

# United States Patent Office

2,965,507

Patented Dec. 20, 1960

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2,965,507

## ADHESIVE SILICATE COMPOSITION

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No Drawing. Filed Jan. 6, 1958, Ser. No. 707,137

7 Claims. (Cl. 106-80)

This invention relates to an aqueous adhesive silicate composition characterized by a high degree of adhesiveness to cellulosic materials while being substantially non-adhesive to heated metal surfaces, to compositions and processes for imparting and improving nonadhesion of aqueous silicate adhesive compositions to heated metal surfaces, and to improvement in the preparation of paper-board via the use of such adhesives and compositions.

In the manufacture of laminated and corrugated paper-board, the term "corrugated board" is used throughout the specification and claims to refer to the corrugated material comprising at least one planar cellulosic liner bonded to a corrugated cellulosic element via the tips of the flutes of the corrugated element. The operations involved in preparing corrugated board generally comprise forming a corrugated element by passing a cellulosic sheet between corrugating rolls and while the sheet is still engaged in the rolls, applying an adhesive to the tips of the thus-formed flutes. Thereafter, a noncorrugated or planar cellulosic liner is applied against the adhesive-coated flutes of the corrugated element as the corrugated sheet passes between the corrugating roll and a pressure roll. The resulting "single-faced" element may then be used as such in certain applications, but more commonly there is subsequently applied to the exposed corrugated side of the single-faced element in a so-called "double backing" operation wherein adhesive is applied to the still exposed tips of the flutes and a second liner sheet is applied thereagainst. The thus-formed structure is passed through a so-called "hot plate" dryer section where it is heated between a continuously moving belt and hot plates or platen surfaces to dehydrate the adhesive and establish an adhesive bond, the assembled structure being held in smooth contact with the hot plates by steel idling rolls riding on top of the continuously moving belt.

Referring more specifically to the various operations involved in forming corrugated board, the initial bonding of a corrugated element to a liner is generally termed "single facing" and comprises adhering a corrugated cellulosic element to a flat cellulosic liner thereby to form a 2-ply structure permitting free bending in one direction. Such a product is known as a "single-faced" board and is typically used as such in wrapping and cushioning. In the formation of the adhesive bond in a single-facing operation, only a very short time is available for cementing the corrugated element to the flat liner as the corrugated roll and the pressure roll momentarily press the sheets into position and apply heat and pressure to the situs of the desired adhesive bond. Typical contact times in which the adhesive bond must be formed in a single-facing operation are of the order of about  $\frac{1}{50}$  to  $\frac{1}{100}$  of a second. In order to form a satisfactory adhesive bond in the short time available, it is generally the practice to apply as high a pressure as possible and to operate at a relatively high temperature, the latter typically varying between about 300° and 500° F., or more, usually between 340° and 400° F. In practice,

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the cellulosic materials being glued frequently have a lineal speed in the range of about 300 to 500 ft. per minute so that it will be appreciated that only a small time is available for forming the desired adhesive bonds.

The other principal operation referred to hereinbefore in forming corrugated board is that of applying a second liner sheet to a single-faced corrugated element. In this operation, which generally is termed "double-facing" and is accomplished in a so-called "double facer" or "double backer," a previously-formed, single-faced corrugated structure comprising a flat cellulosic sheet superimposed on, and bonded to, a corrugated, cellulosic element is provided with the second liner sheet bonded to the exposed flutes of the single-faced corrugated element.

The double-facing or double-backing process can be repeated as desired to form a so-called "double-walled" board comprising two flat liners and two corrugated members bonded to a third flat liner therebetween, or a so-called "triple-wall" board comprising four flat liners and three corrugated elements sandwich-style therebetween having the same or different flute heights, e.g., so-called "A," "B" or "C" flutes therebetween.

