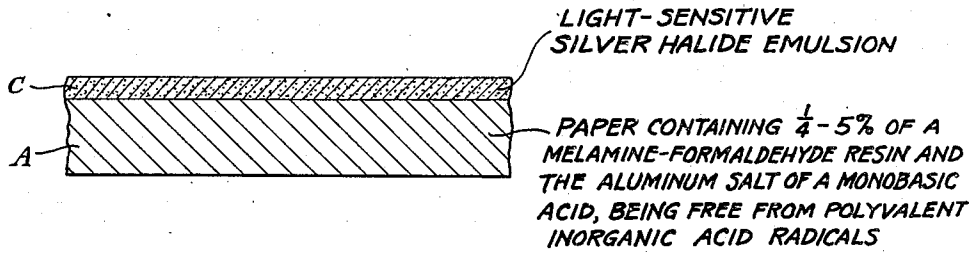
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PHOTOGRAPHIC PAPER

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PHOTOGRAPHIC PAPER

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This invention relates to photographic papers comprising paper having a sizing of a wet strength-imparting melamine resin and an aluminum salt of a monobasic acid and a light-sensitive coating applied to at least one surface of the paper. This application is a continuation-in-part of my application Serial No. 532,299, filed April 22, 1944.

In the past, more or less trouble has been experienced in the processing of photographic papers due to the fact that paper ordinarily is not adapted for the soaking operations which are necessary in developing, fixing and washing the photographic emulsion. Not only has the paper support portion of the photographic paper been susceptible to change, such as loss of wet strength, but also the photographic paper itself has been affected, such as evidenced by blistering, frilling and the like.

Previous attempts have been made to increase the wet strengths of paper, but in many of those previous cases it has also been necessary to incorporate plasticizer in the paper due to the brittleness tendencies induced in the paper in increasing its wet strength because of either the nature of the material incorporated in the paper or the amount of the material which was necessary.

In the case of some papers which have been treated to impart high wet strength thereto, the material employed for that purpose has had a derogatory effect upon sensitized emulsions. In the case of many papers having improved wet strength, a sensitized emulsion coated thereon has been deleteriously affected by the wet strength imparting material therein.

One object of my invention is to provide a photographic paper in which substantially no deleterious photographic effect is exerted by the paper support upon the light-sensitive coating. Another object of my invention is to provide a photographic paper having good wet strength without brittleness or the necessity of plasticization. A further object of my invention is to provide a photographic paper characterized by blister resistance, freedom from frilling or pulling off of the light-sensitive coating, and resistance to scratches and abrasion.

I have found that photographic papers having the above characteristics are obtained by employing, therefor, paper supports containing a melamine-formaldehyde or melamine-monoureide-formaldehyde resin in a proportion within the range of ¼–5% (based on the bone dry weight of the pulp) and the aluminum salt of a monobasic acid, the paper being substantially free from polyvalent inorganic acid radicals.

The accompanying drawing illustrates a photographic paper in accordance with my invention. This photographic paper is made up of support consisting of a paper sheet containing melamine resin and an aluminum salt of a monobasic acid, which paper is substantially free of polyvalent inorganic acid ions, so as to impart high wet strength and resistance to blistering and frilling to the paper, and a light-sensitive silver halide emulsion on the support. The paper support is designated, A, and the emulsion layer is designated, C, in the drawing. If desired, the paper may be further treated, such as with a baryta coating prior to depositing the emulsion layer thereon.

The property of blister resistance is only associated with photographic papers and is not of interest to the general paper industry. This term implies a resistance to the formation of blisters, during photographic processing, within paper stock that has been sensitized with a silver halide carrier photographic emulsion. Photographic paper when processed often develops blisters which might actually rupture the paper sheet. These blisters upon the development of the photographic paper may result from the actual separation of the fibers of the sheet into layers. They may be caused by absorption of water and/or the generation of gas during processing or of steam during the drying of the paper. One of the objects of my invention is to avoid blistering in photographic paper.

