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STAIN-FREE PAPER SIZED WITH STARCH OR GELATIN AND AROMATIC ORGANIC ACIDS

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This invention relates to photographic paper, and more particularly to stain-free photographic paper. It also relates to a method of preparing stain-free photographic paper.

Staining of photographic paper may be caused by the presence of oxidized developer thereon. This problem is especially serious with papers developed by a stabilization process (developing and fixing baths) or a monobath process, including papers used as receiving sheets in black-and-white and color image transfer processes. In these processes no attempt is made, such as washing, to remove any developer which may remain on the print.

Previously, it has been suggested to incorporate an acid in a size for the photographic paper in order to prevent undesirable staining of the paper. Paper thus sized is protected against staining when developed in a monobath process, used as a receiving sheet in black-and-white diffusion transfer processes or as a receiving sheet in color diffusion transfer processes such as those described in British Patents 840,731 and 804,971. However, it is desirable to employ acids having a lower solubility than those previously employed in paper sizes to prevent staining. It is advantageous to employ acids of relatively low water solubility in order to prevent or minimize interaction of these acids with coatings thereover which may contain a photographic silver halide emulsion or physical development nuclei. In addition, acids of low water solubility do not tend to neutralize alkali in the processing solutions.

Sizing paper with acids having low solubility presents serious problems as to the method of application. As is known in the art, it is not desirable to use organic solvents in surface sizing photographic paper. When aqueous sizes are employed, the only acids previously used were those soluble at temperatures of less than about 120° F. since higher temperatures could not be employed due to safety requirements which must be maintained in threading paper through hot sizing solutions.

It thus appears highly desirable to provide an aqueous sizing solution containing acids having low solubility, but which may be applied to paper in good concentration at temperatures less than about 120° F.

One object of my invention is the preparation of stain-free photographic paper. Another object of my invention is to provide a paper size containing acids of low solubility. A further object of my invention is to provide a paper size containing acids of low solubility, which size may be applied from an aqueous solution at temperatures less than about 120° F. Another object of my invention is to provide a paper size containing a high concentration of acid, which size may be applied from an aqueous solution at temperatures less than about 120° F. Other objects of my invention will appear herein.

These and other objects of my invention are accomplished by a size containing a combination of aromatic organic acids soluble at concentrations of about 1 to 6% in water at less than 120° F., and preferably within the range of 100–120° F., at least one of said acids being insoluble at concentrations of 2% or more in water at temperatures under 150° F., and another organic acid soluble at concentrations of at least about 2–3% in water at temperatures under 135° F.

I have found that when at least two aromatic organic

acids are incorporated in an aqueous size, one acid being soluble at concentrations of at least about 2–3% in water at temperatures under 135° F., and the other being insoluble at concentrations of about 2% or more in water at temperatures under about 150° F., the acids in combination are more soluble in the aqueous size than either acid separately. Paper sized with this combination of acids in accordance with my invention provides excellent stain protection and a high concentration of acids having low solubility. The combined lower water solubility of such acid combination permits formulation of aqueous sizing solutions containing high acid concentrations, which sizes may be applied at temperatures under about 120° F.

My invention will be further illustrated by the following examples.

EXAMPLE I

A roll of 21 lb./1000 sq. ft. paper base stock was tub sized with the following composition:

	Percent
Starch	7.0
Phthalic acid	2.475
Benzoic acid	0.525
Water	90.0

The paper thus sized was coated with a gelatin solution containing zinc sulfide nuclei and was employed as a positive receiver in a solvent transfer system which made use of monobath processing. The print showed no stain several days after the processing. For comparative purposes, a paper sized in the same manner, but not containing acid, was coated with a gelatin solution containing zinc sulfide nuclei and employed as a positive receiver in the same solvent transfer system and monobath processing. The paper was badly stained a brownish-yellow color after two days.

EXAMPLE II

The process of Example I was followed except that 1.5% phthalic acid and 0.5% salicylic acid were substituted for the phthalic and benzoic acids of Example I. The paper was coated and processed as in Example I. The positive print obtained showed essentially no stain several days after the processing.

EXAMPLE III

The process of Example II was followed except that 1.5% p-hydroxybenzoic acid and 0.5% salicylic acid were substituted for phthalic acid and salicylic acid. The positive print obtained showed no stain after several days after the processing.