In forming the double-faced board in the double-backer, the problems encountered with respect to adhesive bonding are somewhat different from those involved in single-facing operations in that a longer time is available for forming the adhesive bond, typically from about 5 to 20 seconds. Also, somewhat lower machine temperatures are encountered, typical hot plate temperatures in a double-backer being about 300° to 350° F.

Difficulties in the manufacture of corrugated board arise when aqueous adhesive silicate compositions come in contact with the corrugating, pressure and idling rolls, platens of the hot plate dryers and other apparatus, undesirably forming glasslike, hard deposits thereon, thus fouling the rolls and hot plate sections and necessitating an interruption in production to remove the deposits. Further, as the laminated cellulosic structure passes between the belts and the platens of the hot plate section, some of the adhesive silicate composition frequently exudes from the portions of the laminate nearest the edges thereof, and is deposited upon the heated metal surfaces of the platens. After a relatively short time, these deposits of exuded silicate adhesive accumulate on the surface of the platens and other heated metal surfaces and build up into ridges or mounds near the edges of the moving laminated web and under the influence of the relatively intense heat are dehydrated to a hard, strongly adherent, solid silicate. Such hard deposits are then in a position to destroy the edges of the moving laminated structure passing across the heated surfaces.

Moreover, as the production of corrugated board of lesser and greater widths may be scheduled alternately on the equipment during a given production period, the changeover from the lesser to the greater width may leave hard, adherent silicate deposits of the dehydrated adhesive in position to mar substantial areas of the wider corrugated board formed on such equipment. When the accumulation of the deposits of dehydrated silicate is sufficient to cause a destruction of substantial areas of the wider, laminated web passing thereover, the entire operation must be interrupted and the heated metal surfaces cleaned before the further production of such wider widths may be undertaken. A major difficulty in the cleaning operation arises in the fact that the dehydrated silicate adheres quite strongly to the heated metal surfaces, requiring considerable time and hand labor to dislodge the deposit and refinish the surface. Accordingly, despite the many advantages of silicate adhesives, including, of course, a high degree of adhesion to cellulosic materials, one of the problems limiting their application

heretofore has been this undesirable adhesion to heated metal surfaces.

Accordingly, the principal object of this invention is to avoid the difficulties heretofore encountered with the undesired adhesion of silicate adhesives to heated metal surfaces in paperboard manufacturing apparatus.

Another object of the invention is to provide composi-

more generally available. Because of their lower cost and availability, sodium silicates are more widely used and therefore are preferred in the practice of the present invention.

Silicate adhesive compositions of this invention are set forth, together with desired proportions even more specifically in the following table:

Ingredient	Percent By Wgt.	Preferred Compositions		
		Ingredient	Percent By Wgt.	Specific Percent By Wgt.
Aqueous alkali metal silicate (alkali metal oxide:SiO <sub>2</sub> molar ratio of 1.0:2.5 to 4.0)	At Least 50%	Sodium silicate (Na <sub>2</sub> O:SiO <sub>2</sub> 1:3.3 to 3.5) Solids 35 to 47%	70-85	78.68
Polyhydroxy carboxylic acid	Up to 1.0 <sup>1</sup>	Gluconic Acid (50%)	.10 to .50	0.25
Clay	0-20	Barden Clay	8-14	8.56
Urea	0-8	Urea	3-10	6.86
Alkylolamine	0-3	Triethanolamine	0.1-1.0	0.15
Water (added)	0-10	Water (added)	5-8	5.5

<sup>1</sup> On a 100% basis.

tions and methods for decreasing the adhesion of an aqueous adhesive silicate composition to heated metal surfaces generally.

A further object of the invention is to provide methods and compositions for preventing the adhesion of aqueous adhesive silicate compositions to heated metal surfaces of corrugated board-forming apparatus.

A still further object of the invention is to provide a new and improved method of reducing adhesion of corrugated board manufacturing adhesives to heated metal surfaces of the corrugated board manufacturing apparatus.

A still further object of the invention is the provision of adhesive compositions of improved water and moisture resistance to reduce adhesion of alkali metal silicates to heated metal surfaces while providing a high degree of adhesion between paperboard elements.