Another characteristic which is peculiar to photographic paper is frilling. For instance, it is desirable to have a firm bond between the photographic emulsion layer and the paper support. Photographic paper has a tendency upon processing for the emulsion thereof to reticulate from the edges of the base, or for blisters to be formed between the emulsion layer and the base, in some cases the emulsion even breaking away from the base during processing. One of the objects of my invention is to improve the frilling characteristics of photographic paper.

Another highly desirable characteristic for photographic emulsions is resistance to scratching and abrasion during the preparation of paper sensitized therewith for shipment. The physical hardness of the emulsion portion of the paper, in accordance with my invention, is evidenced by a higher melting point of the emulsion as compared with the melting points of emulsions of other papers at or shortly after the time of preparation of the photographic paper. By thus having an increased physical hardness of the emulsion layer, the photographic paper can be more readily handled, such as in cutting and packing and is better suited to use in the continuously operated manufacturing equipment known in the art.

The paper support portion of my photographic paper may be obtained in the manner described in my application Serial No. 532,299, filed April 22, 1944. This paper support is prepared by first incorporating in paper pulp, particularly high

alpha-cellulose pulp, the melamine resin and the aluminum salt of a monobasic acid followed by forming the paper, such as on the paper machine. The paper should be substantially free of polyvalent inorganic acid ions. Hence, alum, sulfuric acid, ammonium sulfate or the like, which have previously been disclosed as useful in paper making should all be excluded. The disclosure of my copending application Serial No. 532,299 is to be regarded as a disclosure of the making of the paper support employed in photographic paper in accordance with my invention.

The aluminum salt may be incorporated in the paper pulp prior to forming it into paper either as such or in the form of sodium aluminate and a monobasic acid, particularly hydrochloric acid. Other suitable acids, such as nitric or acetic acid, may be employed however. The paper sheet finally obtained which is suitable for use as the paper support for photographic paper in accordance with my invention will be a paper sheet containing therein melamine-formaldehyde or melamine-monoureide-formaldehyde resin, and aluminum chloride, nitrate or acetate. In view of the effectiveness of the resins specified in improving the character of photographic paper when incorporated in the paper support thereof, a proportion of ¼–1%, such as ½% or less of the resin is preferred for use in accordance with my invention.

After the paper has been prepared, it is coated with a silver halide emulsion either with or without further prior treatment of the paper. For instance, it may be desirable to first further size the paper with a tub or surface sizing, so as to close the pores of the paper and render its surface smoother. For instance, the paper, after its formation and drying, may be led through an aqueous gelatin solution containing 4–7% solids at a temperature of 85–120° F. and then passing the paper through squeeze rolls or the like to remove the excess of size therefrom, following which it is dried.

If desired, instead of first drying the paper, it may be directly treated with the gelatin solution after formation on the paper machine. After this treatment, it may then be passed through squeeze rolls and dried. Whether or not a surface and/or tub sizing is desirable in addition to the beater sizing described herein is ordinarily governed by the type of photographic paper desired and is optional with the individual operator.

When desired, a pigment coating may be imparted to the paper, such as by mixing a proportion of baryta or barium sulfate (such as 10%, 20%, 40%, etc.) with the gelatin solution referred to, and applying the baryta coating to the paper. Instead of gelatin-baryta, other types of coating compositions may be employed on the paper if desired, such as, polyvinyl alcohol-baryta as described and claimed in application Serial No. 348,013 of Halford R. Clarke filed July 27, 1940, now U. S. Patent No. 2,358,056, or an aqueous baryta composition comprising a cellulose ester of low acyl content and baryta as described and claimed in U. S. Patent No. 2,346,008, of Halford R. Clarke, or any other pigmented coating composition compatible with photographic emulsions.

