(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
16 May 2002 (16.05.2002)

PCT

(10) International Publication Number
WO 02/38864 A2

(51) International Patent Classification[7]: D21H 21/34

(21) International Application Number: PCT/IL01/01024

(22) International Filing Date:
5 November 2001 (05.11.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
139603 10 November 2000 (10.11.2000) IL

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/38864 A2

(54) Title: FLAME-RETARDED PAPER PRODUCTS AND METHOD AND APPARATUS FOR MAKING THEM

(57) Abstract: A flame-retarded paper product comprises as a fire-retardant (FR) ingredient a compound selected from among inorganic and organic flame-retardant compounds. A method of making a flame-retarded paper product is described, which comprises: a) producing a base paper; b) applying to the paper base at least one FR compound, to form a layer comprising said compound; and c) applying to the base paper, over said layer, a coating color and/or laminate and/or surface sizing

FLAME-RETARDED PAPER PRODUCTS AND METHOD AND APPARATUS FOR MAKING THEM

Field of the Invention

The present invention relates to flame-retarded paper products and to processes and methods for making the same. More particularly, the invention relates to flame-retarded paper products, comprising as an active ingredient a compound selected from among inorganic and organic flame-retardant compounds, particularly ammonium bromide and its mixtures with other ammonium salts, e.g., ammonium sulfate, mono- or diammonium phosphate, ammonium polyphosphate, ammonium sulphate, urea, organic brominated flame retardants and their mixtures. More particularly, it relates to a paper product comprising a paper base, a layer comprising flame-retardant (FR) compound or compounds, and a layer of a coating color and/or laminate and/or surface sizing overlying the FR layer. It also relates to a method and apparatus for making such a product.

Background of the Invention

An unfortunate feature of modern life is the large number of fires which occur in occupied buildings. Statistics show that in many of these fires paper and packaging materials are the first item ignited. The majority of such fires result from ignition using small energy sources such as matches, and many of these fires could have been avoided if the paper had been treated with a flame-retardant additive designed to impart ignition resistance.

The major component of paper is wood fibers , mainly contaning cellulose. Natural cellulose is a polysaccharide consisting of β-glucose units linked by ether bonds. When

cellulose is burned, a mixture of gaseous and solid combustion products result and the burning takes place both at and above the surface. A study of the pyrolysis of cellulose shows that the major product is a tarry substance that consists mainly of laevoglucosan. If the formation of laevoglucosan is prevented, the flammability of cellulose is reduced. This is achieved by the use of phosphorus containing compounds such as ammonium phosphates which release phosphoric acid when strongly heated, and the resultant acid esterifies the glucose units to produce glucose-6-phosphate. The phosphoric acid also promotes the formation of a solid carbonaceous char in the cellulose which does not support combustion.

An important feature of burning paper is after-glow, which occurs usually after the flames are extinguished and which could ignite adjacent materials. Glow is defined as the combustion of a material without flame but with emission of visible light from the combustion zone surface. The phenomenon of after-glow is poorly understood but is believed to involve the carbon at the surface of the cellulose, carbon dioxide, carbon monoxide and oxygen. Phosphorus-based flame-retardants are effective at preventing after-glow and are assumed to function in two ways (a) by forming a film of condensed acid over the surface of the cellulose thereby preventing access of oxygen to the burning site (b) by absorbing some of the heat required for further combustion of the cellulose.

Burning of cellulose in the gas phase proceeds by a free radical chain reaction mechanism involving hydroxy, oxygen and other reactive free radical species. Obviously if these active radicals can be neutralized, combustion will cease. Halogen-based materials, particularly bromo-compounds, are effective in terminating free radical chain reactions and are

widely used as flame-retardant additives for a wide variety of substrates including paper. Chlorine compounds have the same mode of action as bromine compounds. The net effect of the use of these materials is the production of the deactivating halogen free radical.

Flame retardancy cellulosic materials are disclosed in US 3,667,999, in which a basic cellulose structure is treated by immersion in a bath containing, *inter alia*, ammonium bromide. US 4,102,794 teaches impregnation of various materials with an aqueous solution comprising at least three ions selected from ammonium, zinc, bromine, chlorine ions, alkaline-earth metal ions and phosphate ions. US 4,888,136 teaches impregnation of cellulosic materials with a composition comprising ammonium bromide and, at least, one water-soluble aluminum salt of an organic hydroxy acid, such as aluminum citrate or lactate.

