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3,002,860

PAPER SIZED WITH NITREOUS SALT OF MALEIC ANHYDRIDE - STYRENE COPOLYMER AND EPOXY RESIN MIXTURE

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This application relates to sized paper and to a method for preparing same.

In the manufacture of high quality paper, particularly paper that is to be used for photographic purposes, it is customary to apply a sizing thereto. One of the materials which has been proposed as a sizing material for paper is an essentially equimolar copolymer of styrene-maleic anhydride. Paper that is sided with styrene-maleic anhydride copolymers is satisfactory in many respects, but its tensile strength is deficient when the paper is wetted with strong alkaline solutions such as are employed in the development of photographic prints.

It is an object of this invention to provide a sized paper which has good tensile strength when in contact with alkaline solutions.

Other objects and advantages of this invention will be apparent from the following detailed description thereof.

The above and related objects are attained by wetting paper with a dilute aqueous solution of 75-95 parts by weight of a volatile nitrogenous base salt of a maleic copolymer, e.g., a styrene-maleic anhydride copolymer, and, correspondingly, 25-5 parts by weight of a water-soluble polyglycidyl ether of a polyhydric alcohol and subsequently drying the paper at a temperature of at least about 190° F.

The following examples are set forth to illustrate more clearly the principle and practice of this invention to those skilled in the art. Unless otherwise noted, where parts or quantities are mentioned they are parts or quantities by weight.

EXAMPLE I

Part A

A sizing solution is prepared by dissolving 5 parts of an equimolar styrene-maleic anhydride copolymer (molecular weight=about 60,000) and 0.5 part of the diglycidyl ether of glycerol in 95 parts of water and adding sufficient ammonium hydroxide thereto to adjust the pH of the solution to 7.2.

Part B

A control sizing solution is prepared in exactly the same manner as described in Part A above except that the diglycidyl ether of glycerol is omitted therefrom.

Part C

Several water laid sheets of unsized high alpha-cellulose paper having a basis weight of 50 lbs./ream are impregnated with the sizing solution of Part A and dried for 2 minutes at 200° F.

Part D

Part C is repeated except that the paper sheets are sized with the control sizing solution of Part B which contains no diglycidyl ether of glycerol.

Part E

The paper sheets from Parts C and D above are thoroughly wetted with distilled water and excess water is removed therefrom by pressing the paper sheets tightly between large blotters.

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Additional paper sheets from Parts C and D are thoroughly wetted with a dilute sodium hydroxide solution having a pH of 13-14 and the excess water is removed by pressing the sheets tightly between large blotters.

The tensile strengths of the wet sheets are set forth in Table I.

TABLE I

Paper Sample	Wet Tensile, lbs./inch (neutral solution)	Wet Tensile, lbs./inch (alkaline solution)
Part C.....	9.3	6.8
Part D.....	4.2	2.0

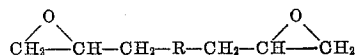
From the above table it is seen that the paper from Part C, which is sized with the mixture of the styrene-maleic anhydride copolymer and the diglycidyl ether of glycerol has a materially higher tensile strength than the paper from Part D, which is sized with only the styrene-maleic anhydride copolymer.

EXAMPLE II

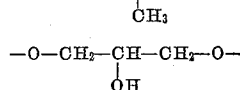
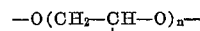
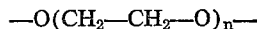
Example I is repeated except that the styrene-maleic anhydride copolymer is replaced with an equivalent quantity of an equimolar copolymer of styrene and the half sec-butyl ester of maleic acid having a molecular weight of about 70,000. Comparable results are obtained.

The first component of the sizing solutions employed in the process of the invention is a volatile nitrogenous base salt of a maleic copolymer. The maleic copolymer moiety is an essentially equimolar copolymer of a monovinylidene aromatic hydrocarbon of the group consisting of styrene, ar-substituted alkylstyrenes, and a maleic monomer of the group consisting of maleic anhydride, maleic acid, half alkyl esters of maleic acids and mixtures thereof. Examples of the ar-substituted alkylstyrenes that can be included in the maleic copolymer include o-, m-, and p-methylstyrenes, o-, m-, and p-ethylstyrenes, 2,4-dimethylstyrene, etc. The half alkyl esters of maleic acid that can be included in the maleic copolymer includes those half esters in which the alkyl group contains 1-8 carbon atoms such as the half methyl maleate, the half sec-butyl maleate, etc. Preferably, the maleic copolymer will have a molecular weight of at least about 10,000. The volatile nitrogenous base moiety should have an atmospheric boiling point not substantially higher than about 175° C. Ammonia is the preferred volatile nitrogenous base for this purpose, but it is also feasible to employ volatile amines such as methylamine, dimethylamine, trimethylamine, the mono-, di-, and triethylamines, isopropylamine, ethanolamine, butylamine, morpholine, pyridine, etc.

