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2,865,753

**PHOTOGRAPHIC EMULSIONS CONTAINING A STYRENE-BUTADIENE LATEX AND PHOTOGRAPHIC PAPER MADE THEREWITH**

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This invention relates to photographic emulsions in which styrene-butadiene polymer has been incorporated and to photographic papers in which those emulsions have been employed as the sensitizing layer.

In various types of photographic papers special paper base is employed to impart particular characteristics to the product obtained. For instance, paper base is employed in the making of some photographic products in which the paper has been treated with a resin to translucentize the paper or with a resin latex to impart water-resistant properties thereto. In some cases paper has been employed which has been melt coated with a resin such as polymethyl styrene or with a cellulose derivative such as cellulose acetate butyrate. In those cases, silver halide emulsion layers are poorly adhesive to the support, often necessitating intermediate layers.

Sometimes photographic papers are manufactured at high rates of production which necessitates fast drying of the emulsion layer after its having been applied to the paper. The rapid drying of a photographic emulsion layer may cause brittleness and in the high-speed production of photographic paper this brittleness may become a serious problem.

One object of our invention is to provide photographic emulsions which exhibit good adherence to resin-treated paper base. Another object of our invention is to reduce the brittleness characteristics of photographic emulsion layers. A further object of our invention is to provide a photographic paper, the base of which is resistant to the effects of water, or is translucent, characterized by adherence of the emulsion layer to the entire paper base and with freedom from frilling. A further object of our invention is to provide photographic emulsions containing styrene-butadiene polymer therein. Other objects of our invention will appear herein.

We have found that by incorporating styrene-butadiene elastomer in gelatin-silver halide photographic emulsions the emulsions so prepared exhibit good adherence to paper particularly paper which has been resin treated. We have found that by incorporating styrene-butadiene elastomers in photographic emulsions the emulsion layers of photographic papers prepared thereby exhibit flexibility properties even after they have been subjected to fast drying in the manufacture of the photographic paper. The elastomers which we employ are prepared by polymerizing together styrene and butadiene in the proportions of 55-65% of the former and 45-35% of the latter. The elastomer is preferably supplied to the photographic emulsion in the form of its primary aqueous emulsion such as an aqueous dispersion or latex in which the latex is formed by the emulsion copolymerization of styrene and butadiene. Styrene-butadiene polymers in latex form are well known in the art having been mentioned in various disclosures such as in U. S. Patents Nos. 2,537,114; 2,685,538; and 2,685,571.

The following examples are illustrative of our invention:

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*Example 1*

To samples of a gelatin-silver halide photographic emulsion of the negative type was added styrene-butadiene latex in amounts varying from 12.5 to 50% solid weight based on the weight of the gelatin in the emulsion. These samples were coated on a resin-treated paper base. The sensitized papers thus obtained were exposed and developed photographically. Good photographic images were obtained and the unexposed portions were free from fog. The preparation of the emulsion and its processing were carried out under darkened conditions.

*Example 2*

Styrene-butadiene resin in the form of its primary aqueous dispersion was added to a gelatin-silver halide photographic emulsion in the proportion of 33% solid weight based on the gelatin in the photographic emulsion. The emulsion so prepared was applied to a paper base which had been sized with Aquapel 380 (stearoyl hexadecyl ethenone). It was found that good bonding was effected between the photographic emulsion applied to the Aquapel-sized paper and the paper itself.

*Example 3*

To two samples of a gelatin-silver halide photographic emulsion was added just before coating a water dispersion or latex of a 60:40 styrene-butadiene copolymer of 48% solids concentration in proportions of 25% and of 50% of the gelatin present. The latex employed is known in the trade as Dow 512K. These emulsions were coated on waterproofed paper. The paper was dried and conditioned at 18% relative humidity at 90° F. for 15 hours together with paper coated and dried under the same conditions but latex had not been added to the emulsion. Strips of the paper were drawn with tension over a 1/2 inch cylinder. The paper coated with emulsion contained 25% and 50% of the latex, showed 16 and 5 cracks per inch respectively whereas the paper coated with emulsion which did not contain latex showed cracking of 34 cracks to the inch.

*Example 4*

To samples of a photographic gelatin-silver halide emulsion was added a styrene-butadiene latex (60:40) having 40% solids which had been prepared by copolymerizing styrene-butadiene under emulsion polymerization conditions. These emulsions were coated on paper and compared with an emulsion to which no latex had been added. The results when tested as described in the preceding example were 9 cracks per inch for the 25% resin level, 2 cracks per inch for the 50% resin level and 31 cracks per inch for the emulsion containing no resin.

*Example 5*

A 60:40 styrene-butadiene latex having a 40% solids content prepared by an emulsion polymerization was added to a photographic emulsion in the proportion of 18% of styrene-butadiene resin based on the weight of the gelatin in the emulsion. Paper base was coated therewith and the paper thus prepared was exposed, processed, ferrotyped, and conditioned as described in Example 3, along with a paper prepared from emulsion to which no latex was added. The conditioned paper was put through a series of small flexing rolls known as a "Morse Print Straightener." The latex-containing sample was rated as "good" for print straightener cracks; the comparison was "bad."

We claim:

1. A composition of matter comprising a gelatin-silver halide photographic emulsion in which has been incorporated a styrene-butadiene latex resulting from the emulsion polymerization of styrene and butadiene in the pro-

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portions of 55-65% of the former and 45-35% of the latter.

2. A gelatin-silver halide photographic emulsion containing therein a styrene-butadiene latex in an amount of 12.5-50% solid weight based on the weight of the gelatin in the emulsion.

3. A method of preparing photographic papers which comprises incorporating in a gelatin-silver halide photographic emulsion a minor proportion of styrene-butadiene latex and coating the paper with a layer of the emulsion.

4. A method of preparing photographic paper which

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comprises adding to a gelatin-silver halide photographic emulsion a styrene-butadiene elastomer prepared by polymerizing together styrene and butadiene in an emulsion polymerization in which styrene constitutes 55-65% and butadiene 45-35% of their mixture, and applying a layer of the emulsion to a paper base.

References Cited in the file of this patent

UNITED STATES PATENTS

10	2,284,877	Martinez -----	June 2, 1942
	2,410,792	Broeck -----	Nov. 5, 1946
	2,604,388	Stahle -----	July 22, 1952