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2,748,029

TUB SIZING OF PAPER

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9 Claims. (Cl. 117-155)

This invention relates to a new process of tub sizing paper. More particularly this invention relates to tub sizing photographic paper.

There are two commonly used methods of paper sizing. According to one procedure, called beater or engine sizing, the paper chemicals, including those which give high dry bursting strength, and high wet strength are added to the pulp slurry at some point prior to sheet formation upon the wire of the paper machine proper. In the other means of application, the dried paper is run through a bath or tub containing the sizing material in aqueous solution, dispersion, or suspension, whereupon the paper absorbs a quantity of the material. Such a process is called tub sizing. Gelatin and starch are often used for this purpose. The use of these materials improves various characteristics of high quality raw stock such as adhesion of other layers later applied, freedom from fibers, plus the usually-measured physical properties of the sheet such as mullen and wet strength.

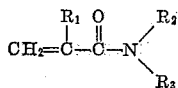
Such materials as gelatin are, however, hydrophilic, being deposited in the interstices of and upon the surface of the raw stock from a water solution. They do not, therefore, result in any substantial improvement in the resistance to moisture of the paper. We have found that, if certain high polymeric aqueous dispersions (hereinafter referred to as hydrosols) are used in place of gelatin for tub sizing paper, a marked improvement results.

An object of this invention is to provide a paper sizing which reduces the paper absorbency toward water. Another object of this invention is to provide a paper having a surface particularly adapted to be coated with a baryta coating in photographic paper manufacturing. A further object of this invention is to provide a sizing which acts as a binder on paper which can be applied by surface treatment. An additional object is to provide a process for coating paper with a sizing to form a hard, abrasive-resistant surface.

The hydrosols which we use in our process are disclosed in patent application Serial No. 272,709 by William F. Fowler, Jr., filed February 20, 1952.

These hydrosols are formed by polymerizing together an unsaturated aliphatic amide and an acrylate, preferably with some unsaturated aromatic monomer therein. When put in the form of an aqueous solution and/or dispersion, this mixture can be polymerized by a simple method whereby there results an emulsion of the polymer in a form for immediate use, such as for mixing with a solution of gelatin or any other water-soluble colloid with which it is to be used. Our process involves the use of:

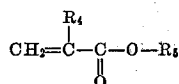
1. An unsaturated aliphatic amide which will be referred to herein as the hydrophilic monomer. This compound will be one having the following structural formula:



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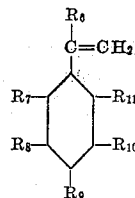
where R₁ is a hydrogen, halogen, alkyl or cyano substituent and R₂ and R₃ may be either hydrogen or alkyl.

2. A monomer having the following structural formula:



wherein R₄ is a hydrogen, halogen or an alkyl substituent, and R₅ is an alkyl, cyano alkyl or halogenated alkyl group. The compounds of this type will be referred to herein as the plasticizing or softening monomer.

3. A monomer having the following structural formula:



wherein R₆ is hydrogen, halogen or an alkyl, and R₇, R₈, R₉, R₁₀ and R₁₁ may each be any of the following: hydrogen, halogen, alkyl, nitro, cyano or dialkyl amino.

In compounding the monomers, the monomers designated 1 and 2 should each be present in a proportion at least 2% of the total monomer composition. However, the sum of these two monomers should constitute at least 30% of the composition. The class of monomers designated 3 should not constitute any more than 70% of the total monomer mixture employed. Although in some cases it may be desirable to entirely dispense with the unsaturated aromatic constituent, it is preferred that at least 5% thereof, based on the total monomer present, be used so as to assure the obtaining of a polymer which is free of tackiness under all conditions of operation. As an example of compounds which are useful as constituent 1, any of the following unsaturated aliphatic amides are useful for this purpose:

1. Acrylamide
2. α-Ethyl acrylamide
3. α-n-Propyl acrylamide
4. α-Isopropyl acrylamide
5. α-n-Butyl acrylamide
6. α-n-Octyl acrylamide
7. N-methyl acrylamide
8. N-ethyl acrylamide
9. N-isopropyl acrylamide
10. N-n-propyl acrylamide
11. N-n-butyl acrylamide
12. N-isobutyl acrylamide
13. N-n-hexyl acrylamide
14. N,N-dimethyl acrylamide
15. N,N-diethyl acrylamide
16. N,N-di(n-propyl)acrylamide
17. N,N-di(isopropyl)acrylamide
18. N,N-di(n-butyl)acrylamide
19. N,N-di(n-butyl)methacrylamide
20. Methacrylamide

