

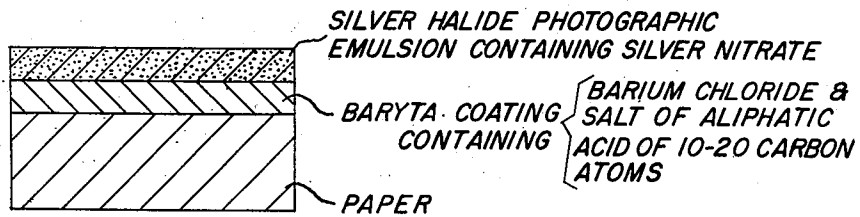
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BARYTA COATED PHOTOGRAPHIC PAPER

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BARYTA COATED PHOTOGRAPHIC PAPER

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This invention relates to a baryta coated paper characterized by the presence of a layer containing barium chloride or some other chloride to prevent the migration of silver salts into or through the paper itself from a photographic emulsion which has been applied thereto.

In the case of photographic papers there is often a tendency for some of the silver material in a photographic emulsion to migrate into and through the paper base which may result in discoloration of the paper or even possibly of the emulsion itself. This has been found to be particularly objectionable in the case of print-out emulsions, such as of the type described in U. S. Patent No. 2,126,319 of Staud and Fallesen, which conventionally may contain not only silver halide but also soluble silver. It has been noted that when print-out emulsions are coated out onto a regular baryta coated paper base the silver salts tend to migrate through the baryta layer and the paper to the back of the paper sheet where they react with the interleaving tissue, ordinarily used, to form objectionable discoloration of the back of the photographic paper or often of the emulsion itself.

I have found that if the baryta coated paper contains a small proportion of barium chloride, preferably in the baryta coating, with or without sodium stearate or like salt that the discoloration of the paper and emulsion which has been noted heretofore is reduced and upon storage no objectionable discoloration occurs. I have found it to be desirable to include sodium stearate or the like with the barium chloride to present a more impermeable layer although prevention of the migration of the silver ions into the paper is appreciably reduced merely by the presence of barium chloride alone. I have found that a barium halide such as barium chloride, bromide, or iodide is eminently suitable for use in the baryta coating for inhibiting the migration of silver salts to the back of the paper sheet. Although aluminum chloride might for example be employed for this purpose, because of its hardening tendencies towards gelatin its field of use is more restricted than in the case of barium chloride.

The accompanying drawing illustrates photographic paper in accordance with my invention. This drawing shows in section the arrangement of the layers therein in which the paper is baryta coated with a composition which contains in addition to the barium sulfate and carrier therefore, barium chloride and a salt of an aliphatic acid of 10–20 carbon atoms over which is applied a silver halide photographic emulsion containing silver nitrate.

One object of my invention is to provide a baryta coated paper which will inhibit the migration of the silver salts from the photographic emulsion layer to the paper base. Another object of my invention is to provide a paper base for photographic products possessing a barrier of a metal halide to bar movement of silver from one layer to another. A further object of my invention is to inhibit the discoloration which has here-

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tofore been exhibited by some types of silver photographic emulsions on the paper support therefor. Other objects of my invention will appear herein.

In its broadest aspects my invention involves a paper support for photographic emulsions to which a metal halide barrier has been supplied prior to the coating of a photosensitive emulsion layer thereon. This barrier should be such that there is .4–1 gram of the metal chloride per sq. meter of the paper. The halide barrier to prevent the migration of silver salts into or through the paper base may conveniently take the form of the prescribed amount of metal halide in the baryta layer applied to a paper base. I have found that the preferred metal halide for use in this connection is barium chloride. I have in addition found that when part of this barium chloride is converted to a barium soap of an aliphatic acid (saturated or unsaturated) of 10–20 carbon atoms that the prevention of the silver salt migration is enhanced. Instead of incorporating barium chloride in the baryta layer some other halide which forms an insoluble soap may be employed such as aluminum chloride although in the case of the latter material hardening properties are exerted on the gelatin when too much of that material is employed. Other metal halides such as sodium chloride, potassium chloride, potassium bromide or sodium iodide can be employed in the baryta layer to prevent the migration of silver salts but preferably when the fatty acid soap is not used in the baryta layer.

