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WATER RESISTANT COATINGS FOR PHOTOGRAPHIC PAPER AND METHOD FOR PRODUCING SAME

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This invention relates to a process for treating paper with a resin latex coating which may or may not be pigmented and which may be waterproof or water resistant.

Waterproof coatings of paper, fabrics and other absorbent materials are well known. Various waxes have been used to impart water resistance by heating the wax treated material so that the wax permeates the interstices of the material. In addition, various synthetic resins have been used commercially especially to treat fabrics in the clothing and weaving industries. Photographic paper has often been made water resistant by coating with a cellulose lacquer, but this process is unsuitable in certain instances for general paper mill use due to the volatile solvents used and resultant hazards.

The above methods have been found generally unsatisfactory in making a water-resistant paper which may be used photographically, and which is compatible with photographic emulsions, dyes and processing chemicals. For instance, the use of a wax treatment may cause a gelatin emulsion to peel from the paper. Other treatments such as resin coatings from solvent solutions or hot melt permit absorption of dyes into the paper coating resulting in staining and other objectionable after effects. It has also been found that some of the water-resistant surfaces permit retention of processing chemicals in the paper which later affect the photographic images.

Accordingly, it is desirable to have a photographic paper base which is either completely or partially resistant to water and particularly to the processing solutions in which the paper is immersed. Such paper could be rapidly processed without retention of the chemicals in the base and could be squeegeed dry for immediate use. For instance, partially resistant stock might be sufficiently temporarily resistant to water or photographic processing solutions to permit contact with a sheet wet with water or chemicals for a few seconds without sufficient wetting of the stock to cause cockle and mottle or similar defects and yet have a water resistance balanced in such a manner as to be receptive to the transfer of a gelatin image.

An object of this invention is to provide a water-resistant paper which will permit the application of gelatin solutions or other similar water based materials without repellency, and to which the gelatin coating will adhere during immersion in water or photographic processing solutions. Another object of this invention is to provide a water-resistant coating which will have low or negligible absorption for chemical dyes, which will have substantially the same thermal expansion properties as gelatin, and which will form a continuous film free of holes. A further object is to produce a water-resistant paper whose sheets will remain separate and individual under pressure in roll form or in cut sheets. Another object is to provide paper which resists the absorption of water or chemical solutions in such quantity as to cause stain or change in physical characteristics during contact periods up to sixty seconds. Another object is to provide a water-resistant paper receptive to the transfer of a gelatin image, but sufficiently water resistant as to eliminate excess wetting.

The above objects are obtained through our process of coating a suitable base material with a mixture of two resins which forms a good, clear, water-white and waterproof film. This mixture contains essentially (1) a soft resin latex formed by the polymerization of styrene with butadiene, and (2) a hard polystyrene latex. This mixed system is unique in that it has better film forming properties than a system containing the same overall ratio of styrene to butadiene that is obtained during a normal polymerization. In the preferred embodiment of our invention, the mixture of the polystyrene resin latex and the styrene-butadiene resin latex was applied by a suitable method to the face of baryta coated stock. The resin latex coating, after drying, was passed in front of a bank of infrared heaters at such a rate as to bring the coated paper to a temperature between 180 to 320° F. This results in a water-resistant paper coating compatible with gelatin coatings suitable for uses as described above.

The following examples are given by way of illustration and it is understood that the invention is not limited thereto.

