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ASBESTOS SATURATING PAPER INCLUDING CELLULAR HOLLOW GAS - CONTAINING RESIN SPHERES

Marsden C. Hutchins, Bound Brook, N.J., assignor to Johns-Manville Corporation, New York, N.Y., a corporation of New York

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10 Claims. (Cl. 162—155)

This invention relates to a novel paper product, and more particularly to means of producing effective paper sheets containing major proportions of bulky filler material, and the filled asbestos paper thereof.

It is a primary object of this invention to provide means of producing asbestos sheets comprising paper, millboard, and the like which have the capacity to take up during web formation and retain appreciably high proportions of very light weight, bulky fillers of generally spherical configuration.

It is a more specific object of this invention to provide asbestos paper compositions of a fiber-binder system which contain major amounts of light weight spherical fillers and at the same time maintain good strength properties both wet and dry, a high degree of porosity and in turn good resin absorption capacity whereby the paper may be handled in a normal manner in forming, pressing, drying, and winding operations on a paper machine and in saturation, drying, and curing in a typical submersion and tower resin impregnating procedure.

It is a further object of this invention to provide high bulk or porous asbestos paper compositions which possess the property of entraining and retaining high ratios of up to about 60% by weight of very light weight, small particle sized, substantially spherical bodies of filler, and in addition thereto also exhibiting the necessary porosity and the like characteristics to take up or absorb appreciable quantities of resin saturant so as to comprise an effectivve high resin content body or lamina for resin molding or lamination.

It is well established in the paper art that asbestos fibers are not comparable in a number of significant aspects to typical organic fibrous material such as cellulose. This is particularly true in the characteristic property of cellulose of its natural affinity for water whereby the natural hydration, normally facilitated by vigorous admixing as in a conventional paper pulp beater to increase penetration, effects the development of minute fibrillae extending from the principal fiber particle and the formation of a gel-like mass on the fiber surfaces. The interlocking or intermeshing of these hydration produced fibrillae and the gelatinized condition of the surface of the fiber bodies upon drying cements and provide the strong self-bonding characteristic of cellulose fibers which is exhibited in a number of paper products including those with considerable proportions of fillers such as bodying clays and pigments. Asbestos fiber on the other hand, lacks this unique characteristic property of cellulosic fibers and extensive beating as typically employed in the development of strength in organic fibers, is ineffective and normally merely results in the shortening of the asbestos fibers with a consequential actual loss of strength in the resulting web or paper. Thus, typical asbestos fibers being inherently different from cellulose fibers in lacking effective bonding capacity normally require appreciable quantities of an extraneous binder to provide integrity and sufficient strength in a paper composed thereof, particularly when an appreciable portion of filler is employed in the product. The inclusion of extensive amounts of binder, however, results in a heavy, dense product lacking porosity which in some applications, such as a saturating paper, constitute a decided and limiting disadvantage.

This invention comprises means of producing an asbestos fiber based paper which when augmented by only a relatively minor proportion of resin size or binder can take up and retain major amounts of bulky, generally spherical fillers while maintaining good strength both wet and dry, and high bulk or porosity and in turn good capacity for saturants. These unique and apparently inconsistent features are achieved through the cooperation or over-all effects of specially selected components comprising the base paper which, through composite action of the components, possess the ability to entrain very light weight spherical bodies in weight ratios greater, or in volume ratios considerably greater, than the base material comprising fiber and size. Moreover, this heavy filling of the paper does not eliminate its useful or effective strength and adsorption characteristics.

Specifically, the method or means of this invention generally comprises the formation of a base paper or sheet product with a combination of a specific classification of asbestos fibers and relatively small, considering the nature of the paper and degree of filling, amount of size. The particular asbestos which can be utilized in amounts ranging from approximately 20 to 75 parts by weight of the sheet, or more commonly approximately 32 to 54 parts by weight, comprises fibers which are identified and classified in the art as "harsh" and consist of the chrysotile, crocidolite, and amosite asbestos. These fibers should be well opened to the point of substantially eliminating any fiber bundles, bodies, or pencils of about 1/32 inch or more in diameter. This requisite can be determined by the Schopper-Riegler freeness test, and to meet the standard should have a freeness value of at least approximately 180 to 560, and preferably between about 350 to 560. Also, these fibers should be refined to the point of providing a size classification or distribution, as determined by a standard Bauer-McNett system of fiber classification, of at least 70% by weight thereof retained on 200 mesh standard screen sieve, with at least about 50% by weight of the fiber retained on the said 200 mesh standard screen sieve passing 28 mesh standard screen sieve but retained on 100 mesh standard screen sieve.

