

1

3,556,934

METHOD OF FORMING A PAPER CONTAINING GASEOUS FILLED SPHERES OF THERMOPLASTIC RESINS

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5 Claims

ABSTRACT OF THE DISCLOSURE

Papers containing expanded thermoplastic microspheres are prepared by incorporating an expandable thermoplastic microsphere within the pulp slurry and the paper dried at about 90° C., causing the microspheres to foam. This phenomenon appears to be peculiar to microspheres having a vinylidene chloride-acrylonitrile copolymer shell.

This invention relates to an improved method for the preparation of paper and an improved paper, and more particularly relates to an improved paper containing small hollow plastic particles and to a method for the preparation thereof.

Various benefits and advantages are obtained by incorporating within paper hollow synthetic resinous particles. The desirability and many of the advantages are set forth in U.S. Pat. 3,293,114 wherein expanded hollow particles are added to a paper making pulp of paper making fibers and a paper sheet or board formed therefrom. Such a procedure provides low density improved opacity, brightness, high stiffness, low thermal conductivity; tear strength is maintained while basis weight is lowered. Alternately, the basis weight may be held constant and the caliper increased by the addition of spheres. When adding hollow gas-filled plastic spheres to paper, there tends to be a nonuniformity of distribution of such hollow particles throughout the paper; that is, the hollow spheres tend to deposit adjacent the top or felt side thereof and provide a sheet having something less than desired symmetry.

It would be desirable if there were available an improved method for the preparation of paper containing expanded hollow synthetic resinous microspheres.

It would also be desirable if there were available a method for the preparation of paper containing hollow microspheres wherein conventional drying techniques could be employed.

These benefits and other advantages in accordance with the present invention are achieved in a method for making paper which comprises depositing paper making fibers upon a screen from an aqueous suspension and subsequently drying and compressing the deposited fibers to form a generally continuous sheet, the improvement which comprises incorporating within the aqueous suspension from which the fibers are deposited a plurality of synthetic resinous particles, each particle having a generally spherical liquid-containing space therein, the synthetic resinous particles comprising a polymer of from about 65 to 90 weight percent vinylidene chloride and from about 35 to 10 weight percent acrylonitrile, and beneficially a polymer of 65 to 75 weight percent vinylidene chloride and 25 to 35 weight percent acrylonitrile, the liquid being a volatile fluid foaming agent which is a non-solvent for the polymer, such a blowing agent advantageously is isobutane present from about 10 to 25 parts by weight, the particles being expandable to hollow gas-filled monocellular spheres by heating to a tempera-

2

ture within the range of from about 85° C. to 100° C., retaining on the resultant fibrous sheet at least a portion of the synthetic resinous thermoplastic particles, the resinous particles being present in a proportion of from about 0.05 to about 60 percent by weight of the weight of the paper making fibers and each of the particles having a diameter of from about 0.5 to about 50 microns, subsequently drying the paper at a temperature sufficient to cause the synthetic resinous particles to expand to form a plurality of gas-filled particles within the paper sheet.

Also contemplated within the scope of the present invention is a paper comprising paper making fibers having incorporated therein a plurality of synthetic resinous thermoplastic particles, each of the synthetic resinous thermoplastic particles having a generally spherical shape and defining a generally spherical liquid-containing space therein, the synthetic resinous particles being a polymer of from about 65 to 90 weight percent vinylidene chloride and from about 35 to 10 weight percent acrylonitrile, and beneficially a polymer of 65 to 75 weight percent vinylidene chloride and 25 to 35 weight percent acrylonitrile, the liquid being a volatile fluid foaming agent, such a blowing agent advantageously is isobutane present from about 10 to 25 parts by weight, and the synthetic resinous particles being expandable to a hollow gas-filled body at a temperature within the range of from about 85° C. to about 100° C., the particles being present in a proportion of from about 0.05 to about 60 percent by weight of the weight of the paper making fibers and each of the resinous particles having a diameter of from about 0.5 to about 50 microns.