Acrylic acid esters which are useful as constituent 2 in the composition referred to above are the following:

1. Methyl acrylate
2. Ethyl acrylate
3. n-Propyl acrylate
4. Isopropyl acrylate
5. Isobutyl acrylate
6. n-Amyl acrylate
7. Isoamyl acrylate
8. n-Hexyl acrylate

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9. 2-ethyl hexyl acrylate
10. n-Octyl acrylate
11. n-Decyl acrylate
12. Methyl methacrylate
13. Ethyl methacrylate
14. n-Propyl methacrylate
15. Isopropyl methacrylate
16. n-Butyl methacrylate
17. Isobutyl methacrylate
18. n-Amyl methacrylate
19. 2-ethyl hexyl methacrylate
20. n-Octyl methacrylate
21. n-Decyl methacrylate
22. β -Cyanoethyl acrylate
23. β -Cyanoethyl methacrylate
24. β -Chloroethyl acrylate
25. β -Chloroethyl methacrylate
26. n-Butyl acrylate

Of the monomers of the unsaturated aromatic type which may be employed as constituent 3 where that is used, any compounds selected from the following list may be employed:

1. o-Methyl styrene
2. m-Methyl styrene
3. p-Methyl styrene
4. 2,4-dimethyl styrene
5. 2,5-dimethyl styrene
6. 3,4-dimethyl styrene
7. 3,5-dimethyl styrene
8. 2,4,5-trimethyl styrene
9. 2,4,6-trimethyl styrene
10. 2,4,5-triethyl styrene
11. o-Ethyl styrene
12. m-Ethyl styrene
13. p-Ethyl styrene
14. 3,5-diethyl styrene
15. p-n-Butyl styrene
16. m-Sec-butyl styrene
17. m-tert-butyl styrene
18. p-hexyl styrene
19. p-n-Heptyl styrene
20. p-2-ethyl hexyl styrene
21. o-Fluoro styrene
22. m-Fluoro styrene
23. p-Fluoro styrene
24. o-Chloro styrene
25. m-Chloro styrene
26. p-Chloro styrene
27. 2,3-dichloro styrene
28. 2,4-dichloro styrene
29. 2,5-dichloro styrene
30. 2,6-dichloro styrene
31. 3,4-dichloro styrene
32. 3,5-dichloro styrene
33. 2,3,4,5,6-pentachloro styrene
34. m-Trifluoromethyl styrene
35. o-Cyano styrene
36. m-Cyano styrene
37. m-Nitro styrene
38. p-Nitro styrene
39. p-Dimethylamino styrene
40. Styrene

The preparation of the polymer is carried out by combining the monomers in an aqueous system. The amide constituent is soluble in water and the softener or plasticizing monomer, and the unsaturated aromatic compound can be incorporated by dispersing those in water, such as by the use of a wetting agent. For this purpose an anionic surface active agent is preferred, such as sodium lauryl sulfate. Other dispersing agents, however, such as (1) cetyl dimethyl ethyl ammonium bromide, (2) sodium stearate, (3) sulfonates of an octyl phenoxy polyethylene glycol, (4) sodium salts of alkyl-aryl sul-

