Bitumen-impregnated cellulose fiber sheets include one of their main surfaces, an adhesive primer layer, and, deposited on this adhesive primer layer, a fireproof coating including expandable graphite. In a preferred embodiment of the invention, the expandable graphite has a trigger temperature lower than 300°C. and the layer of expandable graphite corresponds to a dry matter basis weight of 80 to 140 g/m². The sheets have a fire resistance fulfilling in particular the European Standard EN 13 501-5. They are mainly intended to be used as covering material, and in particular, as roof covering material.
FIELD OF THE INVENTION

The present invention generally relates to fire-resistant, bitumen-impregnated cellulose fiber sheets and their method of manufacturing. Said sheets are mainly intended to be used as covering material, and in particular, as roof covering material.

PRIOR ART

Bitumen-impregnated cellulose fiber sheets are well known by the one skilled in the art. They are generally manufactured from recycled paper and are rectangular in shape. Conventionally, the recycled paper is subjected to a processing step for removing the non-cellulosic elements, such as staples for example, and to a defibrating step, before forming a paper pulp that will be applied on a wire, then let drain and calibrated. It is possible to add other elements to the pulp, such as pigments for example, in order to obtain colored cover sheets, adapted to the architectural environment. The cellulose fiber pulp may be corrugated by means of a machine as described in the patent FR 2,496,551 or in the patent application EP 844,071, so as to obtain rectangular sheets whose corrugations are parallel to the two edges of the length. After drying, a cellulose fiber sheet is obtained, which may be cut at the desired size. The sheets then are soaked in bitumen, then cooled and possibly coated with a layer of paint.

The bitumen-impregnated cellulose fiber sheets are materials offering many advantages for the field of construction and renovation. Such sheets are light-weight, resistant, ultra-flexible, easy to install, and cheap. Their flexibility allows them to adapt to the slight deformations inherent to old woodworks. This is an important characteristic for building renovation. Their light-weight allows them to be installed on a light woodwork. The absence of a high additional load therefore limits the structural reinforcements often required for renovation works. Cutting and drilling such sheets require only very simple tools, such as hammer and saw.

The bitumen-impregnated cellulose fiber sheets are thus very widely used in the field of construction and renovation. However, their low resistance to an external fire poses a real problem regarding the security standards imposed by the national and international authorities, and in particular those imposed by the European Commission. Indeed, such standards are in constant evolution and the requirements imposed are more and more severe.

Therefore, there exists a need for improving the fire resistance of the bitumen-impregnated cellulose fiber sheets.

To provide fire resistance to a material, it is known to cover it with an expandable graphite-based coating. Expandable graphite is an in tuneuscent agent that, after exposure to fire, expanges and creates an isolating barrier.

The U.S. Patent No. 6,436,510 describes cellulose fiber sheets having a fire-resistant coating comprising expandable graphite and a thermoplastic or thermosetting polymer. Once coated with the polymeric binder and the expandable graphite, the cellulose fiber sheets are then coated with bitumen and shaped as flat shingles that can be used as roof covering materials.

Still in the field of construction, the patent US 2011/011021 describes cotton fiber plates. The cotton fibers are covered with expandable graphite by means of a mechanical-bond and/or chemical-bond binder. The binder used may be any thermoplastic polymer capable of forming a film after drying. Further, polyacrylates, epoxy resins, polyvinyl acetate resins, polyurethanes or styrene-based thermoplastic rubbers are mentioned. The plates coated with the fireproof layer may be later coated with modified bitumen and may thus serve as roof covering material.

The patent application WO 2005/0145139 describes fireproof coating similar to those mentioned hereinabove. This coating is prepared from a composition comprising at least one polymer binder of same nature than those used in the U.S. Patent No. 6,436,510, particles of expandable graphite, a vector such as water or a hydrocarbon solvent, according to the nature of the polymer binder, and a pigment such as, for example, titanium dioxide, calcium carbonate, or borates. The coating is then dried at the temperature of conservation of said material, which may further be a modified bitumen or shingles. An additional external layer may be applied to protect the coating from environmental factors such as rain or wind.