The preparation of expandable synthetic resinous particles suitable for the practice of the invention is well known to the art and is described in Belgian Pat. 641,711 which describes in great detail the preparation of many varieties of expandable microspheres and suspension systems therewith. An example of the preparation of expandable microspheres is set forth in U.S. Pat. 3,293,114.

Generally, it is critical and essential to the practice of the present invention that the polymer composition of the shell of the expandable microspheres contain from 65 to 90 weight percent vinylidene chloride and from 35 to 10 weight percent acrylonitrile. Compositions outside of the hereinbefore mentioned scope are not suitable for the practice of the present invention and either do not expand at normal paper drying temperatures, expand slightly and rupture or otherwise given unsatisfactory performance.

A wide variety of expanding agents and volatile fluid foaming agents may be employed in the practice of the present invention. Many of such blowing agents are set forth in Belgian Patent 641,711. Particularly advantageous and beneficial are low molecular weight hydrocarbons such as the pentanes, butanes and mixtures thereof. Halohydrocarbons may also be employed either alone or in admixture with other volatile fluid foaming agents. However, the hydrocarbons are found generally eminently satisfactory. Generally, the plastic particles are utilized in a paper in a concentration of from about 0.05 to 60 percent by weight, depending on the desired characteristics of the resultant paper. If papers of minimum bulk density are desired, a maximum quantity of particles are incorporated therein. If maximum physical strength is desired, generally lower quantities are employed. Beneficially, the incorporation of from about 0.5 to 10 percent by weight of such particles is oftentimes sufficient to reduce the density of the paper sufficiently to provide a sufficient decrease in the cost of milling of the finished printed article, such as a magazine or book, while required physical characteristics of the paper are maintained.

The particles or microspheres employed in the present invention are readily incorporated in either long fiber or short fiber pulps, and also in groundwood pulps and rag pulps. The incorporation of the plastic particles provides on an equal basis weight comparison a significant increase in the stiffness of the paper as well as a significant increase in the caliper. Thus, it makes possible the preparation of papers having greater stiffness, lighter weight, and having increased caliper, all desirable features for many books, magazines and the like.

Employing the method of the present invention, papers are readily dried at a temperature sufficient to cause expansion of the thermoplastic particles concurrently with drying to a moisture content of about 5 weight percent water remaining in the paper. Thus, conventional drying procedures are readily employed without the need of adding moisture to the paper. In the practice of the present invention, it is undesirable to heat the paper during the drying procedure to temperatures substantially in excess of about 100° C. to thereby reduce the moisture content below 5 percent.

Papers prepared in accordance with the method of the present invention are readily smoothed or polished to pro-

box after obvious movement of the slurry has ceased. Handsheets are formed on an 80 mesh screen and subsequently dried by the following procedure. The handsheet and screen are removed from the deckle box and the sheet transferred and pressed against a sheet of blotting paper. The sheet is then placed on a polished chrome plated sheet under a pressure of 60 pounds per square inch for a sufficient length of time to remove by capillary action the majority of water available thereto. The sheet of blotting paper is removed and replaced with one half inch of felt. The felt paper-plated sheet sandwich is placed in a platen press wherein the platen has a temperature of 115° C. A thermocouple is inserted between the test sheet and the felt. The paper is dried for a period of about 4 minutes where the thermocouple indicates a temperature of 95° C. after 6 seconds; a temperature of 100° C. after about 90 seconds and a maximum temperature of 108° C. This procedure is employed with all samples in the following table with the exception of Samples 5 and 6. Sample 5 is removed after 10 seconds and air dried at 25° C. Sample 6 is removed after 90 seconds. Sample 5 is damp to the touch; Sample 6 appears to be dry. The results of this experiment are set forth in the following table.