EXAMPLE IV

The process of Example III was followed except that 1.5% p-hydroxybenzoic acid and 0.5% benzoic acid were substituted for p-hydroxybenzoic acid and salicylic acid. The positive print obtained showed no stain several days after processing.

As will be readily apparent to those skilled in the art, a wide variety of aromatic organic acids may be employed with my invention. The acid combination which I employ involves the use of one aromatic organic acid which is substantially insoluble in water at concentrations of 2–3% at temperatures under about 150° F., and preferable which is soluble at concentrations of 2% or more at 200° F. The other aromatic organic acid which I employ in the combination of my invention is soluble in water at concentrations of at least 2% at 135° F. By employing this combination of acids, a combined solubility is achieved which is greater than the solubility of either acid alone. Hence, such a combination of acids may be coated from an aqueous system, containing a concentration of up to about 6% acid, onto paper at temperatures

under 120° F. to provide a high concentration of acids which affords excellent protection against staining of the paper.

The ratio of the more soluble to the less soluble aromatic organic acid may vary from about 9:1 to 1:1, and preferably is about 3:1 to 7:1. I have found that the combination of 8–38% of benzoic acid and about 92–62% phthalic acid, at about 3% solids concentration in water, are soluble at temperatures under about 120° F., and sizes prepared therefrom provide excellent protection against staining of paper. Other especially useful combinations of acids, employed in about a 3:1 ratio of the acid of greater solubility to the acid of lower solubility, are the following: phthalic acid and salicylic acid; p-hydroxybenzoic acid and salicylic acid; and, p-hydroxybenzoic acid and benzoic acid. However, as mentioned above, a variety of organic acids may be employed in accordance with my invention to provide highly useful results.

Good results may be obtained in accordance with my invention with sizing solutions containing about 1–6% aromatic organic acids, which results in amounts of the acid on the paper of about 0.25–1.5% acid, based on the dry weight of the paper. I prefer to use sizing solutions containing about 2–3% of the acid combination of the invention, which produces papers containing about .5–.75% organic acid, based on the dry weight of the paper.

A number of binders are useful in the sizes in accordance with my invention. I have found that starch or gelatin provide extremely useful results. The paper prepared in accordance with my invention may be coated with ordinary gelatino silver-halide emulsions to provide photographic papers which are highly resistant to stain caused by the oxidation of any developer which may remain on the paper after the developing operation.

Paper sized in accordance with the invention may also be coated with gelatin or other vehicles containing physical development nuclei to produce a highly stain resistance positive sheet for physical development of an image in solvent transfer systems. The development nuclei used in the sensitive elements of our invention are those physical development nuclei for dissolved silver salts which are well known in the art and include colloidal heavy metals, e.g., colloidal silver and gold; colloidal metal sulfides, selenides and tellurides, e.g., lead sulfide, nickel sulfide, cadmium sulfide, silver sulfide, copper sulfide, zinc sulfide, mercury sulfide; metal proteinates, e.g., silver proteinates; compounds forming physical development nuclei with dissolved silver salts, e.g., sodium sulfide, colloidal sulfur, organic sulfur compounds such as thiourea, mercaptans and xanthates. Receiving sheets sized in accordance with our invention are useful in both black and white diffusion transfer systems and color diffusion transfer systems, such as those described in British Patents 840,731 and 804,971.

This invention has been described in detail with particular reference to preferred embodiments thereof but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A stain-resistant paper for use in photography comprising surface of said paper sized with a binder selected from the group consisting of starch or gelatin and .5–.75%, based on the dry weight of paper, of a combination of two aromatic organic acids soluble at concentrations of 1–6% in water at 100–120° F., one of said acids being selected from (A) the group consisting of phthalic and p-hydroxybenzoic acids, and the other acid being selected from (B) the group consisting of salicylic acid and benzoic acid, the ratio of (A) to (B) being from 7:1 to 3:1.

2. A stain-resistant paper for use in photography comprising surface of said paper sized with a starch binder and about .5–.75%, based on the dry weight of the paper, of a combination of acids essentially consisting of about 82% phthalic acid and 18% benzoic acid.

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