The size of the paper products of this invention comprises synthetic resins, viz., acrylic resin and urea formaldehyde resin, and preferably a combination of both. Such resins may be conveniently obtained and employed in liquid, aqueous emulsion or powdered form. However, other size materials, as for example a starch based binder such as corn gum, or a latex, can be substituted in part for resins, as will be demonstrated in the ensuing examples. The size is included in such relatively minor proportions of normally approximately 5 to 7 parts by weight, or possibly from about 4 up to approximately 10 parts by weight, depending of course upon the particular composition and the ultimate requirements of the paper product. Greater amounts of size, although possibly imparting greater strength, decidedly diminish the bulk and porosity and in turn the saturating capacity of the sheet or web and as such are unsuitable.

Additionally, small quantities of paper maker's alum—aluminum sulfate—of up to about 3 parts by weight of the stock solids are typically desirable in the stock slurry to facilitate formation of the web or sheet and may be required for effective binder retention and cure with a size such as urea formaldehyde.

Further, other typical paper components such as pigments and the like to impart some specific property to fulfill the needs of a particular end use or application may be included, and in particular up to about 30 parts by weight of non-asbestos fibers such as synthetic fibers or materials as for example nylon (Du Pont's polyamide resins) fibrous materials, can be included in the paper of this invention.

The specific filler materials of this invention comprise light weight cellular or hollow spheres or rounded bodies of small diameters, i.e., approximately 1 to 500 microns and typically about 25 to 250 microns, of organic or inorganic compositions, preferably of a thermosetting resin composition. Such materials are commercially available in a number of different compositions including synthetic resins, clay or ceramics, glass, silica, and the like, and are further described in the patent literature, for example United States Letters Patent No. 2,101,635, No. 2,261,639, No. 2,676,892, No. 2,797,201, No. 3,030,215, etc. Preferred resinous spheres comprise nitrogen filled phenol formaldehyde spheres sold under the trade designation Microballoons, a product of Union Carbide Corp., and urea fromaldehyde nitrogen filled spheres identified as Colfoam Microballoons, manufactured by Colton Chemical Co., Division of Air Reduction Co.

The means of this invention, i.e., the formation of a single or multi-ply sheet or felt product comprising a paper or millboard of the specific materials given hereinbefore, can conveniently be effected or a product thereof formed on an ordinary paper machine or forming equipment for the production of water-laid felts such as a Fourdrinier, and particularly with a continuous, multicylinder paper manufacturing machine or process.

The following examples comprise several specific illustrations of preferred and typical means and products of this invention, demonstrating the pronounced advantages thereof. It is to be understood, however, that the specific materials and/or proportions thereof are primarily exemplary and are not to be construed as limiting this invention to any specific component or its amount, composition and/or data recited hereinafter.

EXAMPLE I

Laboratory hand sheets produced by preparing an aqueous slurry of the constituents in a beater, vacuum filter molding sheets from the slurry, then pressing and drying the same, were formed comprising the following paper compositions. Sample A comprised a standard or control paper product which did not contain any spherical fillers and is given for comparison with Sample B a like formulation containing an appreciable amount of hollow resinous sphere fillers. The formulations and their respective properties were as follows:

TABLE I

	Standard Sample A	Sample B
Furnish, Percent:		
Asbestos fiber, 3W grade	97	46
Phenolic resin spheres (Microballoons PL-3981) [a]		46
Acrylic resin (Rhoplex WC-9) [b]	3	2
Urea formaldehyde (Parez 615) [c]		5
Alum		1
Physical Properties:		
Basis weight, lb./100 ft.^{2}	2.8	2.9
Caliper, mils	13	27
Bulk, (Thickness in in.×100)÷(Weight lb./100 ft.^{2})	0.47	0.92
Mullen, p.s.i	9	9
Tensile, lb./in	8.2	6.2
Stretch, percent	1.2	2.3
Wet (water) tensile, lb./in	3.5	2.3
Wet (methylethyl ketone) tensile, lb./in	2.6	2.8
Tear, grams	51	41
Gurley stiffness, grams	0.93	1.3
Gurley densometer, sec./100 cc	53	33
Kerosene value, percent	123	151
Ash, percent	84.3	44.4
Asbestos, percent	97.5	51.5

[a] Union Carbide Corp.
[b] Rohm & Haas Co.
[c] American Cyanamid Co.

EXAMPLE II

Papers of similar compositions to those of Example I were prepared on a continuous four cylinder mold pilot plant paper machine simulating a commercial production paper manufacturing process on a reduced scale. The

paper formulations and their physical properties were as follows:

TABLE II

	Standard Sample A	Sample B
Furnish, Percent:		
Abestos fiber:		
3W grade	94	23
4K grade		23
Phenolic resin spheres (Microballoons BJO-0930)		46
Urea formaldehyde resin (Parez 615)	5	5
Acrylic resin (Rhoplex WC-9)		2
Alum	1	1
Physical Properties:		
Basis weight, lb./100 ft.^{2}	2.3	2.0
Caliper, mils	10	13
Bulk, percent	0.43	0.65
Mullen, p.s.i	4	4
Tensile, lb./in. MD	5.8	4.3
Tensile, lb./in. CD	4.2	3.0
Stretch, percent MD	0.5	0.8
Stretch, percent CD	0.4	1.2
Wet (water) tensile, lb./in. MD	1.2	1.2
Wet (methylethyl ketone) tensiles, lb./in. MD	3.2	1.3
Tear, grams MD	29	21
Tear, grams CD	35	24
Gurley stiffness, grams MD	0.3	0.3
Gurley stiffness, grams CD	0.4	0.3
Gurley densometer, sec./100 cc	56	24
Kerosene value, percent	106	145
Ash, percent	84.0	47.5
Asbestos, percent	97.2	55.0

(MD denotes machine direction or parallel to the web formation, and CD denotes cross machine direction or perpendicular to web formation.

EXAMPLE III

A dilute aqueous slurry of a stock comprising the following formulation:

Furnish	Percent	Pounds per Batch
Asbestos fiber, 3W grade	42	800
Phenolic resin spheres (Microballoons VJO-0930)	50	953
Urea formaldehyde resin (Parez 615)	5	95.3
Acrylic resin (Phoplex WC-9)	2	38.1
Alum	1	19.0

was utilized in the formation of a paper on a multicylinder commercial production paper manufacturing machine as follows. The fiber was beaten until free of large clots and pencils whereupon the resin spheres were blended with the fiber in a hydrobeater, the resin sizing subsequently added in the chest and the stock formed into a continuous web or sheet of paper. Upon evaluation the samples of the thus produced paper gave the following typical physical properties:

TABLE III

Physical properties	Sample A	Sample B
Basis weight, lb./100 ft.^{2}	2.1	2.0
Caliper, mils	20	29
Bulk, percent	1.0	0.99
Mullen, p.s.i	2.0	3.0
Tensile, lb./in. MD	2.6	3.4
Tensile, lb./in. CD	1.7	2.8
Wet (water) tensile, lb./in. MD	0.6	0.8
Wet (methylethyl ketone) tensile, lb./in. MD	1.0	1.6
Tear, grams MD	12	20
Tear, grams CD	16	32
Gurley densometer, sec./100 cc	11	18
Gurley stiffness, grams MD	0.4	0.9
Gurley stiffness, grams QD	0.3	0.9
Kerosene value, percent	139	148
Ash, percent	38.1	40.1
Asbestos, percent	45.0	47.3

EXAMPLE IV

Pilot plant scale runs on a four cylinder mold pilot plant forming machine were made preparing papers containing 30%, 40%, 50%, and 60% by weight of hollow

resin spheres. The composition and physical properties of these were as follows:

TABLE IV

	Resin Sphere Content			
	A 30%	B 40%	C 50%	D 60%
Furnish:				
Asbestos fiber:				
3W grade	31	26	21	16
4K grade	31	26	21	16
Phenolic resin spheres (Microballoons BJO-0930)	30	40	50	60
Urea formaldehyde resin (Parez 615)	5	5	5	5
Acrylic resin (Rhoplex GC-9)	2	2	2	2
Alum	1	1	1	1
Physical Properties:				
Basis weight, lb./100 ft.²	2.3	2.2	2.3	2.2
Caliper, mils	16	17	19	21
Bulk, percent	0.71	0.78	0.84	0.97
Mullen, p.s.i.	4	2	2	2
Tensile, lb./in. MD	5.5	2.9	3.2	1.8
Tensile, lb./in. CD	2.8	1.6	1.7	1.2
Stretch, percent MD	0.8	0.9	0.9	0.8
Stretch, percent CD	1.2	1.1	0.9	1.2
Wet (water) tensile, lb./in. MD	1.9	1.1	1.0	0.8
Wet (methylethyl ketone) tensile, lb./in. MD	2.9	1.5	1.6	1.1
Tear, grams MD	38	34	24	18
Tear, grams CD	44	44	28	26
Gurley stiffness, grams MD	0.68	0.44	0.53	0.48
Gurley stiffness, grams CD	0.43	0.40	0.33	0.32
Gurley densometer, sec./100 cc	20	11	12	5
Kerosene value, percent	135	153	176	202

EXAMPLE V

A large scale run on a multi-cylinder commercial paper making machine was carried out with a stock of the formulation:

Furnish	Percent	Pounds per Batch
Asbestos fiber, 4A grade	42	840
Phenolic resin sphers (Microballoons BJO-0930)	50	953
Urea formaldehyde resin, 35% solids (Parez 615)	5	272
Acrylic resin, 40% solids (Rhoplex WC-9)	2	95
Alum	1	19

The average and extremes of the physical properties of a number of samples of paper taken from this run were as follows:

TABLE V

Physical Properties	High	Low	Average
Basis weight, lb./100 ft.²	2.7	1.7	2.2
Caliper, mils	23	16	21
Bulk, percent	0.98	0.87	0.92
Mullen, p.s.i.	3	2	2.5
Tensile, lb./in. MD	3.8	1.9	2.7
Tensile, lb./in. CD	2.8	1.3	1.8
Stretch, percent MD	1.8	1.2	1.5
Stretch, percent CD	2.1	1.3	1.8
Tear, grams MD	23	11	16
Tear, grams CD	30	15	21
Gurley stiffness, grams MD	0.91	0.11	0.49
Gurley stiffness, grams CD	0.71	0.20	0.39
Gurley densometer, sec./100 cc	22	13	17
Wet (water) tensile, lb./in. MD	0.9	0.2	0.5
Wet (methylethyl ketone) tensile, lb./in. MD	1.8	0.8	1.3
Kerosene value, percent	170	135	150
Ash, percent	44.0	37.1	40.1
Asbestos, percent	52.0	43.9	47.4

EXAMPLE VI

A series of papers with each containing a different type of spherical filler material were prepared on a pilot plant multi-cylinder paper making machine and evaluated. The compositions and physical properties of these papers were as given:

TABLE VI

	Sample		
	A	B	C
Furnish:			
Asbestos fiber:			
3W grade	21	21	
4K grade	21	21	26
Silica spheres (Hastings Glob-O-Sil F)	50		
Alumina bubbles		50	
Phenolic resin spheres			40
Nylon polyamide resin floc ⅛" to ½"			13
Nylon polyamide resin Fibrid 201 [a]			13
Urea formaldehyde resin	5	5	
Acrylic resin	2	2	6
Starch (Stayco gum) [b]			1
Alum	1	1	1
Physical Properties:			
Basis weight, lb./100 ft.²	2.1	1.4	4.4
Caliper, mils	18	12	35
Bulk, percent	0.84	0.81	0.80
Mullen, p.s.i.	2	2	10
Tensile, lb./in. MD	3.7	3.5	7.4
Tensile, lb./in. CD	1.8	2.0	4.7
Stretch, percent MD	0.7	1.9	1.5
Stretch, percent CD	1.1	1.0	1.7
Wet (water) tensile, lb./in. MD	1.4	1.5	3.7
Wet (methylethyl ketone) tensile, lb./in. MD	1.9	1.8	2.8
Tear, grams MD	23	18	58
Tear, grams CD	25	29	76
Gurley stiffness, grams MD	0.4	0.2	3.0
Gurley stiffness, grams CD	1.2	0.1	1.5
Gurley densometer, sec./100 cc	16	25	6
Kerosene value, percent	141	146	151
Ash, percent	89.2	84.3	20.0

[a] E. I. du Pont de Nemours & Co.
[b] A. E. Staley Mfg. Co.

EXAMPLE VII

Additional papers embodying silica spheres and with slight formula modifications to enhance specific properties were also prepared on the pilot plant machine. These papers and their properties were:

TABLE VII

	Sample		
	A	B	C
Furnish:			
Asbestos fiber:			
4A grade	21	21	21
4K grade	21	21	21
Silica spheres (Hastings Glob-O-Sil Type F)	50	50	50
Acrylic resin (Rhoplex HA-16)			4
Acrylic resin (Rhoplex WC-9)	2	2	
Urea formaldehyde (Parez 615)	5	5	3
Alum	1	1	1
Physical Properties:			
Basis weight, lb./100 ft.²	2.1	2.3	4.0
Caliper, mils	18	16	22
Bulk, percent	0.84	0.68	0.56
Mullen, p.s.i.	2	2	5
Tensile, lb./in. MD	3.7	3.3	6.5
Tensile, lb./in. CD	1.8	2.0	3.8
Stretch, percent MD	0.7	0.8	1.0
Stretch, percent CD	1.1	1.7	2.2
Wet (water) tensile, lb./in. MD	1.4	1.5	2.9
Wet (methylethyl ketone) tensile, lb./in. MD	1.9	1.6	2.1
Hot wet tensile, p.s.i. MD		38	59
Tear, grams MD	23	21	39
Tear, grams CD	25	24	43
Gurley stiffness, grams MD	0.4	0.4	1.4
Gurley stiffness, grams CD	0.2	0.3	0.8
Gurley densometer, sec./100 cc	16	26	36
Kerosene value, percent	141	155	129
Ash, percent	89.2	87.1	81.6

Further examples illustrating variations in the paper formulations of this invention and techniques of preparing the same are given hereafter.

EXAMPLE VIII

A paper, formulated as follows:

	Percent	Pounds
Asbestos, 3W grade	42	800
Resinous spheres	50	953
Urea formaldehyde resin	5	95
Acrylic resin	2	38
Alum	1	19

was prepared by beating the asbestos for 35 minutes in 10,000 pounds of water, whereupon the resinous spheres were added and an additional 10,000 pounds of water added thereto. After the spheres were well mixed with the fiber, 272 pounds (95 pounds of solids) of urea formaldehyde wet strength resin, 95 pounds (38 pounds of solids) of acrylic resin, and 19 pounds of paper maker's alum were each added to the beater with 5 minutes of mixing between each addition. This stock was then dumped into a chest, further diluted with water and formed into a 0.020 inch thick web of a paper sheet on a multi-cylinder type paper machine.

EXAMPLE IX

Paper comprising:

	Percent	Pounds
Asbestos, 4A grade	63.2	6.0
Resinous spheres	30.6	2.9
Urea formaldehyde resin	2.6	0.25
Acrylic resin	2.6	0.25
Alum	1.0	0.1

was prepared in the laboratory with the 4K grade chrysotile asbestos dispersed in 150 pounds of water in the beater and beaten for 5 minutes whereupon the 2.9 pounds of resinous spheres, 8.2 pounds (0.25 pounds of solids) of urea formaldehyde wet strength resin, 0.71 pound (0.25 pound of solids) of acrylic resin emulsion, and 0.1 pound of alum were each added to the beater with 2 minute intervals between the additions. This stock was diluted in the chest and sheeted out to a 0.005 inch thick web or paper on a multi-cylinder paper machine.