While it is known in the art to use flame-retardant compositions, including those based on ammonium bromide, to impart flame retardancy to paper products all prior art methods are based on the impregnation of the paper product. Impregnation presents several disadvantages: the flame-retardant material is easily leached away from the paper, thus diminishing the flame-retardant effect, and relatively high amounts of flame-retardant material are needed, which are not only expensive, but which adversely affect the properties of the paper product. The paper properties are changed, the brightness and the tensile strength decrease with increased amount of flame retardant.

The flame retardant slowly diffuses under the influence of air and acquires a yellowish color. The accelerated aging causes more rapid diffusion into paper.

It is important that additive flame retardants – hereinafter, briefly, FR - do not impair the desirable characteristics and properties of the paper, such as strength, flexibility and brightness.

It is clear that there is a great need for a method and compositions which permit to reduce the amount of flame-retardant material employed, while maintaining a high level of flame-retardancy with time.

While it is highly desirable to render the paper products flame-retarded to a substantial extent, flame-retarding inevitably results in some deterioration of mechanical properties, particularly tensile strength and tearing strength. It would be important to reduce said deterioration to a minor and possibly irrelevant degree and to maintain the ratio between tensile strength and tearing strength substantially unvaried.

It is therefore a purpose of this invention to provide paper products, particularly in sheet form, that are adequately flame-retarded and have a surface that is coated so as to accept printing, writing and drawing. The term "paper", as used herein, is meant to indicate all kinds of paper products including, but not limited to, paper board.

It is another purpose of this invention to provide flame-retarded paper products having a combination of a high degree of flame-retardancy and mechanical properties that are substantially the same than, or are very close to, the properties of the conventionally coated base paper.

It is a further purpose of this invention to provide a method of applying the FR compound or compounds to the base paper, which will result in a product having industrially acceptable mechanical properties, not substantially inferior to those of paper that does not contain FR compounds, or at least are changed to a very minor and substantially irrelevant degree.

It is a still further purpose of this invention to provide a method of applying the FR compound or compounds to a base paper which will result in a paper product having substantially undiminished, or only slightly diminished, tearing strength and tensile strength and having the same ratio between the two said parameters as the same paper to which the FR compound or compounds have not been applied.

It is a still further purpose of this invention to provide an apparatus for the production of paper products, in particular a coating apparatus, that is modified with respect to the conventional apparatus in such a way as to allow to carry out the aforesaid method.

Other purposes and advantages of this invention will appear as the description proceeds.

Summary of the Invention

This invention relates to flame-retarded paper products comprising as an active ingredient a compound selected from among ammonium bromide, diammonium phosphate, ammonium sulfate, ammonium polyphosphate, urea, brominated organic flame retardants and their mixtures.

Throughout the description to follow, ammonium bromide will be referred to as the flame-retardant but it should be understood that this does not involve a limitation and that the examples and statements made with reference to it apply, *mutatis mutandis*, to other flame-retardants as well.

More specifically, this invention provides a paper product, which comprises a base paper, a layer of an FR compound or compounds, preferably including a first binder, and an uppermost layer of a coating color.

The first binder is preferably starch. The coating color layer also preferably comprises a second binder, which is preferably the same as the said first binder but it could be styrene, acrylate, vinyl acetate, etc.

The invention further comprises a method for making the aforesaid paper product, which method comprises: a) producing a base paper; b) applying to the base paper at least one FR compound, to form a layer comprising said compound; and c) applying to the paper base, over said layer, a coating color.

The base paper is made by conventional processes and apparatus and need not be particularly described. The FR compound is applied preferably by spraying on the base paper a liquid phase comprising the FR compound and a first binder. The first binder preferably starch, but could also be a latex or a polymeric binder or a combination thereof. Other ways of applying the FR compound, e.g. spreading, may be used, but spraying is preferred, particularly because of the low viscosity of the liquid phase. Preferably, the FR compound layer is dried before applying the coating color.

The coating color also comprises a second binder, which may be the same as the first binder and is preferably starch, and a pigment or pigments chosen by conventional criteria, and can be applied in any convenient way, such as by providing an aqueous bath of the color and binder and applying the aqueous phase of the color and binder onto the paper by any convenient coating means, or by spreading said aqueous phase onto said paper. It should be understood that the application of coating color to a base paper is conventional and need not be particularly described. Preferably, the thickness of the coating color layer is controlled by a blade or the like.