The paper is coated with a silver halide emulsion of a type suitable for the particular use desired. For instance, a suspension of silver halide in an aqueous solution of gelatin and sensitized as desired, as disclosed in the prior art, may be applied to the paper to form a coating thereon and may then be set and dried. Instead of a gelatin emulsion, silver halide emulsions using other materials as the carriers for the silver halide may be employed, such as U. S. Patents Nos. 2,253,078, 2,211,323, 2,281,703 and 2,110,491. The emulsions of the non-gelatin type may use as the carrier for the silver halide any suitable colloidal material. Yutzy Patent No. 2,322,085 describes gelatin emulsions which are useful for making the photographic paper of my invention. The following examples illustrate the preparation of a photographic paper starting with the paper pulp, in accordance with my invention:

Example I

Refined sulfite woodpulp having high alpha-cellulose content was placed in a hollander or beater to which was added approximately 1% of hydrogenated rosin size and approximately 1% of sodium aluminate, the percentages being based upon the bone dry weight of the pulp. The hydrogenated rosin size employed was prepared by saponifying hydrogenated rosin with approximately ⅓ its weight of caustic soda. Approximately 5% (based on the bone dry weight of the pulp) of 35% hydrochloric acid was added to the beater, thus precipitating the sizing materials of the pulp. After the beating treatment had been completed and after the pulp had been put through a Jordanning operation, but before the paper stock was brought to the paper machine, there was added thereto 1%, based on the weight of the bone dry pulp, of an acid-aged wet strength-imparting melamine-formaldehyde resin in solution in hydrochloric acid. Nothing was added or was present in the mass to impart polyvalent inorganic acid ions thereto. The paper stock was then applied to the wire of the paper machine and paper was prepared therefrom and passed through the remainder of the machine in the conventional manner.

The paper was dried and a silver halide-gelatin photographic emulsion was applied to one surface of the paper. A paper was obtained having good resistance to blistering and the various other characteristics which characterize photographic paper in accordance with my invention.

Example II

A paper was prepared in a similar manner to that of the preceding example except that aluminum chloride was employed instead of sodium aluminate and hydrochloric acid. A paper was obtained which, when coated with photographic emulsion, formed a photographic paper having the desirable characteristics as specified herein.

Photographic paper is tested for blister resistance ordinarily by subjecting the paper to the following steps and determining the occurrence of blistering therein:

(1) Develop the sheets in an ordinary developing formula, such as formula D–72 (described in Kodak Reference Handbook, page 810, copyright 1940) of 1:2 strength for 1 minute at 70° F.

(2) Immerse the paper in a bath to stop the developing and rinsing in water at 70° F. for 1 minute.

(3) Subject the paper to a hypo fixing bath (formula F–1) and fix for 15 minutes at 70° F.

(4) Immerse the paper in a hypo and alum bath for 20 minutes at 120° F.

(5) Wash at 90° F. for 30 minutes.

(6) Dry on a drier drum.

After subjecting the paper to this series of baths, it is examined for blistering. It has been found that with photographic papers in accordance with my invention subjected to this test, blistering did not occur. For instance, a paper was prepared having a base weight of 52½ pounds per 1000 square feet in which the paper was beater sized with sodium aluminate and hydrochloric acid. In some cases, no melamine resin was incorporated, whereas in other cases both 1% and ½% of melamine-formaldehyde resin was added to the pulp after the Jordanning operation and before placing on the paper machine. After the paper was formed, it was coated with a silver halide gelatin emulsion in the usual manner. The paper containing no melamine resin showed blistering, whereas the photographic papers in which melamine resins were employed in every case exhibited resistance to blistering upon testing in the manner described.

With recording types of papers, the blister test is conducted by subjecting the paper first to double strength developer of the type used therefor, followed by double strength fixing bath of the type employed for recording types of paper.

