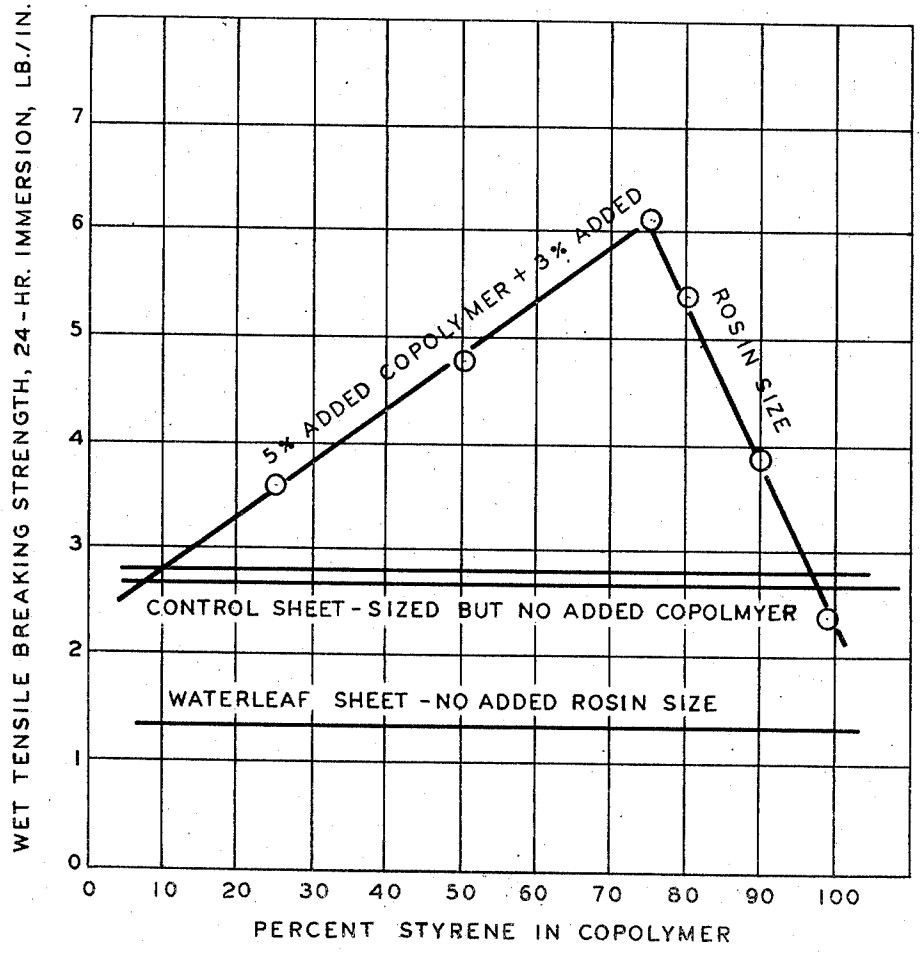
Aug. 25, 1953 E. F. HORSEY ET AL 2,650,163

BUTADIENE-STYRENE SIZED PAPER AND METHOD

Filed May 21, 1947 2 Sheets-Sheet 1

FIG. 1

EFFECT OF BUTADIENE - STYRENE COPOLYMER ON WET TENSILE BREAKING STRENGTH OF PAPER 38 LB. (24 × 36 - 500), SULFITE PULP, 750 CC. S.-R.



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BUTADIENE-STYRENE SIZED PAPER AND METHOD