TABLE I

Sample	0	1	2	3	4	5	6
Caliper.....	3.4	3.7	3.9	4.4	4.7	4.3	4.0
Microspheres added (percent).....	0	2.5	5.0	7.5	10.0	5.0	5.0
Time in press (mins.).....	4	4	4	4	4	10	10
Wt. in grams.....	4,1500	4,3080	4,3425	4,4055	4,5950	4,4590	4,3700
Basis wt. g./m. ²	64.97	67.45	67.99	68.98	71.94	69.81	68.42
Microspheres added (percent).....	0	2.5	5	7.5	10	5	5
Time in press (mins.).....	4	4	4	4	4	10	10
Tensile test to break.....	12.47	12.24	11.67	11.75	12.05	10.37	12.19
Tensile breaking length (meter).....	6,855	6,481	6,130	6,083	5,982	5,305	6,363
Tensile breaking ($\times 10^3$) strength p.s.i.....	7.34	6.61	5.98	5.34	5.12	4.82	6.10

¹ Seconds.

vide uniform thickness by passage between spaced apart forming surfaces such as rolls having temperatures which do not undesirably dehydrate the paper due to the apparent characteristics of the vinylidene chloride-acrylonitrile polymer.

The invention is further illustrated but not limited by

EXPERIMENT 2

The procedure of Experiment 1 is repeated with the exception that 10 weight percent unfoamed microspheres are employed and drying conditions varied in the manner as indicated in Table II.

TABLE II

Sample	1	2	3	4	5	6	7	8
Unfoamed microspheres (10%).....	Control	Control	(1)	(2)	Control	(1)	(2)	(3)
Drying conditions, min. at 140° C.....	All dried	1.5 min. with top platen at 115° C.			34	3	(4)	6
Caliper (mils).....	3.6	3.5	4.5	4.7	3.5	4.9	5.0	5.3
Wt. gms. 9 x 11" sheet.....	4,342	4,354	4,508	4,442	4,294	4,532	4,348	4,411
Basis wt. g./m. ²	67.98	68.17	70.58	69.55	67.23	70.96	68.07	69.03
Lbs. to break.....	11.37	12.54	11.03	10.22	11.91	10.98	9.46	9.07
Tensile breaking length (meters).....	6,025	6,570	5,582	5,248	6,327	5,526	4,964	4,691
Tensile, p.s.i.....	6,316	7,166	4,902	4,349	6,806	4,482	3,784	3,423

¹ Microsphere, 75 percent vinylidene chloride, 25 percent acrylonitrile, 25 percent neopentane.

² Microsphere, 75 percent vinylidene chloride, 25 percent acrylonitrile, 27 percent isobutane.

³ Using a thermocouple with top platen at 140° C., it was determined that sheet surface temperature was: 98° C. in 8 sec.; 100° C. in 12 sec.; 113° C. in 21 sec.; 120° C. in 34 sec.; 125° C. in 1 min.; 24 sec.; 130° C. in 2 min.; 50 sec.; 132° C. in 4 min.

⁴ Top platen only in all cases.

the following examples employing the tests and experimental techniques generally as set forth in U.S. Patent 3,293,114.

EXPERIMENT 1

A plurality of handsheets are prepared from a bleached hardwood soda pulp beaten to 340 milliliters Canadian Standard Freeness. The quantity of microspheres indicated in Table I is added based on the weight of the wood pulp fiber. Two weight percent alum is added to the slurry. The microspheres have a diameter of about 3 microns; the polymer shell is a copolymer of 75 weight percent vinylidene chloride and 25 weight percent acrylonitrile containing about 35 weight percent neopentane based on the total weight of the polymer. The resultant pulp slurry containing the microspheres and alum is transferred to a deckle box and the water drained from the deckle

EXPERIMENT 3

The procedure of Experiment 1 is employed with the following exceptions: one half of one percent rosin is added to the slurry and 10 weight percent microspheres of a copolymer of 70 weight percent vinylidene chloride and 30 weight percent acrylonitrile containing 33 weight percent n-butane is employed in place, with the exception of Sample 1 which is a control, and to which no microspheres are added. Samples 1, 2 and 3 are dried for 4 minutes with a top platen temperature of 115° C. Sheets 4 and 5 are dried for 2 minutes with a top platen temperature of 115° C. Sheet 3, subsequent to drying, is placed between polished chromium plated sheets which are spaced apart by means of 4 mil thick shims and heated at 115° C. for 2 minutes. No change in caliper is observed. The procedure is repeated with both platens

5

heated to 130° C. and the microsphere-containing sheet exposed for a period of 30 seconds. The surfaces of the resultant sheets are very smooth. This procedure is repeated with sheet 4 to provide a smooth surfaced sheet. The results of this experiment are set forth in the following table.