The emulsion melting points are determined as follows: A strip of unprocessed-sensitized paper having dimensions of approximately ¾" by 3" was placed in a water bath having a mechanical agitator at 70° F. The temperature of the bath was raised at the rate of 2° Fahrenheit per minute until the coating melted. The melting point is taken as the point where a sample when touched on the surface of a beaker containing cold water causes a slight white cloud. The following is typical of the melting point increase of freshly prepared photographic paper in accordance with my invention over freshly prepared papers containing no melamine-resin size:

	Melamine resin	Melting point
	Per cent	
A	0	88° F.
B	0	92° F.
C	0	88° F.
D	3	Emulsion softened and separated from the paper base between 180° and 200° F.
E	3	
F	3	

Frilling or the breaking loose of the emulsion layer from paper stock is tested by processing photographic paper in the normal manner as recommended by the manufacturer followed by scratching the surface of the emulsion with a sharp instrument to form a crossline. While the sample is still wet with the final wash water, these crosslines are heavily rubbed with the forefinger and the susceptibility to frilling or pulling loose with the emulsion can be determined therefrom. This test is comparative and of a qualitative nature. It has been found, however, that photographic papers in accordance with my invention in every case exhibit superior resistance to breaking loose of the emulsion from the paper over papers which have not been prepared as described herein.

I claim:

1. Paper having a sizing including ¼–5% (based on the bone dry weight of the pulp) of a melamine resin and the aluminum salt of a monobasic acid, the paper being substantially free of polyvalent inorganic acid ions, and a photographic silver halide emulsion coating applied on said sized paper, said sizing imparting high wet strength and resistance to blistering and frilling to the paper and being chemically inactive to deteriorate the light-sensitive chemicals of said coating.

2. Paper having a sizing including ¼–5% (based on the bone dry weight of the paper pulp) of wet strength-imparting melamine-formaldehyde resin and the aluminum salt of a monobasic acid, the sizing being substantially free from polyvalent inorganic acid ions, and a light-sensitive silver halide photographic emulsion coating applied over said paper, said sizing imparting high wet strength to the paper and resistance to blistering and frilling and being chemically inactive to deteriorate the light-sensitive chemicals of said coating.

3. Paper having a sizing including ¼–5% (based on the bone dry weight of the paper pulp) of wet strength-imparting melamine-monoureide-formaldehyde resin and the aluminum salt of a monobasic acid, the sizing being substantially free from polyvalent inorganic acid ions, and a light-sensitive silver halide photographic emulsion coating applied over said paper, said sizing imparting high wet strength to the paper and resistance to blistering and frilling and being chemically inactive to deteriorate the light-sensitive chemicals of said coating.

4. Paper having a sizing including ¼–5% (based on the bone dry weight of the paper pulp) of a wet strength-imparting melamine resin and aluminum chloride, the sizing being substantially free of polyvalent inorganic acid ions, a light-sensitive silver halide photographic emulsion coating applied over the paper, said sizing imparting to the paper high wet strength, resistance to blistering and frilling, and being chemically inactive to deteriorate the light-sensitive chemicals of said coating.

5. Paper having a sizing including approximately ½% (based on the bone dry weight of the paper pulp) of a wet strength-imparting melamine resin and the aluminum salt of a monobasic acid the sizing being substantially free of polyvalent inorganic acid ions, and a light-sensitive silver halide photographic emulsion coating applied over the paper, said sizing imparting to the paper high wet strength, resistance to blistering and frilling, and being chemically inactive to deteriorate the light-sensitive chemicals of the emulsion coating.

6. Paper having a sizing including approximately ½% (based on the bone dry weight of the pulp) of a wet strength-imparting melamine-formaldehyde resin and aluminum chloride and a light-sensitive silver halide photographic emulsion coating applied over the paper, said sizing imparting to the paper high wet strength, resistance to blistering and frilling and being chemically inactive to deteriorate the light-sensitive chemicals of said coating.

7. Paper having a sizing including approximately ½% (based on the bone dry weight of the pulp) of a wet strength-imparting melamine-monoureide-formaldehyde resin and aluminum chloride and a light-sensitive silver halide photographic emulsion coating applied over the paper, said sizing imparting to the paper high wet strength, resistance to blistering and frilling and being chemically inactive to deteriorate the light-sensitive chemicals of said coating.

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