EXAMPLE X

A high resin sphere content paper composed of:

	Percent	Pounds
Asbestos	36.5	4.0
Resin balloons	57.5	6.3
Urea formaldehyde resin	5.0	0.53
Alum	1.0	0.1

was prepared by beating 2 pounds of harsh, 3W grade chrysotile and 2 pounds of 4K grade crysotile asbestos in 150 pounds of water for 5 minutes, then adding 6.3 pounds of phenolic resin spheres, 1.5 pounds (0.53 pound of solids) of urea formaldehyde resin emulsion, and 0.1 pound of alum to the beater with 2 minute intervals between additions. This stock was transferred to a chest, diluted and formed into a 0.018 inch thick web or paper on a cylinder type paper machine.

The papers of the foregoing examples, in addition to entraining and retaining the significantly high ratios of the light weight, substantially spherical bodied fillers set forth, exhibited adequate dry and wet strength to permit ordinary handling in their formation and to run through resin saturating processes or systems comprising submersion in resin baths and tower drying and curing without extraordinary measures or precautions, and notwithstanding the substantial amounts of filler contained throughout these papers they retained high porosity and in turn capacity for resin saturants as is demonstrated by their good kerosene values. Moreover, they exhibit bulk characteristics of at least 0.40, bulk being measured as the ratio of caliper or thickness to weight, and typically of 0.50 or higher as is apparent from the papers of the examples.

It will be understood that the foregoing details are given for purposes of illustration and not restriction and that variations within the spirit of this invention are intended to be included within the scope of the appended claims.

I claim:

1. The method of producing good wet and dry strength, high bulk asbestos paper containing appreciable amounts of light weight cellular spheres having an average diameter of about 1 to 500 microns, said method comprising forming a dilute aqueous suspension consisting essentially of approximately 20 to 75 parts by weight of refined, harsh asbestos fiber having a Schopper-Riegler freeness value of about 180 to 560, approximately 4 to 10 parts by weight of size of at least one resin selected from the group consisting of acrylic resin and urea formaldehyde resin, and approximately 25 to 65% by weight of light weight cellular hollow gas-containing resin spheres having an average diameter of approximately 1 to 500 microns, then forming therefrom a water-laid sheet containing approximately 25 to 65% by weight of the sheet of the said cellular spheres.

2. The method of claim 1 wherein the asbestos fiber is sized at least 70% by weight retained on 200 mesh standard screen sieve, and at least about 50% by weight of said fibers retained on 200 mesh standard screen sieve pass 28 mesh standard screen sieve and are retained on 100 mesh standard screen sieve.

3. The method of producing a good wet and dry strength, high bulk asbestos paper containing at least about 25% by weight thereof of light weight cellular spheres having an average diameter of about 1 to 500 microns, said method comprising forming a dilute aqueous suspension consisting essentially of approximately 20 to 75 parts by weight of refined, harsh asbestos fiber having a Schopper-Riegler freeness value of about 180 to 560, 0 to approximately 30 parts by weight of synthetic resin fiber, approximately 4 to 10 parts by weight of resin size of at least one resin selected from the group consisting of acrylic resin and urea formaldehyde resin, and approximately 25 to 65% by weight of light weight cellular hollow gas containing resin spheres having an average diameter of approximately 1 to 500 microns, then forming therefrom a water-laid sheet containing approximately 25 to 65% by weight of the sheet of the said cellular spheres.

4. The method of claim 3 wherein the asbestos fiber is sized at least 70% by weight retained on 200 mesh standard screen sieve, and at least about 50% by weight of said fibers retained on 200 mesh standard screen sieve pass 28 mesh standard screen sieve and are retained on 100 mesh standard screen sieve.