In corrugated board manufacturing operations, the speed at which the corrugated board manufacturing apparatus can be operated is directly related to the time required to develop a satisfactory adhesive bond between the several cellulosic elements. Further, it is desirable to reduce the heating time required as much as possible. Accordingly, it is a still further object of this invention to provide new and improved silicate adhesives which not only have the aforementioned desirable characteristics but which also permit greater speed of operation of corrugated board manufacturing equipment.

Broadly, the present invention resides in a new and improved alkali metal silicate-containing adhesive of improved moisture and water resistance characterized by a high degree of adhesion to cellulosic materials, e.g., corrugated board-forming elements, while exhibiting a corresponding nonadhesion to heated metal surfaces.

More specifically, an aqueous silicate adhesive composition of this invention comprises, in combination, a small amount of a polyhydroxy carboxylic acid, a major amount of an aqueous alkali metal silicate, especially one having an alkali metal oxide:silicon dioxide ratio within the range from about 1.0:2.5-4.0, notably, sodium silicate, having an Na<sub>2</sub>O:SiO<sub>2</sub> ratio within the range from about 1:2.5 to 4.0. A preferred range is 1Na<sub>2</sub>O to about 3 to 3.5SiO<sub>2</sub>, the specifically preferred ratio being about 1Na<sub>2</sub>O:3.3SiO<sub>2</sub>, and when employed in the manufacture of paperboard generally including minor amounts of clay and/or urea and, in certain instances, a small amount of an alkylolamine. In addition, in order to obtain a predetermined viscosity, a small amount of water may be added. The term "alkali metal silicate" is intended to refer to silicates of the various alkali metals, i.e., sodium, potassium, lithium, rubidium and cesium, although silicates of potassium and sodium are

The expression "polyhydroxy carboxylic acid" as used in the specification and claims is intended to refer to various carboxylic acids containing at least two hydroxy groups and also to include salts of such acids, especially alkali metal salts, i.e., sodium, potassium, cesium, rubidium or lithium salts of such acids. Illustrative of such compounds are gluconic acid (1,2,3,4,5-pentahydroxycaproic acid), glucono gamma and/or delta lactone, sodium gluconate, ammonium gluconate, copper gluconate, ferrous gluconate, magnesium gluconate, manganese gluconate and potassium gluconate.

Gluconic acid and gluconic acid salts are preferred polyhydroxy carboxylic acid compounds because of their nontoxicity and noncorrosiveness. A specifically preferred additive is an aqueous gluconic acid, e.g., 50% concentration.

The term "clay" as employed in the specification and claims and in the practice of this invention is intended generally to refer to a non-swelling kaolin type clay, generally indicated as consisting essentially of Al<sub>2</sub>O<sub>3</sub>·2H<sub>2</sub>O·2SiO<sub>2</sub>. Suitable commercially-available clays are those available from natural quarries in South Carolina or Georgia. More specifically, the clay preferably in finely-divided, i.e., predominantly aluminum silicate materials of an average particle size of about 2 microns of which Barden clay is an example. It will be understood, of course, that the particle size of the clay can be varied.

In the foregoing table the amount of water specified is in addition to any water normally contained in the aqueous silicate itself which is indicated by the solids content specified. In some instances, it is not necessary to add any water, but generally, addition of a controlled amount of water is desirable to provide a predetermined solids content and thereby regulate the viscosity depending on the intended specific application in the manufacture of paperboard. For example, in single-facing operations it is desirable to have a viscosity not greater than about four poises, preferably 2.0 to 4.0 poises, and even more preferably, 3.0 to 3.5 poises. On the other hand, in double-backing operations it is desired to have an adhesive viscosity of at least 4 poises, desirably within the range from about 4.0 to 8.0 poises, and preferably 5.5 to 6.0 poises, these viscosity determinations measured at 20° C. by a Brookfield viscosimeter (Model LVF) a product of Brookfield Engineering Laboratories, Stoughton, Massachusetts.