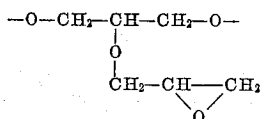
The second component of the sizing agent solution to be employed in the process of the invention is a water-soluble polyglycidyl ether of a polyhydric alcohol conforming to the formula:



where R is a radical of the group



and



and n in the above radicals has a value of 1-2. Typical examples of such polyglycidyl ethers of polyhydric alcohols include the diglycidyl ether of ethylene glycol, the diglycidyl ether of diethylene glycol, the diglycidyl ether of propylene glycol, the diglycidyl ether of glycerol, the triglycidyl ether of glycerol, etc.

The aqueous sizing solutions employed in the invention will contain about 1-25 and preferably about 2-10 weight percent of the above noted two components. The two components will be present in the ratio of 75-95 and preferably 85-95 parts of the volatile nitrogenous base salt of the maleic copolymer and, correspondingly, 25-5 and preferably 15-5 parts of the diglycidyl ether of a polyhydric alcohol.

The sizing solution can be applied to the paper by running either dry paper or wet paper from the paper making machine through the sizing solution. Alternatively, the sizing solution can be applied to the paper by spraying the paper with the sizing solution at any stage in its manufacture or by roll coating the paper. Still other methods of applying the sizing solution to the paper will be apparent to those skilled in the paper making art. After the paper has been sized with the sizing solution, it should be dried at a temperature of at least about 190° F. and preferably by passing the sized paper over heated calendering rolls. The heating step not only dries the paper, but also brings about a reaction between the maleic copolymer and the diglycidyl ether of the polyhydric alcohol.

Although paper of virtually any type can be sized by the method of the present invention, the present process is particularly useful in sizing waterleaf paper and particularly waterleaf paper prepared from a high alpha-cellulose pulp. The invention is particularly useful in the sizing of paper that is to be employed for photographic purposes.

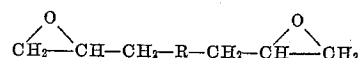
Paper that has been sized in accordance with this invention can be used to manufacture photographic paper by applying a coating of a light sensitive silver halide emulsion thereto. If desired, the paper may be given a baryta coating before applying the photosensitive emulsion thereto, but a particular advantage of the papers manufactured by the method of the invention is that preliminary coatings are not required.

The above descriptions and particularly the examples

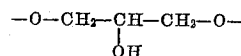
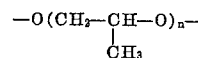
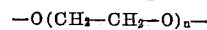
are set forth for purposes of illustration only. Many other variations and modifications thereof will be apparent to those skilled in the art and can be made without departing from the spirit and scope of the invention herein described.

What is claimed is:

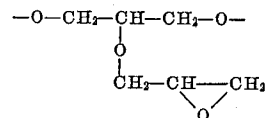
1. The method which comprises wetting paper with a dilute aqueous solution containing 75-95 parts by weight of a volatile nitrogenous base salt of a maleic copolymer and, correspondingly, 25-5 parts by weight of a water-soluble polyglycidyl ether of a polyhydric alcohol and subsequently drying said paper at a temperature of at least about 190° F.; said maleic copolymer being an essentially equimolar copolymer of a monovinylidene aromatic hydrocarbon monomer of the group consisting of styrene, ar-substituted alkylstyrenes and mixtures thereof and a maleic monomer of the group consisting of maleic anhydride, maleic acid, half alkyl esters of maleic acid in which the alkyl group contains 1-8 carbon atoms, and mixtures thereof; said water-soluble polyglycidyl ether of a polyhydric alcohol conforming to the formula:



where R is a radical of the group



and



and n in the above radicals has a value of 1-2.

2. The method of claim 1 in which the water-soluble polyglycidyl ether of a polyhydric alcohol is a diglycidyl ether of glycerol.

3. A sized paper sheet prepared by the method of claim 1.

4. A sized paper sheet prepared by the method of claim 2.

References Cited in the file of this patent

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