Among the patents or patent applications relating to the use of expandable graphite-based coatings for improving the fire resistance of cellular materials, the WO 2004/099491, U.S. Pat. No. 5,886,669 and U.S. Pat. No. 6,084,008 may be mentioned. One of the applications aimed at by the two latter patents is roofing materials.

However, the literature describes no fireproof coating for bitumen-impregnated cellulose fiber sheets. Now, as mentioned above, these sheets offer many advantages in the field of construction but their low fire-resistance does not fulfill the standards imposed by the European authorities.

Therefore, there exists a need for improving the fire resistance of the bitumen-impregnated cellulose fiber sheets.

DETAILED DESCRIPTION OF THE INVENTION

One object of the present invention is thus to improve the fire resistance of bitumen-impregnated cellulose fiber sheets, so as to fulfill in particular the European Standard EN 13501-5.

The European Standard EN 13501-5, described in more details in the examples offire-resistance testing, defines the criteria that must be met by the roofs subjected to an external fire, and allows for a classification of roofs as a function of their fire resistance.

Surprisingly, the applicant has discovered that, to form a sufficiently fire-resistant layer according to the European Standard EN 13501-5, the expandable graphite, which is the most used fire-retardant agent in the field of covering materials, had to be deposited through dry deposition, preferably through fluidized bed spray deposition or through hopper deposition, on an adhesive primer layer. The conventional methods of the prior art, such as spraying the expandable graphite in suspension in water ora dispersion of the expandable graphite in a polymer binder, do not operate because such methods do not allow obtaining a sufficiently homogeneous layer of expandable graphite. In the case of the binary "water/expandable graphite" mixture, the problem mainly lies in an instability of the mixture leading to a separation of the phases in the spraying circuit. This instability may in part be corrected by increasing the viscosity of the dispersing phase, in this case the water. However, this increase of viscosity of the dispersing phase generates difficulties of implementation of spray deposition. In the case of the binary "polymer binder/
expandable graphite" mixture, the main problems are, on the one hand, a problem of dispersion of the expandable graphite particles in the polymer binder due to the electrostatic affinities between the two phases, and on the other hand, a spraying problem. To overcome the technical problem linked to spray deposition and to graphite layer homogeneity, the applicant has developed a method that consists in firstly depositing an adhesive primer layer on the covering sheets, then depositing, through dry deposition, preferably through fluidized bed spray deposition or through hopper deposition, a fireproof coating comprising expandable graphite.

[0016] Accordingly, the present invention has for object bitumen-impregnated cellulose fiber sheets, including at least one of their main surfaces an adhesive primer layer and, deposited on said adhesive primer layer, a fireproof coating comprising expandable graphite.

[0017] Preferably, the adhesive primer layer and the expandable graphite-based fireproof coating are in direct contact. In a particular embodiment, the adhesive primer layer is in direct contact (i) with the fireproof coating comprising expandable graphite, and (ii) with the bitumen-impregnated cellulose fiber sheet.

[0018] As used herein, “fireproof coating” means a coating that allows a fire protection of inflammable materials such as bitumen and cellulose fibers, i.e. retarding or stopping the fire propagation and penetration.

[0019] The present invention has also for object a method of manufacturing sheets as described hereinabove. Said method comprises (a) depositing an adhesive primer on at least one of the main surfaces of the bitumen-impregnated cellulose fiber sheet, (b) depositing through dry deposition, on the adhesive primer layer, a fireproof coating comprising expandable graphite, and optionally, (c) depositing a layer of paint on the fireproof coating.

[0020] The present invention has also for object the use of sheets such as defined hereinabove as roof covering material.

[0021] In the present application, when an article comprises one or several coatings on its surface, the phrase “depositing a layer or a coating on the article” means that a layer or a coating is deposited on the uncovered (exposed) surface of the external coating of the article, i.e. the coating that is the most distant from the substrate.