In order that those skilled in the art may more completely understand the present invention and the preferred methods by which the same may be carried into effect, the following specific examples are offered, the

numerical data being presented in terms of grams unless otherwise indicated:

afforded by an adhesive of this invention when employed in the preparation of corrugated board, as compared

Example No.-----	1	2	3	4	5	6	7	8	9	10	11	12
Aqueous Sodium Silicate <sup>1</sup> -----	2,780	2,780	9,441.6	78.61	77.91	78.41	78.76	1,575	78.66	Percent 75 to 85 5 to 8	Percent <sup>†</sup> 75 to 85 5 to 8	81.16
Water (added)-----	5.25	15.75	660	5.5	5.5	5.5	5.5	110	5.5			5 to 8
Gluconic Acid (50%)-----	10.50	10.50	30	0.30	1.00	0.50	0.3	5	0.25	0.1 to 0.3	0.1 to 0.3	0.25
Triethanolamine-----	5.25	5.0	18	0.15	0.15	0.15	0.15	2.99	0.15	0.1 to 0.2	0.1 to 0.2	0.15
Clay-----			1,027.2	8.58	8.58	8.58	8.58		8.58	8 to 14	8 to 14	8.58
Urea-----			823.2	6.86	6.86	6.86	6.86		6.86	4 to 8	4 to 8	4.86

<sup>1</sup> Na<sub>2</sub>O:SiO<sub>2</sub>=1:3.3, 40.0° B<sub>e</sub>.-41.2° B<sub>e</sub>., specific gravity 1.318-1.397 (av. 37.3% solids).

<sup>†</sup> Na<sub>2</sub>O:SiO<sub>2</sub>=1:3.22, 41.5°-42.5° B<sub>e</sub>., specific gravity 1.40-1.415 (av. 38.8% solids).

The above adhesive compositions exhibit a high degree of adhesion to paperboard-forming elements and, conversely, are substantially nonadhesive to heated metal surfaces.

### Example 13

To illustrate the improvement in moisture resistance imparted to corrugated board formed using an adhesive of this invention, comparative bond strength tests are conducted on corrugated board bonded with an aqueous sodium silicate<sup>1</sup> containing no added gluconic acid and with an adhesive of this invention having the following composition:

	Percent by weight
Sodium silicate <sup>1</sup> -----	77.91
Water-----	5.50
Triethanolamine-----	0.15
Gluconic acid (50% solution)-----	1.0
Clay-----	8.58
Urea-----	6.86

<sup>1</sup> Na<sub>2</sub>O:SiO<sub>2</sub> 1:3.3, 40.0°-41.2° B<sub>e</sub>., specific gravity 1.381-1.397 (average 37.3% solids).

Samples of double-faced corrugated board adhesively bonded with each of the above adhesives are placed in a humidity cabinet (100% relative humidity) for 23 hours at 90° F. and then for two days in a constant temperature room (50% relative humidity and 22.2° C.) before subjected to a so-called "pin test," wherein the strength of the adhesive bond for a given number of flutes is conducted.

The test is conducted on a Riehle testing machine (compression tester). Steel pins, approximately 1/8 inch in diameter sufficient to fit within the flutes of the paperboard samples, alternately long and short as disposed in the sample, the longer pins resting upon a lower support underlying the longer pins at each end, and the alternating shorter pins being contacted by a downwardly extending compression jig engaging the shorter pins at each end. This assembly is placed between the jaws of the compression tester and pressure gradually applied. The pressure for a corrugated board sample 2 1/2" wide with 4 shorter pins applying downward pressure and 5 alternating longer pins being supported from underneath involve a total of 10 inches of glue line.