If desired the halide layer may be separate from the baryta layer. For instance, the metal halide may be incorporated in the stock from which the paper is formed in such amount as to be present in the finished paper in the proportion designated. Also the metal halide may be applied as a layer to the reverse side of the paper preferably employing therewith a small amount of a binder such as gelatin. Alternatively the metal halide can be applied as a layer on the paper prior to the application of the baryta layer. In those cases where a fatty acid soap such as sodium stearate is employed in the baryta coating layer, it is ordinarily advisable to employ a chloride other than that of sodium or potassium as in some cases where alkali metal chlorides are used objectionable foaming has occurred.

As pointed out above my invention relates to the prevention of the migration of silver salts in finished photographic paper but as this phenomena is characteristic of the print-out types of emulsions my invention is especially adapted to papers containing emulsions of that type. The proportion of barium halide specified herein as being useful for preventing the migration of silver salts is ordinarily obtained in a baryta coating composition by the use of at least 4% of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ based on the dry weight of the solid materials in that composition. This minimum would depend upon the concentration at which the baryta coating composition was used and the thickness with which the baryta composition is applied to the surface of the paper. It is desirable to use at least 10 parts of barium chloride per part of sodium stearate or like salt in the coating composition. As has been indicated above the sodium stearate or other soap may be completely omitted although it has been found that the presence of a small amount of soap is desirable to further reduce the penetration of silver salt into or through the paper.

If the halide is employed in the baryta coating composition the baryta coating can be conveniently applied to the paper by any of the conventional coating methods such as by means of a spray, a hopper or by a skim coating such as by the dipping of a roll into a baryta coating solution which roll is then contacted with the paper continuously by passing the paper over the roll wet with

baryta solution, contact being assured by an idling or pressing roll. In any of the baryta coating operations it would be generally advisable to regulate the thickness of the baryta coating by means of a doctor blade, air brush, or the like, after which the baryta coated paper may be dried and collected upon a roll in the preferred preparation of a baryta coated paper. A convenient method of operation is to first coat the paper with a baryta coating containing the metal halide with or without soap and after drying that coating to apply a second baryta coating without the metal halide therein which is then followed by drying and a calendering of the baryta coated paper. This paper may be converted into a photographic paper by applying a layer of sensitive photographic emulsion thereon. As my invention is particularly adapted to the manufacture of photographic papers using emulsions having soluble silver therein in addition to silver halide that type of emulsion would ordinarily be employed for sensitizing the paper. Nevertheless it is to be understood that my invention is adapted to the preparation of photographic paper generally and any photosensitive silver halide emulsion but especially of the gelation-silver type may be used for the photosensitive coating.

When the barrier to the migration of silver salts is to be incorporated in the baryta layer the baryta coating composition may conveniently be prepared in the following manner: A paste of barium sulfate in water is first prepared having a considerable proportion of barium sulfate therein. There is then run into the barium sulfate paste an aqueous solution of barium chloride followed by the addition of a mixture of a gelatin solution and a solution of an alkali metal soap such as sodium stearate with thorough mixing, this mixing preferably taking place at an elevated temperature. After these materials have been thoroughly incorporated in the barium sulfate paste there is then added thereto butyl alcohol and a hardener such as formaldehyde or chromic chloride-formaldehyde while continuing the stirring. The mass is preferably run through a homogenizer to assure a fluid composition. After dilution to the desired degree a baryta layer is applied to the paper.

This method of preparing the baryta coating has been found to be useful with various concentrations of barium chloride and sodium stearate. For instance, the barium chloride ordinarily should constitute at least 4% of the total dry ingredients of the baryta but proportions above this amount may be employed in the method described. In some cases proportions of sodium stearate or barium chloride or both may be employed in which then there may be some tendency towards coagulation in preparing the baryta composition and hence care must be exercised. However, where the proportions are such that there is no danger of coagulation occurring the baryta coating composition may be prepared by combining the constituents thereof in most any desired order particularly as regards the sodium stearate (or like soap) and the barium chloride as is illustrated by the order in which the materials are combined in the examples given. When sodium stearate or some other soap is employed it is desired that the metal halide such as barium chloride be employed in the proportion of 10-20 parts per part of soap.