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fonates, (5) sodium salts of alkyl naphthyl sulfonates and (6) sodium salts of sulfated monoglycerides may be employed in this connection. The monomers ordinarily are present in a dilute solution, such as within the range of 5-60%, the monomer concentration used being not critical but governed by the convenience of the individual operator. Also incorporated in the dispersion is a catalyst adapted to promote the polymerization of the monomers. Either of two methods of polymerization may be used: (1) heating on a steam bath or (2) carrying out at substantially room temperature (15-30° C.). Where a steam bath polymerization is employed, a water soluble per-compound may be employed as the catalyst, as, for example, ammonium persulfate, potassium persulfate, hydrogen peroxide, sodium perborate, sodium peracetic acid or the like. If, on the other hand, the polymerization of the monomer dispersion is carried out at room temperature, a redox system catalyst is employed, such as a mixture of sodium acid sulfite and ammonium persulfate or some other per-compound, a mixture of ascorbic acid and a per-compound or a mixture of a ferrous ion compound and a per-compound, or any other redox system catalyst which has been described as being suitable for promoting the polymerization of monomers. If the amide component of the dispersion is of the N-substituted type, it is advisable to carry out the polymerization by the second method, namely, using room temperature and a redox system catalyst. If, on the other hand, the amide employed is not N-substituted, either carrying out the polymerization at room temperature referred to as method 2 or at an elevated temperature, such as 80-120° C., as referred to as method 1, may be conveniently employed in preparing the hydrosol of the polymer in accordance with my invention. It is desirable in carrying out the polymerization that the mass be vigorously agitated, and that the liquid monomer be added over a comparatively short period. For instance, with vigorous agitation and fairly rapid addition of the monomer, products are obtained having a hydrosol particle size on the order of 0.1 micron or less in diameter. On the other hand, if the agitation is not as vigorous or the monomer is added over a longer period of time, a greater size results. The preparation of the polymer should be carried out using sufficient speed of agitation and of addition of monomer, that the size of the particles of the hydrosol prepared is not more than 1 micron. The time necessary for carrying out the polymerization in accordance with my invention is short, the completion thereof being determined by the absence of the odor of any monomer in the reaction mass. The resulting dispersion obtained may be used directly in mixing with aqueous gelatin compositions or in any other connection in which use thereof is indicated. When the amide employed is acrylamide rather than a substituted acrylamide, it is desirable to use the resulting product shortly after its preparation.

The examples presented herewith are intended to illustrate how our invention may be operated so as to improve the sizing of the sheet. It is, of course, possible to size either (a) waterleaf paper or (b) paper which has already been beater sized. Examples of both processes and results obtained are given below.

Example I.—Tub sizing of waterleaf paper

A hydrosol, containing 20 percent solids, was prepared by the emulsion copolymerization of n-butyl acrylate, styrene, and methacrylamide. The ratio of monomers used was as follows:

	Percent
n-Butyl acrylate	59.1
Styrene	25.2
Methacrylamide	15.7

The hydrosol was diluted to a solid content of 4.4 percent.

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Twelve pound waterleaf paper was cut into 8 in. x 10 in. size, hand dipped into the dilute size, and the excess removed by passing through two power drive press rolls. The sheets were then dried at 220° F. for three minutes on a rotary drum dryer.

Physical tests were run on these sheets:

PHYSICAL PROPERTIES OF TUB-SIZED 12½ LB. WATERLEAF PAPER

Property	Un-tubbed Comparison	2.2% gelatin and Hardener	Tubbing Solution 4.4% Hydrosol
Basis Wt., lb./1,000 ft. ²	13¾	14¾	14¾
Thickness, mils.....	4.1	14.3	4.2
Tear:			
Length.....	44	60	54
Across.....	48	68	54
Mullen, lb./in. ²	14	25	23
Wet Strength, lb./in. ²	¾	2¾	3
Valley Penetration, sec.....	1	2	91
Percent Expansion (2 min. wet).....	3.65	3.30	2.90
Fold:			
Length.....	6	40	38
Across.....	3	11	9
Tensile:			
K 9/50 mm. width, Length.....	3.5	5.6	5.1
K 9/50 mm. width, Across.....	1.3	2.1	2.0

Example II.—Tub sizing of already beater-sized paper

The stock used for tub sizing the already beater-sized paper was white "Insurance R" stock, previously untubbed. This stock was treated with a hydrosol and gelatin mixture having 2.2% Gelatin and 2.2% Hydrosol.

The beater-sized stock was hand dipped into the dilute size, and the excess removed by passing through two power drive press rolls. The sheets were then dried at 220° F. for three minutes on a rotary drum dryer.

The results of physical tests obtained upon the already beater-sized paper after tub sizing are given below.

