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## (54) A process for preparing a non-woven fibrous web from fibers and a latex, and the non-woven fibrous material so prepared.

(57) A high strength, non-woven fibrous material is prepared by (a) mixing an aqueous slurry of a negatively charged, water-insoluble natural or synthetic fiber or blend of fibers with an amount up to the fiber charge reversal point of a structured particle latex having pH independent cationic charges bound at or near the particle surface to form an aqueous suspension, (b) draining water from the aqueous suspension to form a wet web (c) wet pressing the web and (d) drying the web by heating.

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-1-TITLE MODIFIED
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# HIGH STRENGTH NON-WOVEN FIBROUS MATERIAL

This invention is concerned with the use of a cationic latex by wet-end addition in a process for making high strength non-woven fibrous material and the product formed by such a process.

The use of a latex in the manufacture of non-woven materials by wet-end addition, or as a beater additive, is well known. Commonly, the latex has been an anionic latex but a water-soluble cationic deposition aid has been used therewith. Because of the slightly anionic nature of pulp, it has been suggested particularly for paper manufacture that a low-charge density cationic latex should be used in order to get good deposition on the fibers without the use of a deposition aid. However, it has been considered necessary to use a low charge latex to get efficient deposition of the latex. The prior art teaches the utility of bound charge in a wet-end process but does not teach or suggest the advantage of using high levels of bound charge in a structured particle latex to get high strength in the products.

It has now been found that high strength non-woven fibrous materials can be prepared by mixing an

aqueous slurry of a negatively charged fiber with a specific kind of cationic latex in an amount up to the charge reversal point of the fiber, draining water from the resulting aqueous suspension to form a wet web, wet pressing the web and drying the web by heating. The latex comprises structured particles having a non-ionic polymer core encapsulated by a thin polymer layer having a high density of bound, pH independent, cationic charges. The polymer core has a glass transition temperature (Tg) from -80°C to 100°C, preferably from -25°C to 40°C.

Of particular importance is that the cationic latex is used in an amount below that required to cause charge reversal on the fiber. The use of a deposition aid is not a significant factor. An advantage of the process and product of this invention is that the polymer from the latex is uniformly distributed on the fiber and is bonded thereto. Consequently stronger webs are obtained.

The fiber is any kind of negatively charged, water-insoluble, natural or synthetic fiber or blend of fibers which can be dispersed in aqueous slurry. Either long or short fibers, or mixtures thereof are useful. Suitable also are reclaimed waste papers and cellulose from cotton and linen rags, straws, glass fibers and the like. Particularly useful fibers are the cellulosic and lignocellulosic fibers commonly known as wood pulp of the various kinds such as mechanical pulp, steam-heated mechanical pulp, chemimechanical pulp, semichemical pulp and chemical pulp. Specific examples are groundwood pulp, unbleached sulfite pulp, bleached sulfite pulp, unbleached sulfate pulp and bleached

sulfate pulp. The process is valuable in being able to use crude, low quality pulp such as "screenings", i.e., coarse by-product pulp from unbleached chemical pulps.

The cationic latex comprises a water-insoluble copolymer having particles with a high density of pH independent bound charges at or near the particle surface in an amount of from 0.15 milliequivalent to 0.6 milliequivalent, preferably from 0.18 milliequivalent to 0.4 milliequivalent, per gram of copolymer. The composition of the latex copolymer is such as to provide a glass transition temperature (Tg) from -80°C to 100°C, preferably from -25°C to 40°C. Ordinarily, tensile strength of the product increases as the Tg increases up to the point where the polymer does not fuse properly with the times and temperatures encountered in the wet-end process.

The latexes are structured particle latexes having a non-ionic polymer core encapsulated by a thin polymer layer having bound charges as pH independent cationic groups at or near the particle surface. One method of obtaining such latexes is by copolymerizing under emulsion polymerization conditions an ethylenically unsaturated, activated-halogen monomer onto the particle surface of a non-ionic, organic polymer which is slightly cationic through the presence of adsorbed cationic surfactant. The resulting latex is reacted with a non-ionic nucleophile to form a latex suitable for use in the practice of this invention.

Latexes prepared by usual emulsion polymerization conditions have high enough molecular weight to be useful. Usually the degree of polymerization will be greater than 1000. The lower limit can be expressed

as the start of the plateau region when properties are plotted against molecular weight.

The particle size of the latex also has a significant effect. Tensile strength of the product increases as the particle size of the latex decreases. Ordinarily the particle size for best results will be below 1500 Angstroms, especially from 600 Angstroms to 1000 Angstroms.

By "bound" as applied to groups or charges in this specification is meant that they are not desorbable under the conditions of processing. A convenient test is by dialysis against deionized water.