Preferably, in the paper product of the invention, after drying, the FR compound layer is located between the base paper and the coating color layer, which has a thickness of about 5 to about 30 μm . The coating may consist substantially of calcium carbonate, which may or may not comprise additional pigments, e.g., colors or whitening agents, and binders.

The invention also encompasses a flame-retarded paper product comprising a flame-retardant or flame-retardant mixture in an amount of between 0.01% by weight of the paper to about 10% by weight of the paper, on a dry basis.

The invention also provides an improvement to paper coating machines, which comprises adding to said machines, before the coating application components, viz. the coating unit, a spraying device provided with nozzles, and preferably adding dryer means between said spraying device and said coating unit.

The remaining components of the coating machine are the same as in conventional operations. The coating machine can be integrated into the paper machine in a way that is conventional and well known to skilled persons. Such integration therefore will not be described, but should be understood as optionally comprised in the invention.

Brief Description of the Drawings

The drawing (Fig. 1) schematically illustrates a paper coating machine, which comprises all the conventional components of such machines and additionally comprises means for spraying a composition comprising the flame-retardants and the binder onto the paper base, and drying said composition.

Detailed Description of Preferred Embodiments

The present invention will be illustrated by specific examples which are not intended to limit it.

The drawing illustrates schematically a flame-retarding and coating apparatus, which can be inserted into or otherwise coupled to a paper making machine in any convenient way, easily devised by skilled persons to suit the specific paper making machine.

The base paper is a continuous sheet 10 supplied from a drum 11. It travels from right to left looking at the drawing. Numeral 12 indicates guide rollers which bring sheet 10 to a position in which an FR solution 13 is sprayed onto it by a sprayer schematically indicated at 14. The FR solution, with a binder, is supplied from a tank not shown, through a pump not shown.

The paper base 10, which is now coated with a layer of FR solution, passes through IR dryers 15, while being supported by general support 16, and the dryers are so adjusted as to bring the temperature of the paper sheet to 60 - 70°C. The dried base paper then passes through coolers 17, where it is cooled by air blowers substantially to room temperature.

The base paper 10, carrying now a dried layer of FR compound or compounds, including the binder, is indicated by numeral 10'. Coating is applied thereto from a bath 18 through a roller 19, which draws from the bath an aqueous phase comprising pigment and binder transfers it to the base paper. The coated paper is then guided by roller 20. Numeral 21 indicates a blade which scrapes the surface of the paper sheet, carrying the coating color, to control the thickness of said color. Other thickness controlling means could be used. The paper sheet is then guided by roller 22 and passes through dryers 23, which are similar to dryers 15, though they may deliver a different amount of heat. The drying is carried out at this stage, as well as in the previous stage, in such a way as to bring the paper sheet to temperatures from 20 to 90°C and preferably not lower than 60°C. The dried paper then passes through two coolers 24, similar to coolers 17, but that are so controlled, in combination with the other parameters of the process and particularly the traveling speed of the paper web, as to heat the paper, in the drying phase, to temperatures between 20 °C and 90°C, but preferably not lower than 60°C. The weight of the coating is from 5 to 30 g/m^2, preferably 10-15 g/m^2. The coated and dried paper is the final paper product, which is indicated at 10". Paper sheet 10" is wound up on the roller system 25, which has also the task of applying to the paper sheet sufficient traction to draw it through various stages of the apparatus described.

The sprayer 14 is not illustrated, since it may any conventional sprayer. In its simplest form, it may consists of a pipe, preferably of plastic, provided with nozzles, which are spaced at such distances as to coat the whole width of the base paper with a uniform layer of the FR compounds and the binder.

As has been said, a preferred FR compound is ammonium bromide and is applied to the base paper, preferably by spraying, in amounts between 0.01% and 10% of the weight of the paper. It is applied to the paper as an aqueous solution having a concentration between 10 wt% and 80 wt%, but preferably between 20 wt% and 40 wt%.

The coating may be any conventional coating. For example, it may be prepared by providing a pigment slurry and adding to it a binder, preferably starch or e.g. a latex, and mixing well, e.g. for 45 minutes before using. The thickness of the coating layer, when wet, on the paper may be, for example, from 5 μm to 30 μm. The coated paper is dried in drying unite that are preferably IR dryers, which are so controlled, in combination with the other parameters of the process and particularly the traveling speed of the paper web, as to heat the paper, in the drying phase, to temperatures between 20 °C and 90°C, but preferably not lower than 60°C. The weight of the coating is from 5 to 30 g/m^2, preferably 10-15 g/m^2. Preferably, the paper carrying the FR compound or compounds is dried, before applying the coating, in the same way in which the coated paper is dried and in similar drying units.

The sprayed paper is coated with a coating color consisting, for example, of the following formula (Table I):

Table I

Solids content	62%
pH	8.3
	pph (parts per 100 parts of dry pigments)
Pigment	100
Binder	10
Water-soluble polymer	1

The coating color adding to it a binder,latex or starch and mixing , the pigment slurry and adjusting the pH to the right level. The water-soluble polymer is added with the required water addition to achieve the right solids content.

Ignition and non-ignition tests are carried out as described hereinafter.

The amount of starch, when the binder is starch as preferred, in the solution applied to the paper base, is from 0.5 to 20 wt%, preferably 4 – 8 wt%.

Example

The base paper was chemical pulp base paper with a weight of 75 g/m^2. The base paper was sprayed with a solution containing 38 wt% of ammonium bromide and 6 wt% of starch. The speed of travel of the base paper was 100 m/s. The average weight of FR compound and starch on the base paper was 5.5 g/m^2. The mean tear index of the base paper was 9.13 mNn^2/g. The mean tensile index was 53.6 Nm/g. If said base paper is coated in a conventional way, without spraying FR compounds, to an amount of about 8

g/m^2, the mean tear index is lowered to 8.05 mNn^2/g and the mean tensile index to 48.0 Nm/g. After spraying the FR compound and the starch together, as stated hereinbefore, the mean tear index is 8.51 and the mean tensile index is 47.0; but if coating is later applied to the paper, the mean tear index is lowered to 7.45 and the mean tensile index to 41.2. It is seen that both those indices are lowered by the application of FR compound, but not to a considerable extent, while their ratio is lowered only from 5.95 to 5.53.

The mechanical properties of the paper resulting from the Example are set forth more completely in the following Tables II and III.

Table II

Tensile index

Nm/g	coated paper %
18	0
16	2.5
14.9	5
14	10

Table III

Tear index

mNm^2/g	coated paper %
5.1	0
5.7	2.5
5.2	5
5.3	10

The effects of the flame-retardation were determined as set forth hereinafter.

Test method

SF5-EN ISO 6940 textile fabrics - burning behavior determination of ease of ignition of vertically oriented specimens

Samples

Sufficient number of specimens are tested until at least five cases of ignition and five cases of non-ignition occur. Size of the specimens is 80 mm x 80 mm or 200 mm x 80 mm. Specimens are conditioned at a temperature of 20 $\pm 2^{0}$C and a relative humidity of 65 $\pm$2%.

Procedure, surface ignition

Specimen is placed on the pins of the specimen holder so that the specimen is at least 20 mm removed from the frame. The specimen holder is placed vertically in the combustion chamber where a methane gas flame with length of 40 mm is directed to the surface of the specimen. The distance between the gas nozzle and the surface of the specimen is 17 mm. The flame is applied to the specimen of (size 80 x 80 mm) for a time period which preliminary testing indicated will approximate to the minimum ignition time. Ignition shall be deemed to have occurred if either the flame on the specimen persists for a period of at least 5 seconds after removal of the igniting flame, or if the specimen burns to the top of the vertical edges of the specimen, after removal of igniting flame. If the specimen burns to the top edge of the specimen during application of the igniting flame, the sample is retested using a 200 x 80 mm specimen. Ignition of the specimen is recorded. If ignition has occurred then the timer setting is reduced by 1 second. If ignition has not occurred, the timer setting is increased by up to a

maximum time of 20 seconds. Each trial is repeated on a new specimen continuing testing until there are at least five cases of ignition and five cases of non-ignition.

The mean of recorded times at which ignition or non-ignition, whichever has occurred least, was observed is calculated for each direction. If the calculated times relate to ignition, 0,5 is subtracted from the mean value calculated. If the calculated times relate to non-ignition, 0,5 is added to the mean value. The resulting value is rounded to the nearest second.

Flammability tests

The flammability tests were performed for the sprayed paper. The results show that the addition of ammonium bromide affects the flammability point of the paper. The results in Table IV reveal that 2% and 3.3% ammonium bromide shifts the ignition time and it does not ignite.

Table IV

Sample: White paper, 0.7%

Test specimen	Ignition time (s)	Afterflame time (s)	Afterglow time (s)	Ignition/ non-ignition
1	1	2	48	Non-ignition
2	1	2	43	Non-ignition
3	2	2	42	Non-ignition
4	3	1	45	Non-ignition
5	5	1	58	Non-ignition
6	10	0	30	Non-ignition
7	20	0	20	Non-ignition

Sample: White paper, 2.0%

Test specimen	Ignition time (s)	Afterflame time (s)	Afterglow time (s)	Ignition/ non-ignition
1	1	0	7	Non-ignition
2	20	0	0	Non-ignition

Sample: White paper, 3.3%

Test specimen	Ignition time (s)	Afterflame time (s)	Afterglow time (s)	Ignition/ non-ignition
1	1	0	0	Non-ignition
2	20	0	0	Non-ignition
3	20	0	0	Non-ignition

Paper tests

The paper tests show that the basic properties of the coated paper (folding endurance, tearing strength, tensile strength) changes in a way that the tensile strength decreases and tearing strength increases. The changes shown in Tables II and III imply that tensile strength would decrease and the tearing strength would increase, when ammonium bromide is sprayed between the paper and the coating. However, the ratio between them does not vary appreciably.

The minimum ignition time for the paper used in the Example, without flame-proofing compounds, was 1 second. The flame-proofed paper did not ignite after 20 seconds of ignition time. After shorter ignition time, the afterglow time was longer than the afterglow time for a longer ignition time.

The longer ignition time burns a hole through the paper but the damage is not spread.

While embodiments of the invention has been described by way of illustration, the invention may be carried into practice with many modifications, variations and adaptations, without exceeding the scope of the claims.

CLAIMS

1. A flame-retarded paper product, comprising as a fire-retardant (FR) ingredient a compound selected from among inorganic and organic flame-retardant compounds, particularly ammonium bromide and its mixtures with other ammonium salts, mono- or diammonium phosphate, ammonium polyphosphate, ammonium sulphate, urea, organic brominated flame retardants and their mixtures.

2. A flame-retarded paper product according to claim 1 wherein the FR ingredient is ammonium bromide.

3. A flame-retarded paper product according to claim 1 or 2 wherein the concentration of the ammonium bromide solution is between 10 w/w% to 90 w/w%.

4. A flame-retarded paper product according to any one of claims 1 to 3 comprising a flame-retardant or flame-retardant mixture in an amount of between 0.01% by weight of the paper to about 10% by weight of the paper, on a dry basis.

5. A flame-retarded paper product according to claim 4 wherein the flame-retardant is present in an amount of between 1.5% by weight of the paper to about 4% by weight of the paper, on a dry basis.

6. A flame-retarded paper product according to claim 1, which comprises a base paper, a layer of an FR compound or compounds, preferably including a first binder, and an uppermost layer of a coating color.

7. A flame-retarded paper product according to claim 6, wherein the first binder is starch.

8. A flame-retarded paper product according to claim 6, wherein the coating color layer comprises a second binder.

9. Method of making a flame-retarded paper product, which method comprises: a) producing a base paper; b) applying to the paper base at least one FR compound, to form a layer comprising said compound; and c) applying to the base paper, over said layer, a coating color and/or laminate and/or surface sizing.

10. Method of making a flame-retarded paper product according to claim 9, which comprises applying the at least one FR compound preferably by on the base paper a liquid phase comprising the FR compound and a first binder.

11. Method of making a flame-retarded paper product according to claim 10, wherein the first binder is starch.

12. Method of making a flame-retarded paper product according to claim 9, further comprising drying the FR compound layer before applying the coating color.

13. Method of making a flame-retarded paper product according to claim 9, wherein the coating color comprises a second binder and a pigment or pigments, and is applied by passing the paper with the FR compound layer through a bath or by spreading it onto said paper.

14. Method of making a flame-retarded paper product according to claim 9, comprising controlling the thickness of the coating color layer.

15. Method of making a flame-retarded paper product according to claim 9, wherein after drying the FR compound layer is located between the base paper and the coating color layer, and said coating color layer has a thickness of about 5 to about 30 μm.

16. Method of making a flame-retarded paper product according to claim 9, wherein the flame retardant is provided in an aqueous solution.

17. Method of making a flame-retarded paper product according to claim 16, wherein the flame retardant aqueous solution is a solution of ammonium bromide having a concentration from 10 w/w% to 90 w/w%.

18. Method of making a flame-retarded paper product according to claim 17, wherein the concentration of the ammonium bromide solution is between 20 w/w% to about 40 w/w%.

19. Method of making a flame-retarded paper product according to claim 9, wherein the quantity of the FR compound sprayed onto the base paper is from 0.01% by weight of the paper to 10% by weight of the paper.

20. Method of making a flame-retarded paper product according to claim 12, wherein the paper is dried at temperatures between 20°C to about 90°C

21. Use of ammonium bromide as a flame-retarding agent coating layer for paper.

22. Improvement to paper coating machines, which comprises adding a spraying device provided with nozzles to said machines before the coating unit.

23. Improvement to paper coating machines, which comprises adding a dispersion-applying device to said machines before the coating unit.

24. Improvement to paper coating machines according to claim 15, further comprising adding a dryer between the spraying device and the coating unit.

1/1

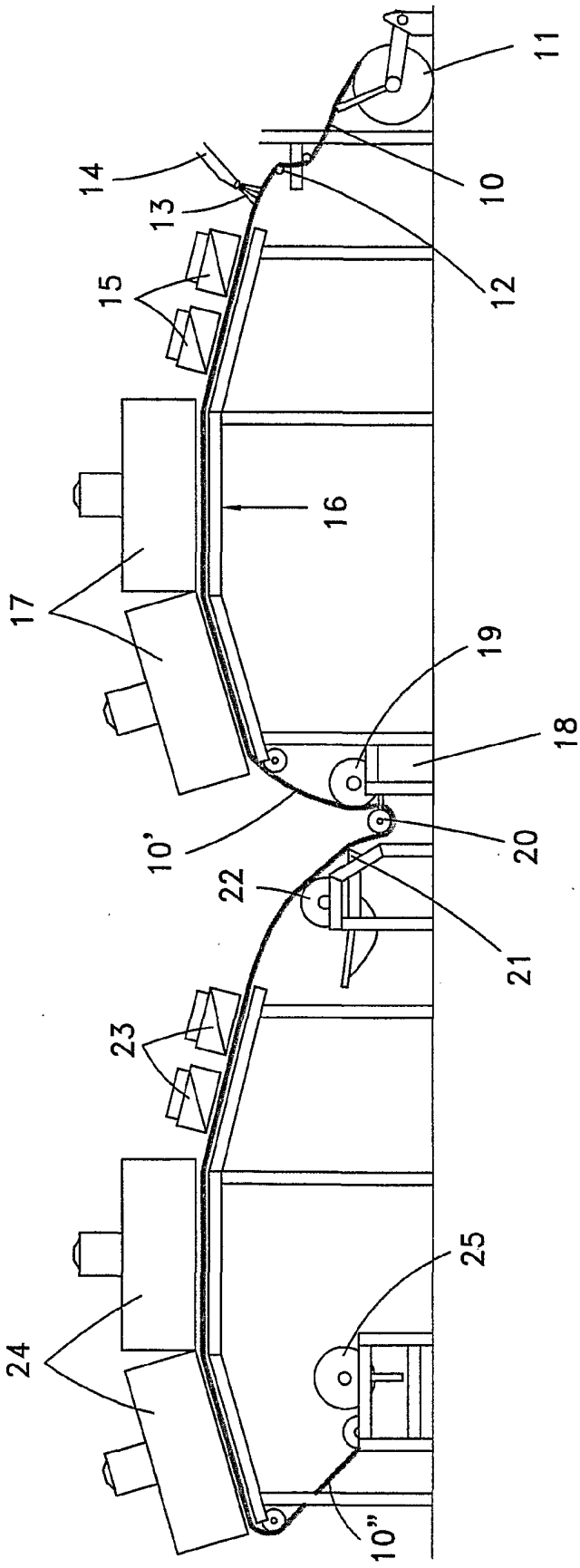

Fig. 1