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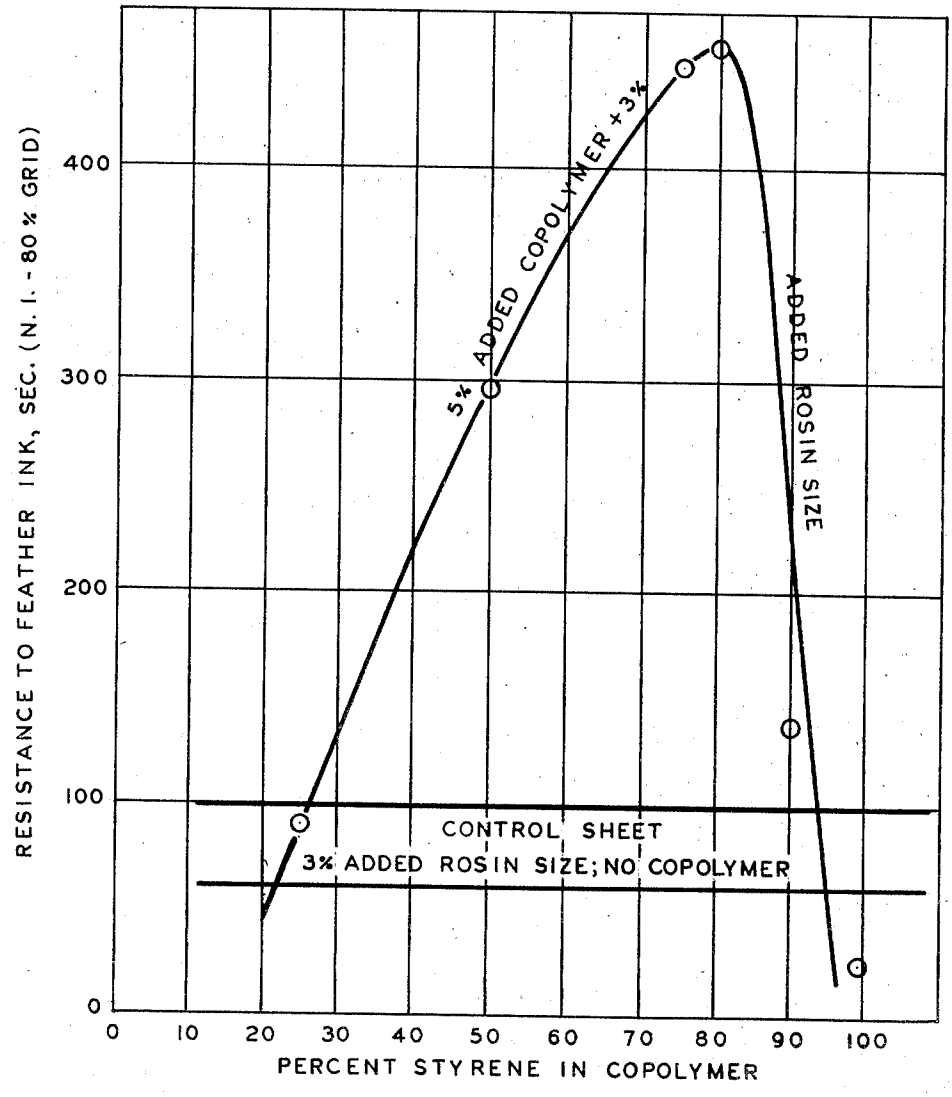


FIG. 2

EFFECT OF BUTADIENE-STYRENE COPOLYMER ON SIZING OF PAPER 38 LB. (24×36-500), SULFITE PULP, 750 CC. S.-R.

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BUTADIENE-STYRENE SIZED PAPER AND METHOD

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11 Claims. (Cl. 92—3)

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This invention relates in general to the sizing of paper and in particular to a new sizing ingredient and a process for its use.

In the sizing of paper with particular reference to increasing the wet strength and related characteristics of the sized paper, it is usual to introduce into the paper a synthetic resin such as, for example, a urea or melamine resin. Likewise, there have previously been attempts to improve the wet characteristics of a sized paper by introducing into the paper natural rubber in the form of rubber latex or a rubber substitute such as, for example, the various synthetic rubbers; the introduction of rubber or a rubber substitute has met with moderate success, although not complete success, and has frequently required the use of special and critical techniques.

Now in accordance with the present invention, it has been found that when a butadiene-styrene copolymer having the proportions of roughly 25% butadiene and 75% styrene is added to paper pulp optionally together with a rosin size, the paper prepared therefrom shows improved sizing and wet strength characteristics such as a greatly increased wet strength and greatly increased resistance to the penetration of water-base inks. It has been found, furthermore, that the sized paper prepared therefrom is highly superior to similar papers containing other sizing agents and, surprisingly, that the superiority is specific to a copolymer having substantially the proportions herein disclosed.

Referring now to the drawing:

Figure 1 is a graphical representation of the sizing characteristics expressed in terms of wet tensile breaking strength in relation to the composition of the added butadiene-styrene copolymer; and

Figure 2 is a graphical representation of the sizing characteristics expressed in terms of resistance to feather ink in relation to the composition of the added butadiene-styrene copolymer.