By the term "pH independent groups" as applied to ionic groups is meant that the groups are predominantly in ionized form over a wide range in pH, e.g., 2-12. Representative of such groups are sulfonium, sulfoxonium, isothiouronium, pyridinium and quaternary ammonium.

By the term "non-ionic" as applied to the monomers in this specification is meant that the monomers are not ionic per se nor do not become ionic by a simple change in pH. For illustration, while a monomer containing an amine group is non-ionic at high pH, the addition of a water-soluble acid reduces the pH and forms a water-soluble salt; hence, such a monomer is not included. The non-ionic nucleophiles, however, are not similarly restricted, i.e., "non-ionic" as used with nucleophiles applies to such compounds which are non-ionic under conditions of use and tertiary amines, for example, are included.

Optional wet-end constituents used in the process to make the products of this invention include pigments and other common wet-end additives. While conventional deposition aids may be used, there is no particular advantage obtained thereby.

The maximum amount of cationic latex used in the practice of this invention is not significantly greater than the amount required to reach the charge neutralization point of the fiber being used. Hence, the amount of latex depends on the charge on the latex and the charge on the fiber. As the charge on the fiber is increased, the amount of a particular latex which can be used is increased with a resulting higher tensile strength in the product. For a particular fiber, as the charge on the latex is increased the amount of latex which can be used is decreased. At a particular level of latex, the tensile strength normally increases with the charge density on the latex particle up to the point where the structured particle morphology is lost, i.e., when the particle becomes soluble or a microgel. The amount of cationic latex usually ranges from 0.5 percent to 5 percent of solids based on the dry weight of the fiber.

The process to prepare the product of this invention preferably is carried out as follows: A dilute aqueous suspension of the fiber is formed in the normal manner often in a concentration of from 0.5 percent to 6 percent. The latex is added at any convenient concentration, often in the concentration as supplied and the resulting mixture is stirred, usually for at least two minutes depending somewhat on the equipment available. The aqueous suspension usually is then diluted further, often with white water from the process.

Optional wet-end additives can be added at any suitable time. A wet web is formed by flowing the resulting suspension over a porous support such as a screen, draining the wet web, wet pressing and completely drying the web by heating. Pressing and heating may be carried out simultaneously. Alternatively, ambient temperature pressing followed by heating to complete drying may be employed. Optionally, other compacting, shaping, tempering and curing steps may be included. The temperatures used for hot pressing, curing and tempering or other heating steps often are from 100°C to 250°C, although higher or lower temperatures are operable. The product is prepared from the resulting suspension, for example, on a paper machine such as a Fourdrinier machine or a cylinder machine or in a laboratory sheet forming apparatus.

The product is a dried, non-woven fibrous web with one dimension much smaller than the other two with the fibers uniformly distributed through the smaller dimension, preferentially oriented in the plane of the web and bonded to a uniformly distributed polymer phase formed from a structured particle latex.

The following examples illustrate ways in which the present invention may be carried out. All parts and percentages are by weight unless otherwise expressly indicated.

Unless indicated otherwise, the latexes for the examples were prepared according to the following summary. A base latex was prepared by batch emulsion polymerization from the monomers shown in Table I using dodecylbenzyldimethylsulfonium chloride as surfactant. The particles of the base latex were encapsulated (capped) with a copolymer of vinylbenzyl chloride by adding "cap monomers" of the kind and in the proportions shown in Table I in a continuously added manner over about one hour

under emulsion polymerization conditions. The resulting latex was mixed with an excess of a nucleophile and was allowed to react to form a bound charge on the latex particles. The reaction was stopped at the desired degree of charge by removing the excess nucleophile by distillation. Except as otherwise indicated the nucleophile was dimethylsulfide and accordingly the resulting pH independent cationic group was sulfonium. In those examples where the quaternary ammonium group is indicated, the nucleophile was 2-(dimethylamino)ethanol.