Although sodium stearate being the more common type of soap would ordinarily be employed where soap is indicated nevertheless any of the alkali metal salts of the aliphatic acids of 10-20 carbon atoms are suitable for use in this connection such as sodium palmitate, sodium myristate, sodium oleate, sodium laurate, sodium palmitoleate or the like.

The following examples illustrate my invention:

Example 1

A baryta coating composition was prepared by soaking and dissolving 36 lbs. of gelatin in 180 lbs. of water at 180° F. After the gelatin has been dissolved there

was added thereto 86.5 lbs. of a 3% aqueous solution of sodium stearate while hot and the mass was well mixed. The above mixture was then introduced into a 630 lb. water paste of barium sulfate having a 45% solid content. The mass was well stirred and heated to 150° F. 13.8 lbs. of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 75 lbs. of water and was added to the barium sulfate paste and mixed for 15 to 20 minutes. There was then added 18 lbs. of butyl alcohol and the mass was run through a homogenizer to improve its characteristics. 58 lbs. of a formaldehyde hardener was added to the mass and it was then thinned with water to the desired consistency for coating onto paper. The baryta material was then applied to paper by applying the baryta from a hopper onto the paper while moving so as to assure the application of .4-1 gram of barium chloride per sq. meter of paper. The baryta coating was then dried in the conventional manner. A second baryta coating but of the conventional kind was applied to the paper, the coating was dried and the paper was calendered by passing through heated rolls. The paper was then collected in the form of rolls.

Photographic print out paper was prepared from the paper so formed by applying thereto in the conventional manner a silver halide gelatin photographic emulsion containing a substantial proportion of unreacted silver nitrate therein. This paper was packaged by inserting interleaving paper sheets between sheets of the photographic paper. It was found that there was no formation of spots or stains in either the emulsion layer or in the paper itself, after storage of the paper for a considerable period of time.

Example 2

A paper was prepared as described in the preceding example by dissolving 36 lbs. of gelatin in 180 lbs. of water and adding thereto 157 lbs. of a 3% aqueous sodium stearate solution in the described manner. This mixture was then poured into 945 lbs. of an aqueous paste consisting of 55% of water and 45% of barium sulfate which mixture was heated to 150° F. and well stirred. 25 lbs. of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 200 lbs. of water. This solution was added to the barium sulfate mass and mixing was continued for 15 to 20 minutes. There was then added to the mass 58 lbs. of a formaldehyde hardener with continued mixing and then 23 lbs. of butyl alcohol. The mass was then improved by subjecting to a homogenization. The mass thus formed was thinned with water to the desired consistency and applied as a coating to paper in the conventional manner. The thus formed paper was coated with a print-out type of silver halide gelatin emulsion containing a substantial proportion of silver nitrate therein. The so formed paper was dried and packaged using interleaving sheets to separate the sheets of photographic paper. After storage for a considerable period of time the paper was found to be free of discoloration and spotting whereas paper of like type prepared without the use of barium chloride and sodium stearate in the baryta coating showed a high degree of discoloration both in the paper and in the emulsion layer.

I claim:

1. A photographic print-out paper comprising a paper base, a baryta coating thereon resulting from applying to the paper a composition of barium sulfate, a binder, a salt of an aliphatic acid of 10-20 carbon atoms and barium chloride, the latter in an amount of .4-1 gram per square meter of surface and a gelatin silver halide photographic emulsion layer containing a substantial proportion of silver nitrate therein.

2. A photographic print-out paper comprising a paper base, a baryta coating thereon resulting from applying to the paper a composition made from barium sulfate, a binder, sodium stearate and barium chloride, which layer was applied to provide .4-1 gram of barium chloride per

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square meter of surface and a gelatin-silver halide photographic emulsion layer containing a substantial proportion of silver nitrate therein.

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