

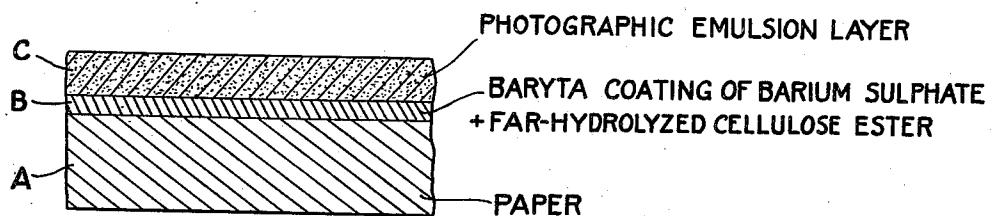
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MANUFACTURE OF PAPER FOR PHOTOGRAPHIC PURPOSES

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MANUFACTURE OF PAPER FOR  
PHOTOGRAPHIC PURPOSES

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This invention relates to the manufacture of paper for photographic purposes. This paper is coated with a baryta coating employing a water-susceptible cellulose ester.

In order to make ordinary paper suitable for use for photographic paper, it is coated with a suspension of blanc fixe or sulfate of barium in a binder, usually gelatin. This coating prevents the infiltration of the photographic emulsion applied thereto into the fiber of the paper and also protects the photographic emulsion against any impurities which might be contained in the paper and which would adversely affect the properties of the emulsion. The coating is applied to the paper by means of a spreading machine. In this way a protective coating is deposited thereon, serving the purposes outlined above.

When photographic emulsions, employing some other medium than gelatin as the carrier for the silver halide, are applied to paper containing a baryta coating consisting of blanc fixe in gelatin, the sensitizing dyes in such emulsions in many cases bleed down into the gelatin layer with unsatisfactory results. Some non-gelatin emulsions, which may exhibit this effect, are described in Salo Patent No. 2,110,491, Fordyce application, Serial No. 221,584, filed on July 27, 1938, now Patent No. 2,211,323 of August 13, 1940, and in Lowe applications, Serial Nos. 318,559, now Patent No. 2,286,215 of June 16, 1942, and 318,560, filed February 12, 1940.

One object of my invention is to provide photographic paper to which non-gelatin emulsions may be applied without any bleeding of the sensitizing dyes or any of the other constituents of the emulsion into the paper or into the baryta coating of the paper. Other objects of my invention will appear herein.

I have found that by coating paper with a dispersion of blanc fixe or barium sulfate in a water-susceptible, lower fatty acid ester of cellulose, the paper is protected from the infiltration of photographic emulsion which is applied thereto and the photographic emulsion is protected from any impurities in the paper. I have also found that bleeding of the sensitizing dyes into the baryta coating or into the paper is prevented thereby. The liquid employed for coating the paper is prepared by dispersing barium sulfate in suitable form in a solution of a far-hydrolyzed cellulose ester, such as cellulose acetate, dissolved in a mixture of an organic solvent and water.

My invention will be more fully understood 55

by reference to the accompanying drawing in which A designates a paper support, B designates a layer of baryta coating thereon of barium sulfate and a far hydrolyzed cellulose ester while 5 C designates the layer of photographic emulsion thereon to form a photographic paper incorporating my invention.

The cellulose ester, which is employed, may be any water-susceptible, far-hydrolyzed, lower fatty acid ester of cellulose. For example, 10 a far-hydrolyzed cellulose acetate, having an acetyl content within the range of 19-30%, may be employed. If a mixed ester, such as cellulose acetate propionate or cellulose acetate butyrate, 15 is employed, a far-hydrolyzed cellulose ester, having substantially the same degree of water-susceptibility, may be used. As a general rule with the mixed esters, those which are suitable are found within the range of 17-30% of acyl. It is desirable, if other esters than the 20 acetates be used, that a major portion of the acyl content be acetyl. With cellulose esters poor in acetyl, the water-susceptibility is not as pronounced and the obtaining of uniform products, having the desired water-solubility, is more difficult than with the higher acetyl content esters. In the case of photographic emulsions which use cellulose esters as the carrier for the 25 silver halide, it is preferred that the cellulose esters employed in the baryta coating correspond thereto as to acetyl content. The cellulose esters may be either high, medium or of low viscosity, the latter being preferred because the baryta coatings containing a low viscosity 30 ester may be applied to the paper using a smaller solvent to solid ratio.

The solvent, which is employed, should be of such a composition that there is little or no blushing; also a better bonding of the coating to 35 the paper is obtained if a solvent mixture is employed in which the cellulose ester is decidedly soluble. The usual ingredients of the solvent employed in the coating of paper are water and a volatile solvent, such as acetone or a water-soluble, aliphatic, monohydroxy alcohol. In 40 some cases it may be desirable to add a minor quantity of a high boiling solvent, such as methyl cellosolve or cellosolve, to aid in the prevention of blushing. Some of the alcohols, 45 which are useful, are methyl, ethyl, normal propyl and isopropyl alcohol.

The amount of solids in the dispersion depends on one hand, as pointed out above, on the viscosity of the cellulose ester. This factor is a

question of technique and resides with the individual operator.

The possibility of coating the paper with more than one coat of the material to obtain a sufficient weight of baryta should be mentioned. For instance, in some cases the use of dispersions, containing 15% of solids, may be employed, while in other cases it may be desirable to use a thinner dispersion, such as a dispersion containing only 9% of solids. In other cases, concentrations between, above or below these values may be desirable.

It may sometimes be desirable to apply more than one baryta coating to the paper so as to obtain a desired thickness or weight of baryta thereon. The application to paper of a plurality of coatings of barium sulfate mixed with a water-susceptible acetyl cellulose is also to be understood as within the scope of my invention. The following examples illustrate the preparation of a photographic paper in accordance with my invention:

*Example I*

100 parts of ethyl alcohol and 70 parts of water are added simultaneously to 30 parts of a 10% solution of a far-hydrolyzed cellulose acetate (acetyl 25%) in a solvent mixture containing 10 parts of ethyl alcohol and 7 parts of water. This mass was well stirred and while stirring, 50 parts of blanc fixe, dispersed in 100 parts of a mixture of equal volumes of ethyl alcohol and water, was added thereto. After thoroughly stirring, the mass was added to 70 parts of the same type of 10% cellulose acetate solution as was previously used and the mixture well stirred. This mixture contained approximately 100 parts of 10% cellulose acetate solution, 120 parts of water, 150 parts of ethyl alcohol and 50 parts of blanc fixe. This dispersion was spread upon a high alpha cellulose paper forming a product upon which a non-gelatin, silver halide, photographic emulsion could be coated.

*Example II*

50 parts of acetone and 50 parts of water were added simultaneously to 30 parts of far-hydrolyzed cellulose acetate propionate (17% acetyl and 9% propional) in a solvent mixture consisting of equal parts of acetone and water. The mass was well stirred and a mixture of 50 parts of blanc fixe dispersed in 50 parts of acetone and 50 parts of water was added thereto. After a thorough stirring the mass was added to 70 grams of the same type of 10% cellulose acetate propionate solution, as was first used, and the mixture was well stirred. The mixture was spread upon paper forming a product upon which a non-gelatin photographic emulsion could be coated.

The far-hydrolyzed cellulose esters, which are employed in preparing baryta coatings in accordance with my invention, may be esters prepared in accordance with the disclosure of Fordyce Patent No. 2,129,052, the hydrolysis being terminated before the point of water solubility is reached.

The photographic papers, prepared in accordance with my invention, have been found to give clear images and there is no bleeding of the sensitizing dye into the baryta coating even on standing. If desired, a gelatin photographic emulsion may be coated over the baryta coating of my invention. However, my invention is par-

ticularly directed to the preparation of a paper, receptive to photographic emulsions which employ some other material than gelatin as the carrier for the silver halide therein.

5 I claim:

1. A photographic paper comprising paper having thereon a coating of barium sulfate mixed with a water-susceptible lower fatty acid ester of cellulose having an acyl content of 19-30% and an overcoating thereover of a photographic silver halide emulsion.

15 2. A photographic paper comprising paper having thereon a coating of barium sulfate mixed with cellulose acetate having an acetyl content of 19-30% and an overcoating thereover of a photographic silver halide emulsion.

20 3. A photographic paper comprising paper having thereon a coating of barium sulfate mixed with a water-susceptible lower fatty acid ester of cellulose having an acyl content of 19-30% and an overcoating thereover of a photographic emulsion composed of silver halide and a far-hydrolyzed cellulose ester.

25 4. A photographic paper comprising paper having thereon a coating of barium sulfate mixed with a cellulose acetate having an acetyl content of 19-30% and an overcoating thereover of a photographic emulsion composed of silver halide carried by a far-hydrolyzed cellulose acetate.

30 5. A photographic paper comprising paper having thereon a coating of barium sulfate mixed with a water-susceptible lower fatty acid ester of cellulose having an acyl content of approximately 25% and an overcoating thereover of a photographic emulsion composed of silver halide and a far-hydrolyzed cellulose ester.

35 6. A paper adapted to support a photographic emulsion on at least one side which comprises paper containing a coating on that side essentially consisting of barium sulfate and a water-susceptible lower fatty acid ester of cellulose having an acyl content of 19-30% so as to prevent the passage of impurities and dye materials to or from the thus coated paper.

40 7. A paper adapted to support a photographic emulsion on at least one side, which comprises paper having a coating on that side essentially consisting of barium sulfate and cellulose acetate having an acetyl content of 19-30% so as to prevent the passage of impurities and dye materials to or from the thus coated paper.

45 8. A paper adapted to support a photographic emulsion on at least one side which comprises paper having a coating on that side essentially consisting of barium sulfate and a water-susceptible lower fatty acid ester of cellulose having an acyl content of approximately 25%.

50 9. A composition for preparing baryta coatings on paper whereby the paper is prepared for an overcoating of a photographic emulsion which comprises blanc fixe dispersed in a solution of a water-susceptible lower fatty acid ester of cellulose having an acyl content of 19-30% in a mixture of water and a volatile solvent.

55 10. A composition for preparing baryta coatings on paper whereby the paper is prepared for an overcoating of a photographic emulsion which comprises blanc fixe dispersed in a solution of cellulose acetate having an acetyl content of 19-30% in a liquid comprising a mixture of water and a volatile solvent.

60 11. A composition for preparing baryta coatings on paper whereby the paper is prepared for an overcoating of a photographic emulsion which comprises blanc fixe dispersed in a solution of

a water-susceptible lower fatty acid ester of cellulose having an acyl content of 19-30% in a mixture of water and ethyl alcohol.

12. A composition for preparing baryta coatings on paper whereby the paper is prepared for an overcoating of a photographic emulsion which comprises blanc fixe dispersed in a solution of a water-susceptible lower fatty acid ester of cellulose having an acyl content of 19-30% in a mixture of water and acetone.

13. A method of preparing paper having use as a support for silver halide emulsions on at least one side, which comprises spreading on that side a dispersion of barium sulfate in a solution of a water-susceptible lower fatty acid ester of cellulose having an acyl content of 19-30%, the liquid portion comprising a mixture of water and a volatile solvent so as to prevent the passage of impurities and dye materials to or from the thus coated paper.

14. A method of preparing paper for use as a support for silver halide emulsions on at least one side, which comprises spreading on that side a dispersion of barium sulfate in a solution of cellulose acetate having an acyl content of 19-30%, the liquid portion comprising a mixture of water and volatile solvent so as to prevent the passage of impurities and dye materials to or from the thus coated paper.

15. A method of preparing paper for use as a support for silver halide emulsions on at least one side, which comprises spreading on that side a dispersion of barium sulfate in a solution of a water-susceptible cellulose acetate propionate, the liquid portion comprising a mixture of water and a volatile solvent so as to prevent the passage of impurities and dye materials to or from the thus coated paper.