[0022] In the present application, a coating that is “on” a substrate/coating or that has been deposited “on” a substrate/coating is defined as a coating that (i) is positioned above the substrate/coating, (ii) is not necessarily in contact with the substrate/coating, that it to say that one or several intermediate coatings may be arranged between the substrate/coating and the coating in question (however, it is preferably in direct contact with said substrate/coating), and (iii) does not necessary fully cover the substrate/coating. When “a layer 1 is located under a layer 2”; it means that the layer 2 is more distant from the substrate than the layer 1.

[0023] According to the invention, the bitumen-impregnated cellulose fiber sheets used for the deposition of the adhesive primer and the deposition of the fireproof coating are manufactured according to a method that is perfectly known by the one skilled in the art. This method that is exemplified in the present application comprises the following main steps:

[0024] manufacturing a cardboard sheet from cellulose fibers;

[0025] coating one of the faces of the cardboard sheet with a thermosetting resin possibly containing pigments;

[0026] optionally, corrugating the cardboard sheet;

[0027] drying and cutting the cardboard sheet;

[0028] deeply impregnating the cardboard sheet with hot bitumen.

[0029] According to the invention, the bitumen-impregnated cellulose fiber sheets used for the deposition of the adhesive primer and the deposition of the fireproof coating typically comprise 40 to 60 wt. % (weight percent) of bitumen relative to the total weight of said impregnated sheets. They typically comprise 40 to 60 wt. % of cellulose fibers relative to the total weight of said impregnated sheets. They typically comprise 0.5 to 2 wt. % of thermosetting resin relative to the total weight of said impregnated sheets.

[0030] In a particular embodiment, the bitumen-impregnated cellulose fiber sheets comprise 0.5 to 2 wt. % of pigments relative to the total weight of said impregnated sheets.

[0031] In another particular embodiment, they comprise 5 to 12 wt. % of mineral fillers relative to the total weight of said impregnated sheets.

[0032] The list of components of the bitumen-impregnated cellulose fiber sheets given hereinabove is of course not limitative.

[0033] The bitumen used is a mixture of hydrocarbon materials of natural origin coming from the heavy end obtained upon petroleum distillation, or coming from natural deposits, in solid or liquid form, of density 0.8 to 1.2. Also admitted as bitumens within the meaning of the invention are the bitumens modified by incorporation of additives of any nature such as additives for improving the adhesiveness characteristics, for artificially providing the required properties for producing a cationic emulsion, by incorporation of elastomers, in the form of rubber powder or other, or the bitumens improved by addition of polymers of various types; this list being of course not limitative.

[0034] The cellulose fibers are typically recycled cellulose fibers coming from old papers, cardboards or newspapers, for example; the list being not limitative.

[0035] The thermosetting resin is a resin or a mixture of resins preferably chosen from epoxy resins, polyurethane resins, polyurea resins, polyurea-formaldehyde resins, melamine-formaldehyde resins, epoxy vinyl ester resins or vinyl ester resins; the list being not limitative.

[0036] The pigments are preferably metal oxides, such as iron oxide or chromium oxide; the list being not limitative. The iron oxide allows obtaining almost all the colors. The role of the pigments is in particular to obtain colored covering sheets that are adaptable to the architectural environment.

[0037] The mineral fillers are mainly provided by the grades of recycled old paper used to form the paper pulp that serves for manufacturing the bitumen-impregnated cellulose fiber sheets. The mineral fillers are typically carbonates, silicates and aluminaes. In a particular embodiment of the invention, these mineral fillers may be added in the recycled cellulose fibers at the defibration step or at the draining step.

[0038] In a particular embodiment of the invention, the bitumen-impregnated cellulose fiber sheets used for the deposition of the adhesive primer and the deposition of the fireproof coating have corrugations intended in particular to collect water. As described in the patent FR 2,755,712, the corrugations may be of irregular form and substantially sinusoidal. The sheets may also have an alternation of waves and
flat regions. Moreover, the corrugations may be different, for example, of the crenellated or V-shaped type.

[0039] In the present invention, the corrugations are preferably sinusoidal. The height of the sinusoidal corrugations is generally of 10 to 100 mm, and preferably of 30 to 45 mm. The ratio between the amplitude and the pitch of the corrugations varies preferably from 1/2 to 1/1.