In carrying out this invention according to a preferred form thereof, a butadiene-styrene copolymer containing approximately 75% styrene and used in the form of the copolymer latex is added to paper pulp in the beater, optionally together with rosin size, and the copolymer and rosin size are precipitated on the pulp with papermakers' alum. The resulting furnish is

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then treated according to conventional papermaking techniques with the optional addition of other paper additives to yield a sized paper having superior sizing characteristics.

Having now indicated in a general way the nature of this invention, the following examples are presented as illustrations but not limitations of preferred embodiments of this invention.

EXAMPLE I

A butadiene-styrene copolymer latex containing the copolymer in the proportion of 25% butadiene and 75% styrene was added to a paper beater containing a sulfite pulp having a freeness of 750 cc. S.—R. The copolymer latex was added to the beater in the amount of 5% based on the dry pulp and, in addition, there was added a conventional rosin size having 18.22% free rosin and added in the amount of 3% based on dry pulp. The pH of this mixture was adjusted to 4.5 with papermakers' alum, and the furnish was then sheeted to form a paper having a basis weight of 38 pounds (24 x 36/500). The paper was tested for its sizing characteristics by standard feather ink, using the Barss, Knobel, and Young News Penetration Tester, and for its wet tensile breaking strength: the test data on this paper as listed under paper No. 8 in Table 1 show that the paper is highly resistant to water-base inks and has an unusually high wet tensile strength.

The above-described procedure was repeated with ten other paper preparations, two of which, namely, papers No. 1 and 2 in Table 1 contained no size or copolymer; three additional papers, namely, papers 3, 4 and 5 to which were added 3% rosin size and no copolymer and the other papers, namely 6 to 11 to which were added 3% rosin size and 5% copolymer having the percentage styrene therein 25, 50, 75, 80, 90 and 99 respectively. The results of sizing tests on the papers thus prepared are set forth in Table 1 and are presented in Figures 1 and 2 wherein there is shown the highly specific relation between the sizing characteristics and the composition of the added copolymer. With reference to the sizing data, it is particularly noted that the sizing characteristics are greatest where the percentage of styrene in the added copolymer lies between about 65 and 85%, preferably between

about 70 and about 85%, reaching an optimum value where the styrene content of the copolymer is about 75 to 80%.

Table 1

Paper Designation	Styrene in Copolymer, percent	Basis Wt. 24 x 36—500	N. I. Sec. 80% Grid	Dry Tensile, lb./in.	Wet Tensile, 24 Hr. Immersion, lb./in.
1	No size	38	1	17.2	1.3
2	do	39	1	19.3	1.3
3	No copolymer	38	97	16.5	2.7
4	do	38	85	17.8	2.7
5	do	39	60	18.7	2.8
6	25	37	90	17.8	3.6
7	50	37	298	19.1	4.8
8	75	38	449	21.8	6.1
9	80	38	456	21.8	5.4
10	90	38	137	21.2	3.9
11	99	38	25	14.3	2.4

EXAMPLE II

The procedure of Example I was repeated, adding to the paper furnish 3% rosin size and a varying percentage of a butadiene-styrene copolymer having the ratio of 25% butadiene and 75% styrene. The copolymer was added in the amount of 2.5, 5, 7.5, 10, and 15% based on the dry pulp, and the sizing characteristics of the corresponding papers are indicated in Table 2 as papers 14 to 18 in comparison with sized papers containing no copolymer. Comparison between the copolymer-containing papers and a conventional rosin sized paper is presented with relation to papers No. 12 and 13 which contain no copolymer, and a comparison with the papers prepared according to Example I is presented with relation to paper No. 15 which corresponds to paper No. 8 in Table 1. An effective degree of sizing was obtained in each case by the addition of small amounts of the copolymer.