EXAMPLE I

A roll of 27 lb. per 1000 sq. ft. photographic base stock was coated with two 20 gm./sq. meter coats of gel-baryta (1:9.6 by weight) on the face side. One 20 gm./sq. meter coat of polystyrene resin latex—styrene-butadiene resin latex combination (45:55 by solids weight) was applied by a suitable method to the face of the baryta coated stock. The resin latex coating, after drying, was passed in front of a bank of infrared heaters at such a rate as to bring the coated paper to a temperature of 300° F. at the last heater. A 1.5 gm./sq. meter coat composed of equal parts (by solids weight) of the above resin latex mixture and gelatin was then applied on the face side. This gel-resin subcoat serves two purposes: (1) To prevent blocking between the face side and wire side coats, and (2) to act as a subcoat (binder) between the resin latex coating and the gelatin emulsion. The subcoat was also heat treated in the above described manner. A 20 gm./sq. meter coat of the same resin latex combination was then applied to the wire side and heat treated. The paper so coated was sensitized with a suitable photographic emulsion. After normal photographic processing and washing, the excess water was removed with a sponge or towel and the print was sufficiently dry for reasonably normal handling. Further testing showed that the paper was equal to or better than regular solvent coated (cellulosic compounds) papers with regard to waterproofness as measured by moisture retention, processing chemical retention, Cobb size, Valley penetration, humidity amplitude, and processing size change.

Waterproofness of resin latex coated paper vs. dope coated (cellulose acetate butyrate in solvent) paper

	Latex Coated	Dope Coated
Moisture Retention [1] ..... percent	15-17	26-28
Hypo Retention [2] ..... mg./in.^{2}	.10-.18	.10-.18
Processing size change:		
L ..... percent	−.04	−.20
C ..... do	−.10	−.30
Humidity Amplitude:		
L [3] ..... do	.02	.06
C ..... do	.04	.18
Cobb Size [4]	.01-.03	.08-.10
Valley Penetration	2,000+	2,000+

[1] After 60 min. in processing solutions, surface wiped with sponge.

[2] After 1 min. in developer, 10 min. in hypo, 2 min. wash. Milligrams per square inch.

[3] Percent change in size per 10% change in relative humidity. (30%-70% R. H.)

[4] 1 min. developer, 2 min. hypo, 3 min. water, consecutive exposures. Moisture gain, grams per 100 sq. cm. (test for water-permeability, Technical Association of the Pulp and Paper Industry method T441m).

The Valley penetration test is described in T. A. P. P. I. Instrumentation Study XVI, "Correlation Between the Degree of Sizing as Determined by Valley, T. A. P. P. I. and Currier Methods."

EXAMPLE II

Photographic base stocks varying in weight from 20 lb. to 40 lb./1000 sq. ft. were baryta coated, resin latex coated, subbed, and sensitized in the manner described in Example I. Testing of the processed photographic stock showed waterproofness comparable to that described in Example I.

EXAMPLE III

A suitable photographic base stock was coated with one 20 gm./sq. meter coat of baryta instead of two 20 gm./sq. meter coats of baryta. After resin latex coating, subbing and sensitizing in the manner described in Example I, the stock so prepared showed waterproofness comparable to that of Example I.

EXAMPLE IV

A suitable photographic base stock was coated with 20 gm. of baryta having a gel:fixe ratio of 1:16 instead of the 1:9.6 ratio described in Example I. After resin latex coating, subbing, and sensitizing in the manner described in Example I, the stock so prepared showed waterproofness comparable to that of Example I.

EXAMPLE V

A suitable photographic base stock was resin latex coated and subbed in the manner described in Example I. A 20 gm. coat of baryta (gel:fixe ratio varying from 1:9.6 to 1:16) was applied over the subbing, and the stock so prepared was sensitized with a suitable photographic emulsion. The stock had waterproofness comparable to that of the stock prepared in Example I.

EXAMPLE VI

A suitable photographic base stock was resin latex coated on the face side only and subbed in the manner described in Example I. A 20 gm. coating of baryta (gel:fixe ratio of 1:16) was applied to the face side and the stock so prepared was sensitized with a suitable photographic emulsion. The stock so prepared was suitable for very rapid processing where the hot processing chemicals are sprayed on the face side of the stock and the wire side receives no wetting. The stock was also suitable for the chemical or photomechanical transfer of photographic images to the face side without mottle, cockle, etc.

EXAMPLE VII

A suitable photographic base stock was coated with 20 gm./sq. meter of baryta (1:9.6, gel:fixe ratio) and then was resin latex coated on the face side only and subbed in the manner described in Example I. The sensitized stock was suitable for the uses described in Example VI.