[0040] The basis weight of the bitumen-impregnated cellulose fiber sheets before the deposition of the adhesive primer and the deposition of the fireproof coating is generally higher than 0.8 kg/m², and advantageously higher than 2.6 kg/m².

[0041] In the present application, all the basis weights are related to the developed surface of the corrugated sheet. In the case where the corrugations are parallel to the length of the sheet, the developed surface of the corrugated sheet is obtained by multiplying the length of the corrugated sheet by the developed width of the corrugated sheet. i.e. by the distance following the closest profile of the sheet corrugation. In the case where the corrugations are parallel to the width of the sheet, the developed surface of the corrugated sheet is obtained by multiplying the width of the corrugated sheet by the developed length of the corrugated sheet, i.e. by the distance following the closest profile of the sheet corrugation.

[0042] The thickness of the bitumen-impregnated cellulose fiber sheets before the deposition of the adhesive primer and the deposition of the fireproof coating is generally at least of 1.5 mm, preferably higher than 2 mm, and better, it varies from 2.5 to 3.5 mm.

[0043] According to the invention, the bitumen-impregnated cellulose fiber sheets described hereinabove are coated with an adhesive primer layer and a fireproof coating comprising expandable graphite.

[0044] The adhesive primer has mainly for role to favor the adhesiveness of the following layers in the final product, in particular the adhesion and the cohesion of the particles of expandable graphite.

[0045] Indeed, when the cellulose fiber sheet according to the invention has just been impregnated with bitumen and is still hot, the bitumen layers present on the main upper and lower surfaces of said sheet are ephemeral and remain only a few seconds. Therefore, said ephemeral bitumen layers cannot serve as adhesive layers to immobilize the fireproof coating, and in particular to immobilize the expandable graphite. This technical problem is not observed in the case of roof sheets or membranes based on polyester and/or polyamide fibers, because, when these latter are impregnated with bitumen, they have on their main upper and lower surfaces sufficiently stable bitumen layers that play, when still hot, the role of adhesive layers and allow the immobilization of the expandable graphite particles.

[0046] The adhesive primer preferably comprises a polymer binder. The polymer binder is preferably a polymer or a mixture of polymers chosen from the thermoplastic resins such as polyvinyl resins, polyvinylidene resins, polyacrylic resins, methacrylic resins or polystyrene resin; the list being not limitative. An example of preferred thermoplastic resin is a polymer of the vinyl acetate type.

[0047] The adhesive primer layer in the final product corresponds to a dry matter basis weight of generally 10 to 200 g/m², and preferably of 20 to 70 g/m².

[0048] The fireproof coating of the invention comprises expandable graphite. This coating is preferably in direct contact with the adhesive primer layer. The method of deposition of the fireproof coating comprising expandable graphite will be described hereinafter.

[0049] The expandable graphite of the present invention has typically a crystalline structure composed of carbon atoms forming planes stacked parallel to each other, in which have been inserted acid molecules, as for example molecules of sulfuric acid or nitric acid. When the expandable graphite is exposed to fire or to a flame, the acid molecules break down and generate gas. The pressure of this gas then forces the graphitic planes to move apart from each other, which generates a dilatation of the graphite. The volume of the graphite particles may then be multiplied by a factor of more than 80 in a few seconds. The thus-dilated graphite has a low density; it is not combustible and forms a good thermal isolator because it reflects a part of the radiating heat.

[0050] Other known advantages of the expandable graphite are, further, that it is of natural origin, it is not polluting, and it does not dissolve in water. The expandable graphite serves as a fire-retardant agent due to an endothermic combustion reaction, but above all due to the formation of an isolating barrier after expansion. It also permits to reduce the thermal conductivity of a material. The flame propagation is limited and the thermal radiation is low. The expandable graphite further guarantees a low density of the smoke and reduces significantly the dripping of the bitumen binder.

[0051] In the present invention, the expandable graphite has preferably an expansion coefficient higher than 70 cm²/g, and advantageously higher than 120 cm²/g, when it is exposed to a temperature of 600°C.

[0052] The expandable graphite is generally in the form of sprayable flakes. The particle size is typically of 50 to 600 μm, and preferably 150 to 400 μm.