The proportions of butadiene and styrene in the copolymer according to this invention are about 25% butadiene and about 75% styrene. As can be clearly seen from Figures 1 and 2, highly satisfactory results are obtained using for the sizing ingredient a copolymer containing between about 65 and about 85% styrene with a preferred range between about 70 and about 85% styrene. Within these limits and critically and specifically within these limits, there is obtained a sized paper having wet characteristics far superior to conventional sized papers, the optimum or peak of the sizing properties being reached with a copolymer containing about 75 to about 85% styrene. It is interesting to note that a sized paper containing a conventional amount of a rosin size and containing a copolymer whose proportions are substantially removed from the preferred range, namely, less than about 25% styrene or more than about 90% styrene shows little if any improvement over an ordinary rosin sized paper and, in fact, may even have impaired sizing properties. Thus, for example, paper No. 11 in Table 1 and in Figures 1 and 2 which is sized with a rosin size and a cooplymer containing 99% styrene has a poorer wet strength than the comparable paper containing only a rosin size and no added copolymer.

It has further been found that the presence of relatively small quantities of the copolymer in a sized paper leads to a measurable improvement in the wet characteristics of the paper. When the amount of the copolymer is about 3 to about 8% based on the weight of the pulp the wet characteristics of the paper are substantially at a maximum, while papers containing amounts of the copolymer under about 3%, for example, about 1 to about 3% are highly satisfactory in that they efficiently size paper with the use of amounts of copolymer in the range ordinarily used in sizing paper with conventional sizing agents. Thus, a range of about 1 to about 8% of added copolymer yields a satisfactory sized paper. The data contained in Example II and Table 2 show that a paper containing 7.5% of a copolymer whose proportions are 25% butadiene and 75% styrene has a resistance to feather ink of almost 600 seconds and a wet tensile breaking strength of slightly over 7 pounds per inch as compared with a simple rosin sized paper whose test values under comparable conditions are under 100 seconds and under 3 pounds per inch, respectively.

Table 2

Paper Designation	Percent Copolymer Added	Basis Wt. 24 x 36—500	N. I. Sec. 80% Grid	Dry Tensile, lb./in.	Wet Tensile, 24 Hr. Immersion, lb./in.
12		38	97	16.5	2.7
13		39	60	18.7	2.8
14	2.5	38	400	22.4	5.7
15	5	38	449	21.8	6.1
16	7.5	37	579	23.0	7.1
17	10	38	360	23.1	6.1
18	15	37	381	22.4	5.8

An amount of copolymer exceeding about 8% is considered not to fall within the scope of this invention. A paper containing the copolymer in excess of this amount does not derive substantially improved sizing properties, but does, on the other hand, lose many of its paper-like characteristics such as writability, etc. to gain, increasingly, many of the properties of an artificial leather, a rubberized sheet material or the like.

The copolymer latex may be prepared according to various procedures as will be apparent to those skilled in the art. For example, latices prepared with fatty acid emulsifiers as well as latices prepared with rosin soap and modified rosin soap emulsifiers have all been found to be satisfactory for addition to the pulp. In general, however, it has been found that at least partial conversion or copolymerization is preferred; thus, a copolymer of the preferred butadiene-styrene proportions is preferably, although not necessarily, largely converted, for example about 90–100% converted.

The use of a rosin size in conjunction with the new copolymer sizing ingredient has been disclosed in the examples as a preferred embodiment of the invention. Thus, a paper containing a rosin size in conjunction with a copolymer has a somewhat greater wet strength than a paper containing no rosin size; the presence of the rosin size in the product is not essential to the development of a certain degree of wet strength, but the presence together of the rosin size and copolymer yields a greatly improved wet strength and also a resistance to feather ink which is far above the total of the separate feather ink resistance. For incorporation into the paper pulp together with the copolymer, there may be used any of the various types of rosin size, such as dry size or a rosin dispersion as saponified rosin, a high free rosin or, if desired, as partially saponified rosin. The preparation and use of rosin sizes of these types are

conventional and need not be further described for a clear understanding of the invention.

In the examples, there has been shown the addition of the copolymer latex to the pulp in the beater engine. It will be understood, of course, that the copolymer, and optionally the rosin size, may be added at various points prior to web formation, as is customary in the use of paper additives in usual paper manufacture.

The paper prepared according to this invention may also contain other conventional paper additives such as, for example, an alkaline filler, a neutral filler, coloring materials, mildew-proofing or five-proofing agents, other wet and dry strengthening agents, or the like, and in all of these various cases a significant improvement in wet properties is attained. The copolymer latex has been found to possess a good degree of compatibility with conventional paper additives, and may be used in the ordinary paper processing without substantial alteration of the usual procedures, being deposited on the fibers by usual size precipitants such as alum or the like, and otherwise favorably adapted for use in paper manufacture.

