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3,597,312

SYNTHETIC FIBROUS FILLER AND PAPER CONTAINING THE FILLER

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10 Claims

ABSTRACT OF THE DISCLOSURE

Synthetic, organic fibrous filler comprising blushed, fibrous polystyrene having high opacity as represented by scattering coefficients of at least about 0.25. The opaque, fibrous polystyrene is suitable for use as filler material in the manufacture of paper.

BRIEF SUMMARY OF THE INVENTION

This invention relates to novel compositions of matter and to their incorporation into paper products. More particularly, it relates to novel and useful synthetic fibrous, white, bright, and opaque filler materials which can be used with or in place of filler pigments in the production of paper and paperboard.

The trend in the paper industry toward lighter weight printing papers has made it necessary to find a means for maintaining in light weight sheets the optical properties normally found in heavier weight papers. The use of conventional filler pigments, such as clay and titanium dioxide, in increased amounts to obtain the desired optical properties, results in severe deterioration of strength properties. Opaque, fibrous fillers, such as the blushed cellulose ester fillers described in U.S. Pat. 3,342,921, provide some opacity without seriously affecting the strength of the paper. However, the blushed fillers previously known do not approach the opacifying power of TiO_2 and, therefore, more suitable synthetic fillers have been sought.

The present invention is based upon the discovery that a particular blushed material, radically different from those known in the past, has an opacity higher than most pigmentary filler materials heretofore known in the paper industry. We have found that polystyrene, when blushed and in fibrous form, has an extremely high opacity, comparable to TiO_2 , as represented by its scattering coefficient. This high opacity for blushed polystyrene fibers is surprising since the refractive index of polystyrene is not particularly high, being about 1.6.

Blushed fibrous polystyrene can readily be incorporated into paper and paperboard to afford opacity without serious losses in strength. Because the new filler is fibrous, it is retained on a paper-forming surface or papermaking machine to a much greater extent than conventional filler pigments. Further, since the blushed, fibrous polystyrene has a microporous structure, it is capable of accepting water and water-based paper coatings.

The novel blushed fibrous fillers of this invention can be prepared by an atomizing spray technique wherein a fiber-forming spray solution of normally transparent polystyrene is sprayed into a bath containing a non-solvent for the solute portion of the spray solution, the non-solvent being miscible with the solvent in the polystyrene solution. As the spray formulation is sprayed from the atomizing nozzle, located just above the non-solvent bath, fibrous-like particles are emitted and collected in the non-solvent bath where the blushing phenomenon continues to completion as the solvent in the fibers is diluted and displaced by the non-solvent. The fibrous fillers of this invention can also be made by adding under shear conditions a solution

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of polystyrene to a non-solvent for polystyrene. Blushed fibers form in the non-solvent. The final product produced by either technique is a white, very opaque, bright, fibrous polystyrene having a fiber length in the range of about 0.01 mm. to 0.41 mm., a width ranging from about 2.6 to 10.5 microns, and a scattering coefficient up to about 0.61. The blushed fibers have these properties without any subsequent mechanical size reduction.

When making blushed, fibrous polystyrene by the spraying technique described above, distances of about $\frac{1}{2}$ to 4 inches between the atomizing spray nozzle and the bath of non-solvent have been employed, with the preferred distance being about one inch. Atomizing spray nozzles having fluid orifice diameters ranging from about 0.028 to 0.100 inch have been used, with a preferred nozzle diameter of about 0.040 inch. Air is supplied to the spray nozzle at pressures varying from about 50 to 120 p.s.i.g.

Many solvents can be used to put polystyrene in solution sufficiently for purposes of this invention. For example, the following classes of solvents have been used: esters such as ethyl, butyl, isoamyl, carbitol, and methyl cellosolve acetates; ethers, such as dioxane, methylal, and bis (2-ethoxyethylether); ketones, such as methyl ethyl ketone, methyl isobutyl ketone, and acetophenone; aromatic hydrocarbons, such as toluene, xylene, Solvesso 100, and Solvesso 150; chlorinated hydrocarbons, such as carbon tetrachloride and ethylene dichloride; mixed solvent systems including mixtures of solvents from above; and mixtures of solvents and swelling agents for polystyrene such as one or more solvents from above mixed with gasoline.

The following non-solvents have been employed in producing the blushed, polystyrene fibers of this invention: water; alcohols, such as methanol, ethanol, and isopropanol; and mixtures of water and alcohol. Also, in some runs, non-solvent has been included in the spray solution, and solvent has been included in the bath of non-solvent in the same or other runs.

When a stream of polystyrene solution is added to a non-solvent under agitation, the blushed, fibrous product is produced in the non-solvent. When a spray formulation of polystyrene is sprayed according to this invention, it is believed that the solution is disrupted by air in the atomizing nozzle and breaks into fluid filaments as the solution is emitted from the nozzle. Some blushing of the polystyrene fibers occurs before the fibers reach the non-solvent due to solvent evaporation, and the blushing continues in the non-solvent.

Conventional mineral pigments can be included in the polystyrene solution before the blushed fibers are formed, with the result that the conventional mineral pigments will be encased in the blushed, fibrous polystyrene. This is one convenient way to pigment the synthetic blushed fibers and to utilize the opacifying abilities of both the blushed, fibrous material and the conventional mineral pigment. The preferred mineral filler for use in this connection is titanium dioxide. Other mineral pigments may be used, such as clay, calcium carbonate, magnesium oxide, hydrated alumina, and hydrated silica. Depending upon the opacity of the blushed polystyrene fibers, the addition of mineral pigment may actually decrease the opacity of the final product since the opacity of the blushed fibers can be much higher than that of a mineral pigment. In such circumstances, the blushed fibers can be utilized as a retention aid for the mineral pigment.

The scattering coefficient (Kubelka-Munk), an indication of opacifying power, of the blushed, fibrous polystyrene of this invention can be as high as 0.61, an opacity heretofore unknown for papermaking filler pigments. A whole range of blushed polystyrene fibrous fillers can be produced having scattering coefficients from about 0.25

to about 0.61. The scattering coefficient for conventional filler clay is normally about 0.19, and for TiO_2 about 0.54. Fibrous fillers, known in the past, have had scattering coefficients up to about 0.27. The scattering coefficients noted above were determined by the method described subsequently in connection with Examples 1-20.

Various polystyrenes have been used for purposes of producing the blushed fibers of this invention. Molecular weights of the polystyrenes have varied from about 5,000 to about 250,000.

DETAILED DESCRIPTION

The invention will be described in greater detail with the aid of the following examples.

Examples 1-20

In the following runs, blushed fibrous polystyrene was produced in a blender under high shear. In each case, 300 milliliters of non-solvent were placed in a Waring blender. With the non-solvent under agitation, 50 grams of a 4 percent solids solution of polystyrene (transparent Dow Styron, general purpose grade, having a molecular weight ranging from 230,000 to 250,000) were metered as a stream into the non-solvent. The blushed, fibrous polystyrene formed immediately upon contact with the non-solvent. In each instance, the resulting blushed product was filtered by use of a Büchner funnel, washed with non-solvent and then washed with water, and then incorporated into hand-sheets of paper for appraisal as to light scattering coefficient (Kubelka-Munk). The solvents in the polystyrene solutions and the non-solvents used in the blender are set forth below for each run, along with the scattering coefficient of the fibrous, blushed polystyrene filler in each case:

Example No.:	Solvent	Non-solvent	Scattering coefficient
1	Ethyl acetate	Methanol	0.48
2	Butyl acetate	do.	0.48
3	Isoamyl acetate	do.	0.34
4	Ethyl acetate	Ethanol	0.46
5	Carbitol acetate	Water	0.32
6	Methyl Cellosolve acetate	do.	0.31
7	Ethyl acetate	55% water, 45% ethanol	0.30
8	Dioxane	Water	0.34
9	do.	Methanol	0.34
10	Methylal	do.	0.40
11	Bis(2-ethoxyethylether)	do.	0.35
12	Methyl ethyl ketone	do.	0.50
13	Methyl isobutyl ketone	do.	0.49
14	do.	90% methanol, 10% water	0.49
15	do.	70% methanol, 30% water	0.48
16	Acetophenone	Methanol	0.47
17	Carbon tetrachloride	do.	0.28
18	80% gasoline, 20% toluene	do.	0.33
19	60% gasoline, 40% toluene	do.	0.25
20	40% gasoline, 60% toluene	do.	0.31
Control			0.035

In the above runs, where mixtures of solvents or non-solvents were used, the percentages noted were by weight.

In the above examples, the fibrous, blushed polystyrene fillers were incorporated into papermaking furnishes, and handsheets of paper were prepared in accordance with Tappi Standard T 205 m-58, the only modification being that the blushed polystyrene fibers were added as filler to beaten cellulosic papermaking fibers to give filler levels of approximately 8% by weight. The screen on the sheet mold on which the handsheets were formed was 150 mesh, and the consistency of the pulp and filler furnish was about 0.15%.

In determining the scattering coefficient for each filler, the opacity of the handsheet containing the filler was first measured according to Tappi Standard T 425 with a B & L opacimeter. Reflectance of the handsheets was

determined at 457 millimicrons by use of an LRL integrating sphere reflectometer. Control handsheets, similar in all respects to the filled sheets except that they contained papermaking pulp only, were also tested for opacity. By use of Tappi Data Sheet No. 65, which contains a graphical solution of the Kubelka-Munk equations relating Tappi opacity, bulk reflectance, and total light scattering power of the handsheet, the latter was determined. Total light scattering power is defined as the product of the scattering coefficient and the basis weight of the handsheet, based on a 3300 square feet ream.

The value for total light scattering power of the Control was divided by the basis weight of the handsheet to arrive at the scattering coefficient of the papermaking pulp. To determine the total scattering power for the filler in a filled handsheet, the scattering coefficient for pulp, determined from the Control, was multiplied by the weight of pulp in the filled sheet, and this value was subtracted from the total scattering power of the filled sheet to obtain the total scattering value for the filler portion of the sheet. The scattering coefficient for the filler was then determined by dividing the total scattering value for the filler by the basis weight of the filler in the handsheet. Scattering coefficients given throughout this specification were determined in the above-described manner.

Examples 21-23

In another series of runs, 200 grams of non-solvent were placed in a blender and highly agitated. Into the non-solvent were metered 10 milliliters of a 4 percent solids solution of polystyrene (Dow Styron). The fibrous polystyrene products produced by use of the solvents and

non-solvents noted below, were blushed and opaque, as shown by the scattering coefficients:

Example No.:	Solvent	Non-solvent	Scattering coefficient
21	Xylene	Isopropanol	0.41
22	Solvesso 100	do.	0.37
23	Solvesso 150	do.	0.49

Solvesso 100 and 150 are narrow cut aromatic hydrocarbon solvents comprising, by volume, respectively, 98.9 percent aromatics and 1.1 percent paraffins, and 97 percent aromatics and 3 percent paraffins.

Examples 24-51

As previously discussed, the blushed fibrous products of this invention can be produced by an atomizing spray technique wherein a solution of polystyrene is sprayed

into a bath of non-solvent for the polystyrene. In the following examples, approximately 1 liter of various solutions of polystyrene (Dow Styron) were sprayed from an air atomizing nozzle, having an internal air mixing chamber and a fluid orifice of 0.040 inch, into approximately 20 liters of non-solvent. In some runs, small amounts of non-solvent were included in the spray formulation. In others, mixtures of non-solvents were used in the non-solvent bath, the percentages noted below being by weight. Air was supplied to the nozzle at pressures varying from about 80–120 p.s.i.g. The distance between the nozzle and the surface of the non-solvent was about 1 inch, so that the sprayed solution passed through the atmosphere for a short period before contacting the non-solvent. Blushed, fibrous polystyrene was recovered from the bath of non-solvent by filtering with a Buchner funnel, washing first with a 50–50 mixture by weight of methanol-water, and then washing with water. Scattering coefficients were then determined in the manner previously described.

Example No.:	Solvent	Non-solvent	Scattering coefficient
52	Xylene	Isopropanol	0.43
53	MIBK	Methanol	0.45
54	Ethyl acetate	Ethanol	0.46

All of the blushed, fibrous polystyrene products of Examples 1–54 were bright, white, and opaque and exhibited fiber lengths ranging from about 0.01 mm. to 0.41 mm., with diameters ranging from about 2.6 to 10.5 microns.

Examples 55–60

In the following runs, conventional mineral pigments were included in polystyrene (Dow Styron) spray formulations. In each case, 30 percent of the solids in the spray formulations was comprised of a mineral pigment, and the total solids of the spray formulations were about 7 percent. After spraying the formulations into non-solvent,

Example No.:	Solvent	Percent polystyrene solids in spray solution	Non-solvent	Scattering coefficient
24	Ethyl acetate	11.8	Methanol	0.28
25	Dioxane	7.0	Water	0.36
26	do	14.0	do	0.25
27	Methyl isobutyl ketone (MIBK)	4.35	Methanol	0.25
28		4.35	70% methanol, 30% water	0.34
29		4.35	50% methanol, 50% water	0.42
30		4.35	40% methanol, 60% water	0.45
31		8.70	Methanol	0.30
32		8.70	70% methanol, 30% water	0.34
33		8.70	50% methanol, 50% water	0.37
34	MIBK	8.70	40% methanol, 60% water	0.41
35		4.35	90% methanol, 10% MIBK	0.28
36		4.35	65% methanol, 25% water, 10% MIBK	0.32
37		4.35	45% methanol, 45% water, 10% MIBK	0.61
38		4.35	80% methanol, 20% MIBK	0.30
39		4.35	60% methanol, 20% water, 20% MIBK	0.38
40		4.35	50% methanol, 30% water, 20% MIBK	0.55
41	80% gasoline, 20% toluene	10.5	Methanol	0.33
42	40% gasoline, 60% toluene	10.5	do	0.35
43	Xylene	4.35	Isopropanol	0.38
44	do	8.70	do	0.40
45	80% xylene, 20% isopropanol	4.35	90% isopropanol, 10% xylene	0.44
46	Xylene	4.35	87% isopropanol, 13% water	0.43
47	80% xylene, 20% isopropanol	4.35	do	0.43
48	Solvesso 150	4.35	Isopropanol	0.44
49	80% Solvesso 150, 20% isopropanol	4.35	do	0.45
50	80% Solvesso 150, 20% isopropanol	4.35	90% isopropanol, 10% Solvesso 150	0.41
51	Solvesso 150	4.35	87% isopropanol, 13% water	0.42

Examples 52–54

In these runs, polystyrenes having various molecular weights were used in the production of blushed, polystyrene fibers. The polystyrene (transparent Borden Styrene

the synthetic blushed polystyrene fibers, pigmented with the mineral fillers, were recovered and scattering coefficients determined. The blushed polystyrene fibers, encasing mineral pigments, had good optical efficiencies.

Example No.:	Solvent	Mineral pigment in spray formulation	Non-solvent	Scattering coefficient
55		Hydrated silica		0.42
56		TiO ₂		0.47
57		Clay		0.40
58		Calcium carbonate		0.32
59		Magnesium oxide		0.32
60		Hydrated alumina		0.44

Polymer No. 7646) used in Example 52 had a molecular weight of about 230,000, the polystyrene (transparent Borden Styrene Polymer No. 8100) used in Example 53 had a molecular weight of about 35,000, and the polystyrene (transparent Piccolastic D-150) used in Example 54 had a molecular weight of about 5,000. In each run, 300 grams of non-solvent were placed in a blender and highly agitated. In to the non-solvent were metered 35 milliliters of a solution of polystyrene prepared by dissolving 8 grams of polystyrene in 200 grams of solvent. The blushed polystyrene fibers produced were quite opaque as shown by the scattering coefficients in the following table:

As can be seen from above, the blushed polystyrene fibers of this invention find great utility in the papermaking field as filler materials. They can be used to replace conventional filler pigments or can be used as retention aids therefor or in conjunction therewith.

While, in the examples above of producing blushed polystyrene fibers by a spraying technique, a one inch spray distance between the atomizing spray nozzle and the surface of the non-solvent has been set forth, distances ranging from about ½ to 4 inches have been used successfully to produce the blushed fibers. Also, while a fluid nozzle diameter of 0.040 inch has been illustrated, diameters ranging from about 0.28 to 0.100 have been used.

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Various changes may be made in the examples specifically set forth above without departing from the spirit of our invention or the scope of the appended claims.

We claim:

1. A composition of matter comprising synthetic, blushed fibers of polystyrene having a microporous structure which is bright, white and opaque, said fibers having lengths ranging from about 0.01 mm. to about 0.41 mm. and widths ranging from about 2.6 microns to about 10.5 microns and produced by preparing a fiber-forming spray solution of polystyrene dissolved in a solvent which is then sprayed from an atomizing nozzle into a non-solvent bath so that fibers are emitted therefrom and collected in the non-solvent which is miscible with the solvent where the blushing continues to completion as the solvent in the fibers is diluted and displaced by the non-solvent.

2. The blushed polystyrene fibers of claim 1 characterized as having a scattering coefficient from about 0.25 to 0.61.

3. The blushed polystyrene fibers according to claim 2 further characterized by the fact that the polystyrene has a molecular weight ranging from about 5,000 to about 250,000.

4. The blushed polystyrene fibers according to claim 3 further characterized by the fact that the blushed fibers encase a mineral pigment in the amount of about 30% by weight of said polystyrene fibers.

5. The blushed polystyrene fibers according to claim 4 wherein the mineral pigment is selected from the group consisting of clay, calcium carbonate, hydrated silica, hydrated alumina, titanium dioxide, and magnesium oxide.

6. Paper comprising cellulosic fibers and synthetic, blushed polystyrene fibers in the amount of approximately 8% by weight of said paper, said blushed polystyrene fibers being opaque and of microporous structure and having lengths ranging from about 0.01 mm. to about 0.41 mm. and widths ranging from about 2.6 microns to about 10.5 microns and produced by preparing a fiber-forming spray solution of polystyrene dissolved in a solvent which is then sprayed from an atomizing nozzle into a non-solvent bath so that fibers are emitted therefrom and collected in the non-solvent which is miscible with the sol-

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vent where the blushing continues to completion as the solvent in the fibers is diluted and displaced by the non-solvent.

7. Paper according to claim 6 wherein the blushed polystyrene fibers have a scattering coefficient from about 0.25 to about 0.61.

8. Paper according to claim 7 wherein the polystyrene has a molecular weight ranging from about 5,000 to about 250,000.

9. Paper according to claim 8 further characterized by the fact that the synthetic, blushed polystyrene fibers encase particles of a mineral pigment in the amount of about 30% by weight of said polystyrene fibers.

10. Paper according to claim 9 wherein the mineral pigment is selected from the group consisting of clay, calcium carbonate, hydrated silica, hydrated alumina, titanium dioxide, and magnesium oxide.

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