5. The method of producing good wet and dry strength, high bulk asbestos paper containing at least about 40% by weight thereof of light weight cellular spheres having an average diameter of about 1 to 500 microns, said method comprising forming a dilute aqueous suspension consisting essentially of approximately 32 to 54 parts by weight of refined, harsh asbestos fiber having a Schopper-Riegler freeness value of about 350 to 560, approximately 5 to 7 parts by weight of synthetic resin size of at least one resin selected from the group consisting of acrylic resin and urea formaldehyde resin, approximately 40 to 60 parts by weight of light weight cellular hollow unicellar gas-containing resin spheres having an average diameter of 1 to 500 microns, and approximately 1 part by weight of alum, then forming therefrom a water-laid sheet containing approximately 40 to 60% by weight of the sheet of the said cellular spheres.

6. The method of claim 5 wherein the asbestos fiber is sized at least 70% by weight retained on 200 mesh standard screen sieve, and at least about 50% by weight of said fibers retained on 200 mesh standard screen sieve pass 28 mesh standard screen sieve and are retained on 100 mesh standard screen sieve.

7. A good wet and dry strength, high bulk asbestos

paper product containing at least approximately 25% by weight thereof of light weight cellular spheres having an average diameter of about 1 to 500 microns, said paper product consisting essentially of approximately 20 to 75 parts by weight of refined, harsh asbestos fiber having a Schopper-Riegler freeness value of about 180 to 560, approximately 4 to 10 parts by weight of size of at least one resin selected from the group consisting of acrylic resin and urea formaldehyde resin, and approximately 25 to 65 parts by weight of light weight cellular hollow gas-containing resin spheres having an average diameter of approximately 1 to 500 microns.

8. The asbestos paper product of claim **7** wherein the asbestos fiber is sized at least 70% by weight retained on 200 mesh standard screen sieve, and at least about 50% by weight of said fibers retained on 200 mesh standard screen sieve pass 28 mesh standard screen sieve and are retained on 100 mesh standard screen sieve.

9. A good wet and dry strength, high bulk asbestos paper product containing approximately 40 to 60% by weight thereof of light weight cellular spheres having an average diameter of about 1 to 500 microns, said paper product consisting essentially of approximately 32 to 54 parts by weight of refined, harsh asbestos fiber having a Schopper-Riegler freeness value of about 350 to 560 and sized at least 70% by weight retained on 200 mesh standard screen sieve and at least about 50% by weight of said fiber retained on 200 mesh standard screen sieve pass 28 mesh standard screen sieve and are retained on 100 mesh standard screen sieve, approximately 5 to 7 parts by weight of synthetic resin size of at least one resin selected from the group consisting of acrylic resin and urea formaldehyde resin, approximately 1 part by weight of alum, and approximately 40 to 60 parts by weight of light weight cellular hollow unicellular gas-containing resin spheres having an average diameter of approximately 1 to 500 microns.

10. A good wet and dry strength, high bulk asbestos paper product containing approximately 50% by weight thereof of light weight cellular sphers having an average diameter of about 25 to 250 microns, said paper product consisting essentially of approximately 42 parts by weight of harsh asbestos fiber having a Schopper-Riegler freeness value of about 350 to 560, approximately 7 parts by weight of acrylic resin and urea formaldehyde resin size, approximately 1 part by weight of alum, and approximately 50 parts by weight of hollow gas-containing resin spheres sized about 25 to 250 microns in diameter.

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DONALL H. SYLVESTER, *Primary Examiner.*

M. O. WOLK, *Examiner.*

H. R CAINE, *Assistant Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,365,358 January 23, 1968

Marsden C. Hutchins

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, TABLE I, first column, line 5 thereof, "Acrylic Resin (Rhoplex WC-9)[b]" should be indented even with "Asbestos fiber, 3W Grade" in line 2; column 4, Example III, in the table, first column, line 2 thereof, for "(Microballoons VJO-" read -- (Microballoons BJO- --; same Example III, in the table, first column, line 5 thereof, for "(Phoplex WC-9)" read -- (Rhoplex WC-9) --; same column 4, TABLE III, first column, line 13 thereof, for "Gurley stiffness" grams QD" read -- Gurley stiffness grams CD --; column 5, TABLE IV, first column, line 8 thereof, for "(Rhoplex GC-9)" read -- (Rhoplex WC-9) --.

Signed and sealed this 22nd day of July 1969.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents