United States Patent Office

3,306,812

Patented Feb. 28, 1967

3,306,812

PROCESS OF SIZING SHAPED FIBROUS ARTICLES WITH POWDERED FATTY ACIDS OF 18 TO 24 C ATOMS

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No Drawing. Filed Feb. 10, 1964, Ser. No. 343,484

7 Claims. (Cl. 162—165)

This invention relates to the manufacture of hardboards or other shaped articles from fibrous materials particularly those containing cellulose, and more particularly relates to the sizing of shaped articles and in particular hardboards during their manufacture.

There is considerable variation in the water-sorption properties of hot pressed hardboards made by standard wet-forming processes. In many instances the water sorption of unsized hardboards is greater than that permissible under various building codes and accordingly in most instances it is necessary to size or waterproof hardboards at some stage in their manufacture to meet building code requirements.

There are presently a number of known methods for sizing hardboards. One commonly used method is that of adding a rosin to the hardboard stock prior to forming it and to precipitate the rosin in the stock or on the fibres by using a precipitating agent, most commonly alum (aluminum sulfate), and/or mineral acids which lowers the pH of the stock. Frequently, the rosin is fully or partially replaced by a wax emulsion. Generally the amount of rosin or wax utilized varies between one and three percent and the amount of alum between three and six percent of the total solids content of the stock; the amount depending upon a number of factors such as the mill and the type of raw material being utilized to manufacture the hardboard.

Other less commonly utilized sizing compounds include vegetable waxes, lower fatty acids and esters thereof, vegetable oil, tallows, petroleum oil, etc., which, in most instances, are incorporated into the hardboard in a manner similar to that utilized with rosin and wax emulsion. In the past the lower fatty acids were saponified or emulsified before addition and precipitated in the pulp stock using precipitating agents.

Also known is a method of treating hardboard after it is made which involves its immersion in, or spraying with, a drying oil and its subsequent heating to a temperature high enough to polymerize the oil. This process is sometimes referred to as a tempering process. Also known is the use of a process which involves incorporating a drying oil into the pulp with some type of carrying agent before the forming process. An example of this process is described in United States Patent No. 2,987,382, issued April 4th, 1961, to Harland H. Young et al. on Incorporating Oil in Hardboard.

It has also been suggested that suitable sizing may be accomplished by vapor sizing paper and fibreboard after forming with a medium chain length fatty acid of 10 to 16 carbon atoms.

As indicated above the most commonly used method for precipitating the sizing involves the use of a metallic salt and/or mineral acid to lower the pH of the pulp stock and it has been found to have a number of faults, one very serious one being that apparently the precipitated sizing agent adheres to the stock fibres at a point which blocks

subsequent bonding of the fibres during forming of the stock. This results in a substantial loss of strength of the sized product as illustrated in the following table.

TABLE 1

Treatment and Quantities (Poplar), Wood Fibres	Density, gm./cc.	Modulus of Rupture, lbs./in.^{2}	Water Sorption, Percent by Weight
Check Hardboards (no sizing)	0.95	4,048	64.0
Hardboards Sized with 1% wax (emulsion) and 3% alum	0.96	3,024	4.3

It is common practice to counteract this loss of strength by adding a small amount of phenol-formaldehyde or other thermosetting resin to the pulp stock, this normally being added together with the sizing compound.

Another practical disadvantage of the commonly used sizing process discussed above is that careful adjustment of the pH of the pulp stock to the proper level before and after the sizing compound is added, is necessary. Also the pulp stock normally must be adjusted to a fairly low pH, sometimes as low as pH 4.5, before the forming and hot-pressing steps. The use of stock having a pH this low frequently results in a substantial amount of corrosion of the forming and pressing equipment with the consequent expense of premature repair and replacement.

It is an object of this invention to provide a process for sizing hardboards and other shaped fibrous articles to a low level of water sorption which substantially decreases and under some circumstances eliminates the particular disadvantages noted above as being associated with present commonly used hardboard sizing processes. A further advantage of the process of this invention results from the fact that no alteration in the normal forming or hot-pressing steps is usually required in carrying out this invention.

It has now been found that it is possible to size hardboards by a process which involves the use, as a sizing agent, of a normal, long chain saturated fatty acid. The particular long chain saturated fatty acids which have been found suitable for use in accordance with this invention range from stearic, C–18 to lignoceric, C–24 with behenic acid, C–22, normally providing the best results. Some, although admittedly very little sizing effect is obtained in accordance with the present invention through the use of stearic acid whereas the use of lignoceric acid is severely limited at the present time as the result of its scarcity and high cost. Consequently the preferred acids are arachidic, C–20 and behenic, C–22 with behenic having been found most suitable. Unsaturated fatty acids have not proven effective and the methyl ester of the behenic acid was found much less effective than the free fatty acid. Presumably, esters of the other saturated fatty acids of this invention are less effective than their corresponding free acids.

Mixtures of long chain fatty acids are also utilizable and may be preferable for use in commercial processes because suitable mixtures are available at a more reasonable cost than pure behenic or arachidic acid. Mixtures of long chain fatty acids within the above-mentioned range and with less than 15% of acids with fewer than 20 carbon atoms are very effective and preferred for use in accordance with the present invention. One example of such a mixture is "Hystrene 9022" sold by Humko Products which, although not highly satisfactory in its pur-

chased form has proven to be very satisfactory after having been recrystallized from an organic solvent such as acetone. In the examples, unless otherwise noted, reference to "Hystrene 9022" will mean this product after having been recrystallized once from acetone. This mixture (recrystallized) consists of C–16, 2%; C–18, 10%; C–20, 72%; C–21, 3%; and C–22, 13%. Also utilizable is "Hydrofol Acid 560" obtainable from Archer-Daniels-Midland Co., which contains 80% behenic C–22, 12% arachidic C–20, and 8% stearic C–18 acids.

Although the amount of sizing agent which must be added in accordance with the present invention to obtain good results may vary, depending upon the type of pulp stock being utilized and the forming and pressing methods used, it has been found that normally about 1% by weight of the total solids content of the pulp stock, will result in a well sized hardboard with a suitable range being from 0.5 to 2%.

Table 2 shows the sizing effect obtained by adding different amounts of various fatty acids to hardboard stock.

TABLE 2.—HARDBOARDS FORMED FROM POPLAR FIBRES

[Except as Noted]

Fatty Acid (or mixtures)	Chain Length (Carbon Atoms)	Amount Added, percent by Weight	Water Sorption, percent by Weight
Check Boards (mean)			46.4
Lauric	12	0.5	68.2
Do	12	1.0	73.0
Palmitic	16	0.5	60.6
Do	16	1.0	46.5
Palmitic Stearic 50:50	16, 18	0.5	17.7
Do	16, 18	1.0	11.2
Behenic	22	0.5	11.6
Do	22	0.75	7.7
Do	22	1.0	6.7
Hydrofol 560	18, 20, 22	1.6	7.7
Hystrene 9022 (Jackpine)	16-22	1.0	6.1

As indicated above, best results are obtained with the addition of approximately 1% by weight of fatty acid.

The fatty acid sizing agents utilized in accordance with the present invention are normally added as a powder to the pulp stock before the stock is formed. The powder must be well mixed into the pulp stock and as it will normally be somewhat difficult to disperse, it is preferable that the powder be ground fine enough to pass through a fifty mesh sieve. Normally, if a mixture of fatty acids is utilized in which the percentage of medium chain length, i.e., below C–20, fatty acids is too high, difficulty will be encountered in rendering the solid mixture fine enough to be readily dispersable. After the sizing agents have been mixed into the pulp stock, the stock is shaped and hot-pressed in the normal manner and at the usual temperatures utilized in known hardboard forming processes.

A particularly important advantage obtainable through the use of the present invention resides in the fact that the pH of the pulp stock when the sizing agent is added is not as critical as with previously known processes in that it can range from between about 4 and 10 depending on the particular pulp stock. Normally a pH of from 7 to 8 has been found satisfactory. (For example best sizing with behenic acid was obtained using jackpine pulp at a pH of about 7 and using poplar pulp at a pH of about 8. Furthermore with jackpine pulp the strength of the resultant board increased as the pH increased from 5 to 10 although with poplar pulp there was no significant change in strength from a pH of 4 to 10). The preferable pH range is from 5 to 8 which is the natural range for most pulps (as received) to be used for manufacturing hardboards and this fact makes the process of the present invention particularly suitable for commercial application.

If an exceptionally strong hardboard is desired the fatty acid sizing agents of the present invention can be added to the pulp stock together with a suitable thermosetting resin such as phenol-formaldehyde with which they are compatible, and the resulting board will have increased

strength over a board which has been prepared using only the fatty acid sizing agent. The amount of phenol-formaldehyde added will normally be from about 1 to about 3% although, as with the sizing agent, from the standpoint of cost it is obviously preferable to utilize as little as possible bearing in mind the final requirements for the water sorption and strength characteristics of the hardboard being produced.

Table 3 shows the effect of utilizing phenol-formaldehyde and behenic acid for the combined purpose of increasing the resultant hardboards' strength and sizing it.

TABLE 3.—HARDBOARDS FORMED FROM JACKPINE PULP

	Density, gm./cc.	Modulus of Rupture, lbs./in.^{2}	Water Sorption, percent by Weight
Unsized Check Boards (mean values of number of samples checked)	0.93	5,206	18.3
1% Behenic Acid	0.93	4,741	6.7
2% Phenol-formaldehyde and 1% Behenic Acid (mean value of number of samples checked)	0.92	6,515	7.6

Alum may also be added together with the fatty acid sizing agents to obtain even better sizing. Alum improves the sizing but usually reduces the strength of the boards with the strength loss being normally greater with soft wood fibers than with hard wood fibres. Of course, some of the benefits resulting from the use of the process of this invention may be diminished to some extent through the addition of alum.

It is also possible to add a commercial wax emulsion such as Paracol 404N together with the fatty acid sizing agents and alum in order to achieve a hardboard possessing a combination of characteristics which may be desirable under some circumstances. When a commercial wax emulsion is utilized it is necessary to lower the pH of the pulp stock to about 4.5–5 by adding alum or some other suitable agent if the wax emulsion is to be effective.

It is suggested that what occurs in the process of this invention is that the fatty acid sizing agents, having a relatively low vapor pressure, do not react or vaporize within the board until the temperature within the board reaches a certain level. When this temperature level is reached enough vapors are released to attach the molecules of the fatty acids to the hydrophilic groups on the fibres thus rendering them hydrophobic. As there is normally little loss in strength resulting from the use of these fatty acid sizing agents it is believed that only the groups, presumably hydroxyl because they take up water, which have not previously reacted to give the board strength, react with the fatty acid molecule. It is also suggested that perhaps a number of the large fatty acid molecules block the penetration of water molecules into the hardboard. Fatty acids below C_{18} may vaporize or dissolve and be lost.

The following examples are given only for the purpose of illustrating certain embodiments of the invention and are not to be considered as limiting the invention, whose scope is as defined in the appended claims.

Example I

The data in Tables 1, 2 and 3 was obtained from hardboard which was made from jackpine or poplar fibres.

The pulp was prepared by putting the fibres or chips through an Asplund defibrator at a steam pressure of 125–135 p.s.i. and the resultant pulp was then refined by passing it through an eight inch Bauer refiner having a plate clearance of 0.030 inch. The sizing agent, and when required the strengthening agent in the form of phenol-formaldehyde was added to the pulp stock and stirred in for approximately five minutes before forming the wet mat on an 8 x 8 inch deckle former. After being formed the boards were cold pressed at 100 p.s.i. and then hot-pressed at 800 p.s.i. for the initial pressure and 200

p.s.i. for the holding pressure at 400° F. Standard methods (Canadian Government Specification Board No. 9-GP-17P) of testing were utilized in every respect except the size of the coupons and the submersion time for the water sorption test. Unless otherwise specified water soptions were done on a 2½ by 2½ inch coupon under one inch of water for two hours and expressed as a percent by weight of the coupon prior to submersion.

Example II

Hardboards were prepared from poplar and spruce chips. The pulp was prepared by putting the chips through an Asplund defibrator at a steam pressure of 135 p.s.i. and the resulting pulp was refined by passing it through a twelve inch Sprout-Waldron refiner having a plate clearance of 0.020 inch. One batch of pulp stock, obtained from poplar chips, had added to it 1% phenol-formaldehyde, 2% alum and 1% behenic acid. The second batch of pulp stock prepared from spruce chips had added to it the same amount of phenol-formaldehyde, alum and behenic acid. A third batch of pulp stock made from spruce chips had the same amount of phenol-formaldehyde and alum added to it and 1% Hystrene 9022 instead of the behenic acid. A fourth batch of pulp stock prepared from spruce chips had the same amount of phenol-formaldehyde and alum added to it and 1% wax (Paracol 404N), a commercial wax-emulsion instead of the acid. The boards were formed in an 8 x 8 inch deckle former, cold pressed at 100 p.s.i. and then hot pressed at 200 p.s.i. and 400° F. after a primary press at 800 p.s.i. for one minute. Standard methods of testing were used in every respect (see Example I) and the following data obtained.

TABLE 4

	Water Sorption percent (24 hr. submersion period)	Thickness Expansion, Percent	Modulus of Rupture, lbs./in.²
Poplar 1% Behenic	14	10	4,000
Spruce 1% Behenic	15	12	3,500
Spruce 1% Hystrene	18	12	5,100
Spruce 1% Wax (Paracol)	25	13	5,200

Example III

Spruce chips were put through an Asplund defibrator at a steam pressure of 135 p.s.i. and the resultant pulp was then refined by passing it through a twelve inch Sprout-Waldron refiner at a plate clearance of 0.020 inch. One batch of pulp stock was then formed into boards on an 8 x 8 inch deckle former, cold pressed at 100 p.s.i. and then hot pressed at 800 p.s.i. for the initial high pressure and 200 p.s.i. for the holding pressure for twenty minutes at 400° F. Another batch of the same pulp stock was formed into boards in the same manner after having added to the pulp stock 1% behenic acid.

The properties of the resultant boards were found to be; density 0.92 gm. per cc.; modulus of rupture 4988 p.s.i., water sorption (7 x 7 inch coupon submerged for 24 hours) of control board 62% by volume, and water sorption of behenic acid sized boards less than 30% by volume thus indicating the substantial sizing effect of belhenic acid.

Example IV

Hardboards were made as in Example III from three types of wood chips, poplar, spruce and jackpine. One group of boards was not sized, a second group was sized with behenic acid, a third group with behenic acid and alum and a fourth group with commercial wax (Paracol 404N), and alum. Tests were made on 7 x 7 inch samples submerged for 24 hours under one inch of distilled water at 25° C. The water sorptions noted below were obtained (being expressed as percent by volume, taking the density of water as 1).

TABLE 5.—WATER SORPTION

Type of Wood	No Sizing	1% Behenic	1% Behenic, 2-3% Alum	1% Commercial Wax, 2-3% Alum
Poplar	64	28	16	55
Spruce	52	23	15	22
Jackpine	52	21	12	16

Example V

Hardboards were made from spruce wood chips as in Example III. One group of boards was not sized, a second group was sized with 1% Hystrene 9022, and a third group was sized with 1% Hystrene 9022 and 2% alum. The test data on these groups of boards are presented in the following table to show the effect of sizing with commercial mixed fatty acids and also to show that these commercial mixtures will size hardboards well enough to meet Canadian Government Specifications for either Type A, Class I or Class II hardboards. All tests were made according to those described in C.G.S.B. Schedule 9-GP-17.

TABLE 6

	Modulus of rupture, lbs./in.²	Water sorption, percent by volume*	Thickness expansion, percent
Control boards, no sizing	5,478	59.2	28.7
Sized with 1% Hystrene	4,866	21.6	13.6
Sized with 1% Hystrene plus 2% Alum	4,760	10.6	7.9
Canadian Government Specification Requirements for Type A, Class I	4,000	16	8
Type A, Class II	2,700	30	15

*7 x 7 inch coupons submerged for 24 hours.

Example VI

This example illustrates the sizing effect obtained with a mixture of Paracol (wax emulsion) and behenic acid. Hardboards were prepared from poplar pulp similarly to Example III. The amount of sizing agent is based on total solids of these agents on a percentage of dry fibre. Water sorption tests were made on 2½ x 2½ inch coupons submerged for two hours.

TABLE 7

Sizing agent:	Water sorption Percent by weight
Control	73.2
1% Behenic acid	9.5
1% Behenic acid, 2% alum	5.6
1% Paracol, 2% alum	15.4
0.5% Paracol, 0.5% behenic acid, 2% alum	8.1

In summary new and significant advances have been provided in the sizing of hardboards which consist essentially in the use as a sizing agent of a saturated long chain fatty acid or mixtures thereof and in particular behenic acid and mixtures containing high percentages of C-20 and/or C-22 acids, this agent being mixed into the pulp stock before forming. The invention is particularly effective with hardwood pulps such as Poplar in terms of effective sizing with low strength loss. Tests have shown that compared to the free acids of the present invention, their esters are not good sizing agents.

We claim:

1. A process for sizing relatively rigid shaped fibrous articles such as hardboards, prepared from a slurry of fibrous pulp stock comprising mixing into said slurry while at a pH of from about 4 to about 10, about 0.5 to 2% by weight of the total solids content of the slurry of a sizing agent consisting of a dry powdered, free, saturated, long

chain fatty acid having from 18 to 24 straight chain carbon atoms in its molecule, forming the pulp into a shaped article and hot pressing said shaped article at a temperature sufficient to cause said fatty acid to vaporize within the shaped article.

2. The process of claim 1 wherein said fatty acid is sufficiently finely powdered to pass through a fifty mesh sieve.

3. The process of claim 1 wherein mixtures of said fatty acids are used with there being less than about 15% of said fatty acids having fewer than 20 carbon atoms.

4. The process of claim 1 wherein said fatty acid has from 20 to 22 carbon atoms.

5. The process of claim 1 wherein a sizing amount of a wax emulsion and a precipitating amount of alum are also mixed into said slurry.

6. The process of claim 1 wherein about 1 to 3% by

weight of a thermosetting resin based on the total solids content of the slurry is also mixed into the slurry.

7. The process of claim 1 wherein about 1 to 3% by weight of phenol-formaldehyde based on the total solids content of the slurry is also mixed into the slurry.

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