What we claim and desire to protect by Letters Patent is:

1. In a process for sizing paper, the step comprising adding to a fibrous material in aqueous medium a latex whose dispersed phase comprises a copolymer of butadiene and styrene in such an amount that there is present from about 1% to about 8% of the copolymer based on the fibrous material, said copolymer being formed from between about 65 and about 85% styrene and the remainder butadiene.

2. In a process for sizing paper, the steps comprising adding to a fibrous material in aqueous medium a latex whose dispersed phase comprises a copolymer of butadiene and styrene in such an amount that there is present from about 1% to about 8% of the copolymer based on the fibrous material, said copolymer being formed from between about 65 and about 85% styrene and the remainder butadiene, and subsequently adding alum to precipitate the copolymer on the fibers.

3. In a process for sizing paper, the steps comprising adding rosin size and a latex to a fibrous material in aqueous medium, said latex having as its dispersed phase a copolymer of butadiene and styrene, the copolymer being formed from about 65 to about 85% styrene and the remainder butadiene, said latex being added in such an amount that there is present from about 1% to about 8% based on the fibrous material, and subsequently adding alum to precipitate the rosin size and the copolymer on the fibers.

4. In a process for sizing paper, the steps comprising adding rosin size and a latex to a fibrous material in aqueous medium, said latex having as its dispersed phase a copolymer of butadiene and styrene, the copolymer being formed from about 75 to about 80% styrene and the remainder butadiene, said latex being added in such an amount that there is present from about 1% to about 8% based on the fibrous material, and subsequently adding alum to precipitate the rosin size and the copolymer on the fibers.

5. In a process for sizing paper, the steps comprising adding up to about 3% rosin size and about 1 to about 8% of a copolymer latex to a fibrous material in aqueous medium, the precentages being based on the weight of solids in the respective compositions with respect to the weight of fibrous material in the furnish, said copolymer latex having as its dispersed phase a copolymer formed from about 75 to about 80% styrene and the remainder butadiene, and subsequently adding alum to precipitate the rosin size and the copolymer on the fibers.

6. In a process for sizing paper, the steps comprising adding up to about 3% rosin size and about 3% of a copolymer latex to a fibrous material in aqueous medium, the percentages being based on the weight of solids in the respective compositions with respect to the weight of fibrous material in the furnish, said copolymer latex having as its dispersed phase a copolymer formed from about 75 to about 80% styrene and the remainder butadiene, and subsequently adding alum to precipitate the rosin size and the copolymer on the fibers.

7. A paper, characterized by high sizing and wet strength, comprising cellulosic fibrous material and a high styrene copolymer of butadiene and styrene distributed substantially uniformly throughout the fibrous material, said copolymer being formed from between about 65% and about 85% styrene and the remainder butadiene, said copolymer being present in the amount of from about 1% to about 8% based on the cellulosic fibrous material.

8. A paper, characterized by high sizing and wet strength, comprising cellulosic fibrous material and a high styrene copolymer of butadiene and styrene distributed substantially uniformly throughout the fibrous material, said copolymer being formed from between about 75% and about 80% styrene and the remainer butadiene, said copolymer being present in the amount of from about 1% to about 8% based on the cellulosic fibrous material.

9. A paper, characterized by high sizing and wet strength, comprising cellulosic fibrous material, rosin size, and a high styrene copolymer of butadiene and styrene distributed substantially uniformly throughout the fibrous material, said copolymer being formed from between about 75% and 80% styrene and the remainder butadiene, said copolymer being present in the amount of from about 1% to about 8% based on the cellulosic fibrous material.

10. A paper, characterized by high sizing and wet strength, comprising cellulosic fibrous material, rosin size, and a high styrene copolymer of butadiene and styrene in the amount of about 1% to about 8% distributed substantially uniformly throughout the fibrous material, said copolymer being formed from between about 65% and about 85% styrene and the remainder butadiene.

11. A paper, characterized by high sizing and wet strength, comprising cellulosic fibrous material, rosin size, and a high styrene copolymer of butadiene and styrene in the amount of about 3% distributed substantially uniformly throughout the fibrous material, said copolymer being formed from between about 75% and 80% styrene and the remainder butadiene.

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