PHYSICAL PROPERTIES OF PRODUCT OF TUB SIZING ALREADY BEATER-SIZED PAPER

Property	37-100 Gelatin (4.4%) (Check)	2.2% Gelatin, 2.2% Hydrosol	4.4% Hydrosol
Weight, lb./1,000 ft. ²	20¾	21	22¾
Thickness:			
Wet mils.....	5.2	5.2	5.2
Dry mils.....	6.8	6.6	6.7
Tear:			
L.....	68	76	68
C.....	68	72	72
Mullen, lb./in. ²	34	34	33
Wet Strength, lb./in. ²	15	14	15½
Penetration, sec.....	135	135	213
Expansion, percent.....	3.02	2.81	2.91
Tensile:			
6P K 9/50 mm. width.....	7.8	7.9	7.8
C K 9/50 mm. width.....	4.2	4.0	3.9
Wet Tensile:			
L K 9/50 mm. width.....	2.23	2.15	2.22
C K 9/50 mm. width.....	1.34	1.33	1.33
Porosity, sec.....	112	39	28
Cobb Size, 5 min. Distilled H ₂ O grams.....	0.227	0.239	0.169
Fold:			
L.....	60	47	58
C.....	37	44	43
Permanence, percent:			
L.....	88	85	85
C.....	76	73	73
UV Reversion:			
B..... percent.....	87.9	87.9	87.1
R..... do.....	85.5	86.1	85.2
Diff..... do.....	2.4	1.8	1.9

Portions of the already beater-sized, subsequently tub-sized samples, were directly sensitized with a photographic emulsion. These were tested sensitometrically and for general photographic quality, fresh and after various incubation periods at 120° F. and 35 percent relative humidity up to 32 days. Results of these tests showed that, in general, no marked changes have been brought about in the photographic characteristics of the emulsion, through the use of this hydrosol either as partial or total replacement for gelatin in the tub-sizing process.

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Results of the physical tests of tub-sized waterleaf paper show that the hydrosol serves as a very effective sizing agent, particularly in comparison with gelatin. When one-half the gelatin is replaced by the hydrosol in tub sizing already beater-sized raw stock, there was an increase in porosity of the paper. Total replacement of gelatin by the hydrosol has (a) improved the sizing (as measured either by Valley Penetration or Cobb size), (b) greatly increased the porosity, and (c) left the rest of the properties essentially unaltered. (Porosity as used in this sense means porosity of the dry sheet to air.)

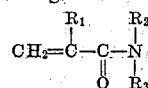
It should be understood that our invention should be more broadly construed than to only include the particular hydrosol composition used in the above examples. Any of the hydrosols described in application No. 272,709 might easily be substituted for this one; the degree of sizing depending to a considerable extent upon the relative amounts of hydrophilic and hydrophobic monomers used.

The Cobb size test is described in T. A. P. P. I. Method T441m45.

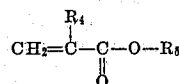
Valley penetration test is described in T. A. P. P. I. Instrumentation Study XVI, "Correlation Between the Degree of Sizing as Determined by Valley, T. A. P. P. I. and Currier Methods."

We claim:

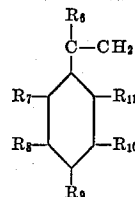
1. A process for tub sizing photographic paper wherein the paper is sized by a hydrosol prepared by polymerizing together in an aqueous system an unsaturated aliphatic amide having the following structural formula:



wherein R₁ is a substituent selected from the group consisting of hydrogen, halogen, alkyl and cyano, and R₂ and R₃ are selected from the group consisting of hydrogen and alkyl, a monomer having the structural formula:

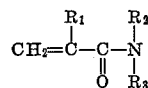


wherein R₄ is a substituent selected from the group consisting of hydrogen, halogen and alkyl, and R₅ is a substituent selected from the group consisting of alkyl, cyano, alkyl and halogenated alkyl, and a monomer having the formula:



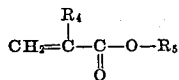
wherein R₆ is a substituent selected from the group consisting of hydrogen, halogen and alkyl, and R₇, R₈, R₉, R₁₀ and R₁₁ are substituents, each of which is selected from any of the following: hydrogen, halogen, alkyl, nitro, cyano and dialkyl amino, each of the first two monomers constituting at least 2% of the total monomer present, and their sum being at least 30% thereof, and the third monomer being no more than 70% of the total monomer present and using the hydrosol as originally formed.

