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(54) Title: SILICATE-DEXTRIN ADHESIVE COMPOSITIONS		
(57) Abstract An adhesive composition comprising (in percent by weight) from about 0.05 to about 0.5 % sodium silicate, from about 10 to about 47 % dextrin, from about 17 to about 70 % alkali metal silicate, from about 0.05 to about 0.5 % sodium metaborate octahydrate or sodium metaborate tetrahydrate, and from about 18 to about 62 % water; and a process for preparing the same. The adhesive composition is useful in the manufacture of paper products, such as paper tubes, corrugated boards and corner boards.		

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SILICATE-DEXTRIN ADHESIVE COMPOSITIONS

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to silicate-dextrin adhesive compositions and
5 process for producing the same.

Reported Developments

Aqueous alkali metal silicates, particularly sodium silicates, are very old in
the art and have many technical applications including their use as binders in coatings
and as adhesives for solid fiber and corrugated boxes and cartons and plywood
10 manufacture. They are versatile adhesives, combining convenience for use with
strength and rigidity. However, in their use in the manufacture of paper products,
such as paper tubes, they do not provide sufficient initial tack and may cause
breakdown of the manufacturing process.

Dextrin and modified dextrans have also been used as adhesives for
15 various applications, including many uses in the paper industry. While these
adhesives quickly develop initial tack, they are difficult to clean from the processing
machinery. They also do not have the strength and rigidity which the silicate-type
adhesives have, and their use is rather limited in the paper industry where strength
and rigidity are required.

20 In order to provide the desirable characteristics of quick initial tack,
rigidity and strength in adhesives intended for use in the paper industry, aqueous
alkali silicates were combined with dextrin, as in U.S. Patent 3,433,691. In so doing,
the prior art has found that at least about 1% of dextrin is required to improve the
initial tack quality over that obtained with straight silicate adhesives. While the initial
25 tack requirement could be improved with the addition of more than 1% dextrin,
thereby enabling a fast, automatic process in the manufacture of paper laminates,
another problem arose. When the composition contained more than about 0.5%
dextrin, the dextrin "floated out," rising to the surface of the adhesive composition.
This floating out was observed both at the time of application of the adhesive to paper

products and on storage of the adhesive. The floating out has resulted in faulty paper products and clogging of the complex dispensing apparatus.

U.S. Patent 3,767,440 reports that the floating-out problem has been overcome by the addition to the aqueous alkali metal silicate/dextrin adhesive composition of a clay slurry consisting of a swelling type clay and a kaolin type clay. The addition of the clay slurry renders the adhesive composition thixotropic and prevents floating out of the dextrin from the adhesive composition.

The prior art also addresses the need of flame-resistant adhesive compositions, such as disclosed in U.S. Patent 4,066,463, which discloses the combination of asbestos fibers with alkali metal silicate, starch, carboxymethyl-cellulose and dextrin.

Other references are directed to the use of vegetable proteins in silicate-containing adhesives, such as U.S. Patents 2,457,108 and 2,681,290. These adhesives require heat on application to the surfaces to be joined to form the necessary bond between the surfaces. Still other references disclose the use of cellulosic material, such as wood pulp to control viscosity, for example, U.S. Patent 3,241,990, or soy polysaccharides, for example, U.S. Patent 4,437,893, in combination with alkali metal silicates.

The object of the present invention is to provide a silicate-dextrin based adhesive composition having superior initial tack, adhesive strength and other desirable characteristics heretofore not quite satisfactorily provided for use in the paper industry including but not limited to tube winding, corrugated boards and corner boards.

SUMMARY OF THE INVENTION

The adhesive composition of the present invention comprises a mixture of:

- a. from about 0.05 to about 0.5% w/w, and preferably about 0.2% w/w of sodium metasilicate;

- b. from about 10 to about 47% w/w, and preferably about 21% w/w of dextrin;
- c. from about 17 to about 70% w/w, and preferably about 58% w/w of an alkali metal silicate, preferably sodium silicate;
- d. from about 0.05 to about 0.5% w/w of sodium metaborate octahydrate or sodium metaborate tetrahydrate; and
- e. from about 18 to about 62% w/w, and preferably about 21% w/w of water.

The adhesive composition of the present invention is prepared by the following steps, the order of which is critical:

1. adding from about 0.05 to about 0.5% w/w of sodium metasilicate to from about 18 to about 62% w/w water, while vigorously stirring, to obtain a solution of the sodium metasilicate;
2. adding with continuous stirring from about 10 to about 47% w/w dextrin to obtain a solution of sodium metasilicate/dextrin;
3. adding with continuous stirring from about 17 to about 70% w/w of an alkali metal silicate, preferably sodium silicate, to obtain a solution of sodium metasilicate/dextrin/alkali metal silicate; and
4. adding with continuous stirring from about 0.05 to about 0.5% w/w of sodium metaborate octahydrate.

The adhesive composition so prepared may be stored at any temperature, including temperatures below freezing, as long as the temperature is maintained below 38°C.

The components are readily available commercially and may also be prepared by methods known in the art.

Sodium metasilicate is well known and used commercially and is described, for example, by Faith, Keyes & Clarks' *Industrial Chemicals*, F.A.

Lowenheim, M.K. Moran, Eds.; Wiley-Interscience, New York, 4th Ed., 1975, pp. 755-761.

Sodium silicate in dry form of Na_2SiO_3 , $\text{Na}_6\text{Si}_2\text{O}_7$ and $\text{Na}_2\text{Si}_3\text{O}_7$ having a 2.0 to 5.5 ratio of SiO_2 to Na_2O is preferred for use in the adhesive compositions of the present invention. However, sodium silicate solutions may also be used, in which case the water content of the solution should be considered so that the above-identified composition ranges are satisfied.

Typical commercial alkali metal silicates are shown in Table 1.

TABLE 1

	Alkali Metal	Wt. Ratio $\text{SiO}_2:\text{M}_2\text{O}$	SiO_2 (%)	Na_2O (%)	Density (lb/gal)	Viscosity (centipoise)
10	Sodium	3.75	25.3	6.75	11.0	220
		3.25	29.9	9.22	11.8	830
15		3.25	28.4	8.7	11.6	160
		3.22	27.7	8.6	11.5	100
		2.87	32.0	11.1	12.4	1,250
		2.58	32.1	12.5	12.6	780
		2.50	26.5	10.6	11.7	60
20		2.40	33.2	13.85	13.0	2,100
		2.20	29.2	13.3	12.5	--
		2.00	29.4	14.7	12.8	400
		2.00	36.0	18.0	14.1	70,000
		1.90	28.5	15.0	12.7	--
25		1.80	24.1	13.4	12.0	60
		1.60	31.5	19.7	14.0	7,000
	Potassium	2.50	20.8	8.3	10.5	40
		2.20	19.9	9.05	10.5	7
		2.10	26.3	12.5	11.5	1,050

Sodium metaborate octahydrate is also available commercially and is made by fusing borax and sodium carbonate.

Dextrin is available in various forms such as canary yellow and white dextrin and is produced by the dry heating of unmodified starches. It is preferred to

use white dextrin for certain paper end products, and the highly soluble linear dextrin sold under the trademark AMAIZO® 1752-S Dextrin sold by American Maize-Products Co., Hammond, Indiana.

EXAMPLES

- 5 The following examples demonstrate by way of illustration some of the preferred adhesive compositions of the present invention, and the process of their preparation. The sodium metasilicate in the amount of from 0.05 to about 0.5% w/w must be added and dissolved in water prior to the addition of dextrin.

Example 1

- 10 Five-tenths (0.5) gram of sodium metasilicate is dissolved in 35 grams of water followed by the addition of 65 grams of dextrin with stirring. Then 23.08 grams of the mix is added to 76.92 grams of silicate and mixed with stirring until the mixture becomes homogeneous. Then 0.30 grams of sodium metaborate octahydrate is added and mixed well with the homogeneous mixture at room temperature.

15 Example 2

- Eight hundredths (0.08) gram of sodium metasilicate is dissolved in 35 grams of water followed by the addition of 65 grams of dextrin with stirring. Then 34.64 grams of this mix is added to a mixture of 57.69 grams of sodium silicate, 0.3 gram of sodium metaborate tetrahydrate and 7.39 grams of water. The combined
20 mixtures are then mixed at room temperature to homogeneity.

Example 3

- One-tenth (0.1) gram of sodium metasilicate is dissolved in 35 grams of water followed by the addition of 65 grams of dextrin with stirring. Then 46.15 grams of this mix is added to 38.36 grams of potassium silicate, 0.35 gram of sodium
25 metaborate octahydrate and 15.03 grams of water. The ingredients are mixed at room temperature until the mixture becomes homogeneous.

Example 4

- Two-tenths (0.2) gram of sodium metasilicate is dissolved in 35 grams of water followed by the addition of 65 grams of dextrin with stirring. Then 15.38

grams of this mix is added to 51 grams of sodium silicate, 0.28 gram of sodium metaborate tetrahydrate and 33.33 grams of water. The ingredients are mixed at room temperature until the mixture becomes homogeneous.

Example 5

- 5 Five-tenths (0.5) gram of sodium metasilicate is dissolved in 35 grams of water followed by the addition of 50 grams of dextrin with stirring. Thirty (30) grams of this mix is added to 70 grams of sodium silicate. The ingredients are mixed at room temperature until the mixture becomes homogeneous.

Example 6

- 10 Three tenths (0.3) gram of sodium metasilicate is dissolved in 35 grams of water followed by the addition of 20 grams of dextrin with stirring. Twenty (20) grams of this mix is added to 79.7 grams of sodium silicate and 0.3 gram of sodium metaborate octahydrate. The ingredients are mixed at room temperature until the mixture becomes homogeneous.

Example 7

- 15 Four tenths (0.4) gram of sodium metasilicate is dissolved in 35 grams of water followed by the addition of 20 grams of dextrin with stirring. Fifty (50) grams of this mix is added to 49.7 grams of sodium silicate and 0.3 gram of sodium metaborate octahydrate. The ingredients are mixed at room temperature until the
20 mixture becomes homogeneous.

Example 8

- To a large container having a mixer capable of operating at variable speed are added 15 gallons of water and 1.25 lb sodium metasilicate. The components are stirred at moderate speed at room temperature until the sodium metasilicate dissolves.
25 Then 125 lbs of dextrin is added and the mixture is stirred at slow speed for about 30 minutes followed by the addition of 305 lbs of sodium silicate with stirring for another 10 minutes. One and three-tenths (1.3) lb of sodium metaborate is added while stirring the mixture for an additional 10 minutes.

The adhesive formulations of the present invention are utilized in making paper products, such as paper tubes, corrugated boards and angle boards, comprising layers of paper adhered to each other by the adhesive formulation. The properties of the final product are a function of the paper used, number of layers of the paper and the particular adhesive used. It was found that an adhesive formulation of the present invention having a solids content of from about 30% w/w to about 44% w/w is required to satisfy the various requirements in the final product. Experiments performed using various solids contents in the formulations showed the following viscosities which indicate the operable utility range. Table 2 shows percent solids content and associated viscosities of Examples 9-14, the preparations of which are analogous to Examples 1-7.

TABLE 2

	Example	Viscosity (cps)	Solids % w/w
15	8	3400	44.0
	9	766	41.8
	10	368	38.4
	11	721	40.5
20	12	332	37.8
	13	220	35.0
	14	150	33.2

Stability testing was performed on samples at 0°C, 5°C, 21°C, 38°C and 70°C using IR spectroscopy and visual inspection methods for determining stability. The data obtained is shown in Table 3.

TABLE 3

0°C	stable for more than 6 months
5°C	stable for more than 6 months
21°C	stable for more than 6 months
38°C	stable for more than 6 months
70°C	unstable after one hour as shown by IR; appearance dark brown

The invention has been described with reference to its preferred embodiments; it is to be understood that modifications within the scope of the invention will be apparent to those skilled in the art.

CLAIMS

I claim:

1. An adhesive composition comprising:
 - a. from about 0.05 to about 0.5% w/w of sodium metasilicate;
 - 5 b. from about 10 to about 47% w/w of dextrin;
 - c. from about 17 to about 70% w/w of an alkali metal silicate;
 - d. from about 0.05 to about 0.5% w/w of sodium metaborate octahydrate or sodium metaborate tetrahydrate; and
 - e. from about 18 to about 62% w/w water.
- 10 2. The composition of claim 1 comprising:
 - a. 0.5% w/w of sodium metasilicate;
 - b. 21% w/w of dextrin;
 - c. 58% w/w of an alkali metal silicate;
 - d. 0.5% w/w of sodium metaborate octahydrate; and
 - 15 e. 21% w/w water.
3. The composition of claim 1 wherein said alkali metal silicate is sodium silicate.
4. The composition of claim 1 wherein said alkali metal silicate is potassium silicate.
5. The process of making an adhesive composition comprising:
 - 20 a. adding from about 0.05 to about 0.5% w/w sodium metasilicate to from about 18 to about 62% w/w water, while vigorously stirring, to obtain a solution of the sodium metasilicate;

- b. adding with continuous stirring from about 10 to about 47% w/w dextrin to obtain a solution of sodium metasilicate/dextrin;
 - c. adding with continuous stirring from about 17 to about 70% w/w of an alkali metal silicate to obtain a solution of sodium metasilicate/dextrin/alkali metal silicate; and
 - d. adding with continuous stirring from about 0.05 to about 0.5% w/w sodium metaborate octahydrate or sodium metaborate tetrahydrate.
- 5
6. The process of claim 5 wherein said alkali metal silicate is sodium silicate.
 7. The process of claim 5 wherein said alkali metal silicate is potassium silicate.

INTERNATIONAL SEARCH REPORT

 International application No.
PCT/US96/10974
A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : Please See Extra Sheet.

US CL : 106/205, 209, 213, 214, 617

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 106/205, 209, 213, 214, 617

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 2,078,836 (CARTER) 27 APRIL 1937, see abstract and the claims.	1-7
A	US, A, 3,433,691 (REESE) 18 MARCH 1969, see abstract and the claims.	1-7
A	US, A, 3,767,440 (OLIX) 23 OCTOBER 1973, see abstract and the claims.	1-7
A	US, A, 4,066,463 (CHOLLET) 03 JANUARY 1978, see abstract and the claims.	1-7
A	US, A, 4,828,616 (YAMASOE) 09 MAY 1989, see abstract and the claims.	1-7
A	GB, A, 1,268,127 (FOSECO INTERNATIONAL LIMITED) 22 MARCH 1972, see entire document.	1-7

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER:
IPC (6):

C09J 103/02