TABLE I

| Latex | Base Latex[a] St % | Bd % | Tg °C | Cap[a] St % | Bd % | VBC % | Structured-Particle Latex Composition Cap % | VBC % | Bound Charge meq/g | Particle Size Angstroms |
|---|---|---|---|---|---|---|---|---|---|---|
| A-1 | 65 | 35 | 2 | 15 | 35 | 50 | 10 | 5 | 0.102 | 1360 |
| A-2 | 65 | 35 | 2 | 15 | 35 | 50 | 10 | 5 | 0.112 | 1360 |
| A-3 | 65 | 35 | 2 | 15 | 35 | 50 | 10 | 5 | 0.127 | 1360 |
| B-1 | 65 | 35 | 2 | 15 | 35 | 50 | 20 | 10 | 0.160 | 1480 |
| B-2 | 65 | 35 | 2 | 15 | 35 | 50 | 20 | 10 | 0.265 | 1480 |
| B-3 | 65 | 35 | 2 | 15 | 35 | 50 | 20 | 10 | 0.298 | 1480 |
| C | 65 | 35 | 2 | | 50 | 50 | 13 | 6.5 | 0.221 | 800 |
| D | 65 | 35 | 2 | | 50 | 50 | 13 | 6.5 | 0.171 | 910 |
| E | 65 | 35 | 2 | | 50 | 50 | 13 | 6.5 | 0.178 | 1480 |
| F | 65 | 35 | 2 | | 50 | 50 | 13 | 6.5 | 0.142 | 1880 |
| G | 65 | 35 | 2 | | 50 | 50 | 13 | 6.5 | 0.203[b] | 1360 |
| H | 50 | 50 | -21 | | 50 | 50 | 13 | 6.5 | 0.204 | 1230 |
| I | 55 | 45 | -15 | | 50 | 50 | 13 | 6.5 | 0.172 | 1190 |
| J | 60 | 40 | -8 | | 50 | 50 | 13 | 6.5 | 0.173 | 1335 |
| K | 65 | 35 | 2 | | 50 | 50 | 13 | 6.5 | 0.199 | 1360 |
| L | 70 | 30 | 20 | | 50 | 50 | 13 | 6.5 | 0.193 | 1320 |

a Monomers: St = styrene; Bd = butadiene; VBC = vinylbenzylchloride

b Bound quaternary ammonium group; others are sulfonium

Example 1

An aqueous dispersion containing 1393 parts of water having a hardness of 106 ppm (calculated as calcium carbonate) and an alkalinity of 48 ppm (calculated as calcium carbonate) and 7 parts (dry basis) of unbleached Canadian softwood kraft having a Canadian Standard Freeness (CSF) of 540 milliliters was stirred at such rate that the kraft was just turning over gently. To the moving kraft suspension was added 0.2 part (3 percent of fiber), dry weight basis, of the latex shown in Table II and the resulting mixture, having a pH between 7 and 8 (unadjusted), was stirred for an additional 2.5 minutes. The resulting furnish was made into a handsheet (3.3 grams, 20.32 cm x 20.32 cm).

A handsheet (Comparative Example 1-C) was prepared in the same manner except the latex was omitted.

Data are shown in Table II.

Examples 2-6

Additional handsheets were made in the same manner using the same components in the same proportions except that a different latex was used. Data are shown in Table II.

TABLE II

| Ex. No. | Latex | Bound Charge meq/g | Tensile (a) |
|---|---|---|---|
| 1 | A-1 | 0.102 | 9,384 |
| 2 | A-2 | 0.112 | 9,741 |
| 3 | A-3 | 0.127 | 9,831 |
| 4 | B-1 | 0.160 | 10,479 |
| 5 | B-2 | 0.265 | 11,082 |
| 6 | B-3 | 0.298 | 10,724 |
| 1-C | none | - | 8,959 |

(a) Breaking length, meters

All of the handsheets shown in Table II (except 1-C) showed uniform distribution of the latex on the fiber.

Examples 7-10

Additional handsheets were prepared in the same manner as described in Example 1 except that different latexes with differing particle sizes were used and the pH of the furnish was adjusted to 4.5 to 5 with sulfuric acid.

Data are shown in Table III.

All of the handsheets of these examples showed uniform distribution of the latex polymer on the fibers.

A comparative handsheet (7-C) was prepared in the same manner except that no latex was used. Data for this comparative example also are shown in Table III.

TABLE III

| Ex. No. | Latex | Bound Charge meq/g | Particle Size Angstroms | Tensile (a) |
|---|---|---|---|---|
| 7 | C | 0.221 | 800 | 10,791 |
| 8 | D | 0.171 | 910 | 10,501 |
| 9 | E | 0.178 | 1480 | 10,233 |
| 10 | F | 0.142 | 1880 | 10,054 |
| 7-C | none | - | - | 9,049 |

(a) Breaking length, meters

Examples 11-16

Handsheets were prepared in the same manner except different latexes were used and the size of each handsheet was 30.48 cm x 30.48 cm (7.5 grams). The latex for Example 11 had bound quaternary ammonium groups and the other examples had sulfonium groups. The handsheets showed uniform distribution of latex in the fibers.

Data are shown in Table IV for the above examples and also for comparative Example 16-C which was prepared in the same manner except that no latex was used.

TABLE IV

| | Latex | | | Handsheet |
|---|---|---|---|---|
| Ex. No. | Kind | Core Tg °C | Bound Charge meq/g | Tensile (b) |
| 11 | G | 2 | 0.203(a) | 10,751 |
| 12 | H | -21 | 0.204 | 9,843 |
| 13 | I | -15 | 0.172 | 9,932 |
| 14 | J | - 8 | 0.173 | 10,109 |
| 15 | K | 2 | 0.199 | 10,529 |
| 16 | L | 20 | 0.193 | 11,657 |
| *16-C | - | - | - | 9,821 |

* Not an example of this invention
(a) Quaternary ammonium rather than sulfonium
(b) Breaking length, meters

Tests referred to in the examples were carried out as follows:

Tensile:

Tensile values are recorded as breaking length, in meters, and are determined according to TAPPI Standard T 494-os-70 except the values are the average of 3 samples rather than 10 and the jaw gap is 5.08 cm rather than 20.32 cm.

Canadian Standard Freeness (CSF):

The values are determined according to TAPPI Standard T 227-M-58 except where variations in the procedure are indicated.

Glass Transition Temperature (Tg):

The values are derived from "Encyclopedia of Polymer Science and Technology", John Wiley & Sons, N.Y., 1970, Vol. 13, page 322, especially figure 8.

1. Process for preparing non-woven fibrous webs from fibers and a latex characterized by:

(a) mixing an aqueous slurry of a negatively charged, water-insoluble, natural or synthetic fiber or a blend of such fibers with a structured particle latex having particles consisting of a non-ionic organic polymer core encapsulated by a thin polymer layer having bound charges of pH independent cationic groups, said charges being present in an amount of from 0.15 milliequivalent to 0.6 milliequivalent per gram of polymer in the latex; the non-ionic polymer core having a glass transition temperature of from -80°C to 100°C; the amount of said latex being not greater than the amount required to cause charge reversal on the fiber;

(b) draining water from the aqueous suspension to form a wet web;

(c) wet pressing the web; and

(d) heating the wet web; whereby there is formed a non-woven fibrous web having polymer uniformly distributed and bonded to the fiber.

2. Process of Claim 1 characterized in that the fiber is a paper-making pulp and the product is paper.

3. Process of Claims 1 or 2 characterized in that the pH independent group is sulfonium.

4. Process of Claims 1 or 2 characterized in that the pH independent cationic group is quaternary ammonium.

5. Process of any one of Claims 1 to 4 characterized in that the diameter of the latex particle is less than 1500 Angstroms.

6. Process of Claim 5 characterized in that the particle diameter is from 600 Angstroms to 1000 Angstroms.

7. Process of any one of Claims 1 to 6 characterized in that the amount of latex is from 0.5 percent to 5 percent of the weight of the fiber, calculated on a dry weight basis.

8. Process of any one of Claims 1 to 7 characterized in that the glass transition temperature of the non-ionic polymer core is from -25°C to 40°C.

9. Process of any one of Claims 1 to 8 characterized in that the amount of bound charge is from 0.18 milliequivalent to 0.4 milliequivalent per gram of polymer in the latex.

10. A non-woven fibrous material characterized in that it has been obtained by:

(a) mixing an aqueous slurry of a negatively charged, water-insoluble, natural or synthetic fiber or a blend of such fibers with a structured particle latex having particles consisting of a non-ionic organic polymer core encapsulated by a thin polymer layer having bound charges of pH independent cationic groups, said charges being present in an amount of from 0.15 milliequivalent to 0.6 milliequivalent per gram of polymer in the latex; the non-ionic polymer core having a glass transition temperature of from -80°C to 100°C; the amount of said latex being not greater than the amount required to cause charge reversal on the fiber;

(b) draining water from the aqueous suspension to form a wet web;

(c) wet pressing the web; and

(d) heating the wet web.

European Patent Office

# EUROPEAN SEARCH REPORT

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Application number
EP 78 10 0677

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim |
|---|---|---|
| | US - A - 3 130 117 (C.G. HUMISTON et al.)<br>* Claims 1 to 7; column 7, table VI * | 1-3,7, 10 |
| | FR - A - 2 308 660 (DOW)<br>* Page 2, line 5 to page 18, last line; examples II to XIX * | 3-6,8, 9 |
| | US - A - 3 772 143 (H.H.ROTH)<br>* Entire document * | 1-3,7, 10 |

CLASSIFICATION OF THE APPLICATION (Int. Cl.²)

D 21 H 3/40
C 08 F 257/02
C 08 F 279/02
C 08 F 8/00//
(C 08 F 257/02
C 08 F 212/14
C 08 F 279/02
C 08 F 212/14)

TECHNICAL FIELDS SEARCHED (Int.Cl.²)

D 21 H 3/38
D 21 H 3/64
C 08 F 257/00
C 08 F 279/00
C 08 F 8/00

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| The Hague | 10-11-1978 | NESTBY |

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