Using the above procedure, it is observed that a pressure of 25.9 lbs. is required to break the bond of the unmodified sodium silicate while the adhesive of this invention requires a higher pressure of 28.4 lbs. Thus, there is a 67% deterioration of the bond strength due to effect of moisture in the adhesive bond formed with unaltered sodium silicate while there is but a 61.5% deterioration in a comparable bond formed with an adhesive of this invention.

A similar test is made using an adhesive of this invention containing a smaller amount of gluconic acid (0.5% of a 50% solution of gluconic acid) and the latter exhibits a higher dry bond strength than the former gluconic acid-containing adhesive of this invention and moreover, in an 8 hour exposure to 100% relative humidity at 90° F. a pressure of 33 lbs. is required to break 10" of glue line bond, thus exhibiting only a 57% bond strength deterioration.

### Example 14

To illustrate the improvement in dry bond strength

with a corresponding unmodified sodium silicate,<sup>1</sup> experimental samples of double-backed corrugated board are subjected to the same compression test of adhesive bond strength described in the preceding example. The adhesive of this invention employed is the following:

- (1) 78.68% by weight sodium silicate<sup>1</sup>
- (2) 6.86% urea
- (3) 5.5% water (added)
- (4) 8.56 (or 8.58%) clay
- (5) 0.15% triethanolamine
- (6) 0.25% gluconic acid (50% solution)

It is found that the dry bond strength of the comparable corrugated board samples, differing only in the adhesive employed, require an average of 66.4 lbs. to destroy the bond in the gluconic acid-containing adhesive of this invention compared to 52.5 lbs. to destroy the same length of adhesive bond using the unmodified sodium silicate, thus indicating a marked improvement in adhesive dry bond strength.

It is to be understood that although the invention has been described with specific reference to particular embodiments thereof, it is not to be so limited, since changes and alterations therein may be made which are within the full intended scope of this invention as defined by the appended claims.

What is claimed is:

1. An adhesive composition consisting essentially of an aqueous alkali metal silicate containing about 30% to 50% solids and having an alkali metal oxide:SiO<sub>2</sub> ratio within the range from about 1:2.5 to 4.0, about 0.1% to 1% of gluconic acid and about 0.1% to 3% of triethanolamine.

2. An adhesive composition consisting essentially of, an aqueous sodium silicate, having an alkali metal oxide:SiO<sub>2</sub> ratio within the range from about 1:2.5 to 4.0 and containing about 30% to 50% solids, about 8% to 14% of clay, about 3% to 10% of urea and about 0.1% to 1% of gluconic acid.

3. An adhesive composition consisting essentially of, in combination, about 70% to 85% by weight of an aqueous sodium silicate containing about 35%-47% solids, and having an Na<sub>2</sub>O:SiO<sub>2</sub> ratio within the range from about 1:2.5 to 4.0, about 0.1% to 0.5% by weight of gluconic acid, about 3% to 10% by weight of urea, about 8% to 14% by weight of clay, about 0.1% to 1.0% by weight of triethanolamine.

4. An adhesive composition consisting essentially of, in combination, about 75% to 80% of an aqueous sodium silicate having a Na<sub>2</sub>O:SiO<sub>2</sub> ratio within the range from about 1Na<sub>2</sub>O:3.3 to 3.5SiO<sub>2</sub>, about 0.1% to 0.2% triethanolamine, about 0.1% to 0.3% gluconic acid, about 8% to 14% clay and about 5% to 8% added water.

5. The method of preparing paperboard which includes the step of applying to cellulosic elements to be joined as the adhesive therefor the composition of claim 2.

6. The method of preparing paperboard which includes the step of applying to cellulosic elements to be joined as the adhesive therefor the composition of claim 3.

<sup>1</sup> Na<sub>2</sub>O:SiO<sub>2</sub> 1:3.3, 40.0°-41.2° B<sub>e</sub>., specific gravity 1.381-1.397 (average 37.3% solids).

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7. The method of preparing paperboard which includes the step of applying to cellulosic elements to be joined as the adhesive therefor the composition of claim 4.

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