[0053] Expandable graphite particles are commercially available with a great number of suppliers. They have a “trigger” temperature (temperature at which the graphite expansion starts after exposure to a flame during a few seconds) generally ranging from 130°C to 500°C.

[0054] The inflammation temperature of a bitumen-impregnated cellulose fiber sheet according to the invention is lower than that of a bitumen sheet or membrane based on polyester and/or polyamide fibers. The inflammation temperature of a bitumen-impregnated cellulose fiber sheet according to the invention is typically lower than 300°C, in particular lower than 190°C. For example, it is of 130°C to 270°C. Therefore, the expandable graphite according to the invention has preferably a trigger temperature lower than 300°C. For example, it is of 120°C, 130°C, 140°C, 150°C, 160°C, 170°C, 180°C, 190°C, 200°C, 210°C, 220°C, 230°C, 240°C, 250°C, 260°C, 270°C, 280°C, 290°C, 300°C. In particular embodiments, it is of 160°C or 220°C. Particularly satisfying results are obtained for expandable graphite trigger temperatures ranging from 120°C to 220°C, in particular from 160°C to 220°C or from 120°C to 180°C. Very good results are obtained for a minimum trigger temperature of 160°C. The layer of expandable graphite in the final product corresponds to a dry matter basis weight generally ranging from 50 to 300 g/m², and preferably from 80 to 140 g/m². This basis weight corresponds to a “mean basis weight” over the whole developed surface of the sheet according to the invention. The best results of flame holding and thus fire resistance of the sheets according to the invention are obtained when the homogeneity of the expandable graphite distribution is optimum, i.e. when the “local basis
weight” of the layer of expandable graphite in the final product is at least of 80 g/m² in dry matter weight, in any point of said sheet. According to the invention, the term “point” means a developed surface ranging from 1 cm² to 900 cm² (for example, 30 cm x 30 cm, i.e. the size of a firebrand used for the fireproof tests described hereinafter), in particular from 1 cm² to 100 cm², preferably from 1 cm² to 2 cm². The measurement of the local basis weight of the expandable graphite may for example be made by means of adhesive labels whose size corresponds to the size of the developed surface to be tested (for example, of 2 cm² if it is desired to test areas having a developed surface ranging from 1 cm² to 2 cm²). This measurement is made by differential calculation. For example, on the one hand, an adhesive label is applied on a bitumen-impregnated cellulose fiber sheet comprising an adhesive primer layer. The label is removed, which allows taking a sample of the adhesive primer present on the tested area. The quantity of adhesive primer is then calculated by weighing the label before and after the sample has been taken. On the other hand, the same operation is carried out with a label of same size on the same sheet, which further comprises, this time, a layer of expandable graphite on the adhesive primer layer. This second operation allows quantifying the quantity of adhesive primer and of expandable graphite present in the tested area. The mass quantification of the expandable graphite is then obtained by difference between (i) the measurement of the quantity of adhesive primer and of expandable graphite, and (ii) the measurement of the quantity of adhesive primer.

In a particular embodiment, the bitumen-impregnated cellulose fiber sheet coated with the adhesive primer layer and the fireproof coating may also include a layer of paint deposited on the fireproof coating. The layer of paint has for main role to improve the good resistance of the graphite over time. It is also used for aesthetic effect. The paint that can be used in the present invention is typically of vinyl or acrylic nature. The polymer present in the layer of paint is generally the same as that of the adhesive primer. The layer of paint corresponds to a dry matter basis weight generally ranging from 50 to 300 g/m², and preferably from 100 to 200 g/m².

The present invention has also for object a method of manufacturing fireproof-coated, bitumen-impregnated cellulose fiber sheets as described hereinabove.

This method comprises (a) depositing an adhesive primer on at least one of the main surfaces of the bitumen-impregnated cellulose fiber sheet and (b) depositing through dry deposition, on the adhesive primer layer, a fireproof coating including expandable graphite.

In a particular embodiment of the present invention, the method comprises a step of depositing a layer of paint on the fireproof coating.