EXAMPLE VIII

A roll of suitable photographic base stock was baryta coated as in Example I except that an additional 20 gm. coat of baryta was coated on the wire side. The stock was then resin latex coated, subbed, and sensitized as in Example I with comparable waterproofness.

EXAMPLE IX

Samples of suitable photographic base stock were baryta coated with two 20 gm. coats of baryta (1:9.6 gel:fixe ratio). The paper was then coated with resin latex combinations in which the polystyrene resin latex to styrene-butadiene latex ratio was varied from 50:50 to 0:100 (by solids weight). The coatings were heat treated, subbed, and sensitized in the manner described in Example I. While the waterproofness was comparable on all samples, it was found that the optimum range with regards to non-blocking, color, heat and light stability, and general handling properties was from 50–50 to 40–60 (styrene—styrene-butadiene by solids weight). Below the

40–60 ratio the coatings had a tendency to be yellow and tacky.

EXAMPLE X

Baryta coated photographic paper, prepared as in Example I, was coated with a 20 gm./sq. meter coat of polystyrene resin latex—styrene-butadiene resin latex combination (45:55 by solids weight). Samples were heat treated at temperatures ranging from 180° F. to 350° F. (temperature of coated paper at last heater). The samples were then subbed; heat treated at the same temperatures as for the face coating; coated on the wire side and heat treated at the same temperature; and sensitized with a suitable photographic emulsion. All samples showed waterproofness comparable to that of Example I. However, it was found that a temperature range of 240°–300° F. was optimum to provide good gloss, antiblocking qualities, and adequate adhesion between the subcoat and latex coat.

EXAMPLE XI

Suitable photographic base stock was baryta coated as in Example I. Using a polystyrene resin latex—styrene-butadiene resin latex (45:55) combination, coating weights varying from 10 gm./sq. meter to 30 gm./sq. meter were applied to the face side. Similar weights of the same latex were applied to the wire side after subbing. It was found that the 10 gm. coatings offered temporary water resistance for some purposes but that 15–20 gms. was optimum for good waterproofness.

EXAMPLE XII

Photographic base stock was baryta coated and resin latex coated on the face side as in Example I. Subcoatings (1.5 gm./sq. meter) were applied in which the resin latex to gel ratio was varied from 60–40 to 30–70 (by solids weight). The wire side coating was then applied and heat treated as in Example I. After sensitizing with the proper photographic emulsion, it was found that the entire range of resin-gel ratios provided adequate emulsion adhesion for some purposes. However, it was found that the optimum range for best adhesion was from 50–50 to 30–70 resin to gel.

EXAMPLE XIII

Photographic base stock was baryta coated as in Example I. A resin latex coating composed of from 70 to 80 parts of the poly-styrene resin latex and styrene-butadiene latex combination, and from 30 to 20 parts of gelatin by weight was applied at a laydown of 20 gm./sq. meter. The coating was heat treated as described in Example I and the wire side coating was applied and heat treated. The resulting stock was sensitized with a proper photographic emulsion and was found to have waterproofness comparable to that of Example I. In addition, it was found that the addition of gelatin to the resin latex combination provided adequate adhesion (for some purposes) of the photographic emulsion to the resin coating without the use of a 1.5 gm. gel-resin subbing intermediate layer.

EXAMPLE XIV

A roll of suitable photographic base stock was baryta coated, resin latex coated on the face side, and subbed with proper heat treatment between coatings. Then two consecutive 10 gm./sq. meter coatings of the same resin latex were applied to the wire side instead of one 20 gm./sq. meter. Each coating was heat treated separately. After sensitizing with the proper photographic emulsion, it was found that the dual 10 gm. coatings prevented the penetration of the processing chemicals through weak spots in the coating when the stock was under the cinching pressure of the standard roll processing equipment or when there was considerable hydro-static pressure as in deep tank processing.