TABLE III

Sample	1	2	3	4	5
Microspheres added (percent)---	None	10	10	10	10
Initial drying, mins. at 115° C.---	4	4	4	2	2
Initial caliper (mils)-----	3.4	4.5	4.6	4.6	4.6
Caliper after post heat with shims-----			4.1	4.2	
Wt. gms. 9 x 11" sheet-----	4.1860	4.3880	4.4523	4.4794	4.5335
Lbs. to break-----	11.60	10.44	10.43	11.35	11.33
Basis, wt. g./in. ² -----	65.54	68.70	69.71	70.13	70.98
Tensile breaking length (meters)-----	6,321	5,428	5,344	5,780	5,701
Tensile, p.s.i. (X10 ³)-----	6.63	4.54	5.09	5.40	4.93

Smoothing or expansion of the sheets beneficially is accomplished at lower temperatures to prevent collapse of the microsphere and provide optimum caliper and surface smoothness.

In a manner similar to the foregoing illustrations, beneficial and advantageous papers are obtained employing microspheres of the following composition: 65 weight percent vinylidene chloride, 35 weight percent acrylonitrile; polymer shells containing encapsulated therein 38 weight percent isobutane, 90 weight percent vinylidene chloride, 10 weight percent acrylonitrile, 34 weight percent n-butane, 84 weight percent vinylidene chloride, 16 weight percent acrylonitrile, polymer shell containing 27 weight percent dichlorofluoromethane.

Similar beneficial results are obtained when paper making fibers other than wood pulp or cellulosic fibers are employed, such as asbestos, synthetic resinous fibers such as nylon, cellulose acetate, polypropylene and the like.

As is apparent from the foregoing specification, the present invention is susceptible of being embodied with various alterations and modifications which may differ particularly from those that have been described in the preceding specification and description. For this reason, it is to be fully understood that all of the foregoing is intended to be merely illustrative and is not to be construed or interpreted as being restrictive or otherwise limiting of the present invention, excepting as it is set forth and defined in the hereto-appended claims.

What I claim is:

1. In a method for making paper which comprises depositing paper-making fibers upon a screen from an aqueous suspension and subsequently drying and compressing the deposited fibers to form a generally continuous paper sheet, the improvement which comprises

6

incorporating within the aqueous suspension from which the fibers are deposited a plurality of synthetic resinous particles, each particle having a generally spherical liquid-containing space therein, the synthetic resinous particles comprising a copolymer of from about 65 to 90 weight percent vinylidene chloride and from about 35 to 10 weight percent acrylonitrile, the liquid being a volatile fluid foaming agent which is a non-solvent for the copolymer, the particles being expandable to hollow gas-filled monocellular spheres by heating to a temperature within the range of from about 85° C. to 100° C.,

retaining in the resultant fibrous sheet at least a portion of the synthetic resinous thermoplastic particles, the resinous particles being present in a proportion of from about 0.05 to about 60 percent by weight of the weight of the paper-making fibers and each of the particles having a diameter of from about 0.5 to about 50 microns, subsequently

drying the paper sheet at a temperature sufficient to cause the synthetic resinous particles to expand to form a plurality of gas-filled particles generally uniformly within the paper sheet.

2. The method of claim 1 wherein the paper sheet is subsequently smoothed by confining between heated surfaces.

3. The method of claim 1 wherein the copolymer is a copolymer of from about 65 to 70 weight percent vinylidene chloride and from about 25 to 35 weight percent acrylonitrile.

4. The method of claim 3 wherein the particles contain from about 10 to 25 weight percent isobutane, based on the weight of the copolymer.

5. The method of claim 4 wherein the paper making fibers are wood fibers.

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