2. A process for tub sizing photographic paper wherein the paper is sized with a hydrosol prepared by polymerizing in an aqueous system a mixture of monomers having the following formula:

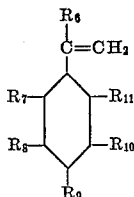


wherein R₁ is a substituent selected from the group consisting of hydrogen, halogen, alkyl and cyano, and R₂

and R₃ are selected from the group consisting of hydrogen and alkyl, a monomer having the structural formula:



wherein R₄ is a substituent selected from the group consisting of hydrogen, halogen and alkyl, and R₅ is a substituent selected from the group consisting of alkyl, cyano alkyl and halogenated alkyl, and a monomer having the formula:



wherein R₆ is a substituent selected from the group consisting of hydrogen, halogen and alkyl, and R₇, R₈, R₉, R₁₀ and R₁₁ are substituents, each of which is selected from any of the following: hydrogen, halogen, alkyl, nitro, cyano and dialkyl amino, the first and second monomers each constituting at least 2% and their sum constituting 30-95% of the total monomer present, and the third monomer constituting 5-70% of the total monomer present and using the hydrosol as originally formed.

3. A process for sub sizing photographic paper wherein the paper is sized with a hydrosol prepared by polymerizing 40 parts of methacrylamide, 5.04 parts of sodium lauryl sulfate and 1.26 parts of potassium persulfate in 1000 parts of hot water while heating this solution, introducing thereto 150 parts of n-butyl acrylate and 64 parts of styrene, and continuing the heating of the mass until a white opaque hydrosol is obtained.

4. A process for sub sizing photographic paper wherein the paper is sized with a hydrosol prepared by polymerizing together a mixture of the following: 20 parts of N-isopropylacrylamide, 75 parts of n-butyl acrylate, 32 parts of styrene, 500 parts of cold water, .127 part of potassium persulfate, .127 part of sodium acid sulfite and 2.5 parts of sodium lauryl sulfate until no odor of monomer is present in the mass and a white opaque hydrosol results.

5. A process for tub sizing photographic paper wherein

the paper is sized with a hydrosol prepared by polymerizing together with agitation 1000 parts of hot water, 1 part of potassium persulfate, 5 parts of sodium lauryl sulfate, 40 parts of methacrylamide, 77.5 parts of p-chlorostyrene and 136 parts of n-butyl acrylate, and supplying heat to this mixture until a white opaque hydrosol results.

6. A paper containing as a sizing agent a hydrosol prepared by polymerizing together in an aqueous solution of an unsaturated aliphatic amide, the mixture of the amide, an aliphatic acrylate and a styrene monomer, the amide and the acrylate each constituting at least 2% of the monomer present, and their sum constituting at least 30% thereof, and the styrene monomer constituting not more than 70% of the total monomer present therein and using the hydrosol as originally formed.

7. A process of sizing paper comprising tub sizing the paper with a hydrosol obtained by polymerizing n-butyl acrylate, styrene and methacrylamide in an aqueous system and using the hydrosol as originally formed.

8. A process for sizing photographic paper comprising tub sizing the paper with a hydrosol formed by polymerizing together in an aqueous solution of an unsaturated aliphatic amide, a mixture of the amide, an aliphatic acrylate and a styrene monomer, the amide and the acrylate each constituting at least 2% of the monomer present, and their sum constituting at least 30% thereof and using the hydrosol as originally formed.

9. A process for tub sizing photographic paper wherein the paper is sized with a hydrosol prepared by polymerizing in an aqueous system methacrylamide, n-butyl acrylate and styrene, the methacrylamide and n-butyl acrylate constituting at least 2% and their sum at least 30% of the total monomer present and using the hydrosol as originally formed.

References Cited in the file of this patent

UNITED STATES PATENTS

2,123,599	Fikentscher	July 12, 1938
2,140,048	Fikentscher	Dec. 13, 1938
2,343,095	Smith	Feb. 29, 1944
2,550,652	Dreschel	Apr. 24, 1951
2,592,218	Weisgerber	Apr. 8, 1952

OTHER REFERENCES

Serial No. 397,138, Fikentscher (A. P. C.), published May 9, 1943.