The above examples show our use of the water-re-

sistant coating to paper to be used for photographic purposes. However, the coating mixture shown above could also be applied to any suitable absorbent base material such as cloth, leather and the like. In addition, various coating methods may be used in applying this resin composition to the paper. As can be seen from the above examples, there may be variations in the paper stock weight, number and weight of baryta coatings, gel:fixe ratio in the baryta, position of the resin and baryta coatings, ratio of polystyrene to styrene-butadiene, temperature of heat treatment, resin coating weight, subbing formula and amount of gelatin, if any, added to the coating mixture.

The polystyrene resin which we use for 100% polystyrene contains from 32 to 50% resin solids. The styrene butadiene latex contains from 60 to 67% styrene and from 40 to 33% butadiene and has 48–55% solids.

Various coating means may be used which are within the scope of our invention. For example, a reverse roll coater, air knife doctor, coating hopper or the like may be used. Heating methods include infrared heaters, infrared blankets, and any other suitable method to obtain the desired temperature. Heat treating temperature is referred to above as the "temperature of the coated paper as it passes in front of the last heating unit." Generally, the paper is passed in front of the heaters at such a rate as to obtain the temperature in about fifteen seconds, but this time is not considered critical and other time periods may be used to accomplish the purposes of this invention.

In photographic uses it is advantageous to apply a subbing coat over the waterproof coating as shown above in Example I. This subbing coat is applied from a water system and acts as a binder between the resin coating and photographic emulsion coating. However, it is also advantageous to add gelatin to the resin coating mixture. The resulting coating permits the application of a photographic emulsion directly on the water resistant surface without additional subbing.

This process for forming a water-resistant and waterproof coating for paper meets a need in the photographic industry for a waterproof surface which is compatible with a gelatin emulsion, and which resists staining by photographic dyes and chemicals.

In view of the many changes and modifications which may be made without departing from the principles underlying the invention, reference should be made to the appended claims for an understanding of the scope of the protection afforded this invention.

We claim:

1. A process for preparing a photographic fibrous sheet base material comprising the successive steps of coating the material with a coating containing baryta, drying, coating with a mixture containing from 40 to 60% polystyrene resin latex and from 60 to 40% styrene-butadiene resin latex, drying, and heating to a temperature between 180 to 320° F., applying a subcoating containing from about 30 to 70% gelatin and from 70 to 30% of a mixture containing from 40 to 60% polystyrene resin latex and from 60 to 40% styrene-butadiene resin latex, drying, and heating to a temperature between about 180 to 320° F., and coating with a photographic gelatin emulsion containing light-sensitive silver salts over the subcoating.

2. A process according to claim 1 wherein the base material is paper.

3. A process for making a photographic fibrous sheet base material comprising the successive steps of coating the material with a mixture containing from 40 to 60% polystyrene resin latex and from 60 to 40% styrene-butadiene resin latex, drying, and heating to a temperature of about 180 to 320° F., applying a subcoating containing gelatin and a mixture of from 40 to 60% polystyrene resin latex and from 60 to 40% styrene-butadiene resin latex, drying, and heating to a temperature between 180 to 320° F. and coating with a photographic gelatin emulsion containing light-sensitive silver salt.

4. A process according to claim 3 wherein the base material is paper.

5. A process for making a photographic paper comprising the successive steps of coating the paper with a mixture containing from 30 to 70% gelatin and from 70 to 30% of a mixture containing from 40 to 60% polystyrene resin latex and from 60 to 40% styrene-butadiene resin latex, drying, and heating to a temperature between about 180 to 320° F., and coating with a photographic gelatin emulsion containing light-sensitive silver salts.

6. A water resistant photographic paper produced in accordance with the process described in claim 1.

7. A water resistant photographic paper produced in accordance with the proces described in claim 2.

8. A water resistant photographic paper produced in accordance with the process described in claim 3.

9. A water resistant photographic paper produced in accordance with the process described in claim 4.

10. A water resistant photographic paper produced in accordance with the proces described in claim 5.

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