating with an alkaline formaldehyde solution, and thereafter reacting the deacetylated chitin in the colloid with an acid formaldehyde solution.

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