The deposition of the adhesive primer is carried out through spray deposition, through coating using further a roll or a brush, or through any other mode known by the one skilled in the art, the preferred mode being spraying. This spray deposition is implemented, for example, by means of sweeping nozzles such as those conventionally used by the one skilled in the art for the deposition of a layer of paint on a covering sheet. An exemplary implementation of the adhesive primer spray deposition is detailed hereinafter in the present application. The adhesive primer is sprayed over at least one of the main surfaces of the bitumen-impregnated cellulose fiber sheet, preferably at least the surface of the sheet having the possibly pigmented thermosetting resin layer described hereinabove. The nozzles are oriented in such a manner that the adhesive primer layer is the most homogeneous possible. The adhesive primer layer corresponds to a dry matter basis weight generally ranging from 10 to 200 g/m², and preferably from 20 to 70 g/m².

The dry deposition of the fireproof coating comprising expandable graphite is carried out on a bitumen-impregnated cellulose fiber sheet including on at least one of its main surfaces an adhesive primer layer, said sheet having preferably a temperature lower than 160°C, in particular lower than 120°C. Indeed, the graphite expansion phenomenon is not reversible, i.e. once the expandable graphite has reached its trigger temperature, it expands and will not recover its non-expanded initial state if cooled to a temperature lower than its trigger temperature. During the manufacturing of a bitumen-impregnated cellulose fiber sheet according to the invention, the drying temperature of the cellulose fiber sheet is about 260°C and the temperature of the bitumen during the step of hot impregnation is about 190°C. The trigger temperature of the expandable graphite according to the invention being preferably lower than 300°C, for example ranging from 120°C to 180°C or from 160°C to 220°C, for the hereinabove-mentioned reasons of inflammation temperature of the sheet according to the invention, the expandable graphite can be deposited only after the step of drying the cellulose fiber sheet and hot impregnation with bitumen. The expansion of the expandable graphite is thus avoided during the manufacturing of the sheet according to the invention and before the use of said sheet as a fireproof roof covering.

The dry deposition of the fireproof coating comprising expandable graphite is preferably carried out through gravity deposition, in particular through hopper deposition, or through spray deposition, and advantageously through fluidized bed spray deposition of the expandable graphite. The fluidized bed spray deposition of the expandable graphite is preferred to the hopper deposition because it allows obtaining a layer of expandable graphite that is more homogeneous and thus more fire-resistant.

The gravity deposition, in particular hopper distribution, consists in carrying the sheet having the adhesive primer layer as defined hereinabove, under a hopper (or tank) filled with the expandable graphite; the surface of the sheet having the adhesive primer layer being exposed to the hopper so that the deposition of the expandable graphite is carried out on the adhesive primer layer. The hopper is preferably equipped, at the lower end, with a knurled roll, whose speed and position relative to the hopper wall (corresponding to the lip opening size) may be varied, the knurled roll serving to distribute the graphite as a function of the required quantities and of the speed of advance of the sheet. The knurled roll also allows obtaining a better distribution of the expandable graphite and thus improving the fire resistance of the sheet according to the invention.

The fluidized bed spraying of the expandable graphite consists in putting the expandable graphite in suspension in a gas flow swirl in such a way that the expandable graphite, which is a solid, behaves as a liquid. The dry particles of expandable graphite are placed in a fluidized bed container. The gas flow is preferentially injected under the particles of expandable graphite, so as to propel the particles in the gas flow swirl and to form a cloud of particles in suspension in the gas flow. The gas flow used in the present invention is preferentially a flow of air having a pressure varying from 2 to 3
Bar, and still better a pressure of 2.5 Bar. The suspension of expandable graphite in the gas flow is then sprayed over the main surface of the sheet having the adhesive primer layer. The spraying is preferably carried out by means of nozzles having an opening that is preferably not circular and whose surface area varies from 45 to 60 mm², preferably from 50 to 52 mm², and still better of 51.17 mm². A flow of air of 2 to 3 Bar allows a flow rate of dry particles of expandable graphite varying from 400 to 500 g/min per nozzle. The quantity of expandable graphite deposited depends on the quantity and the nature of the polymer binder of the hereinabove defined adhesive primer layer. For example, for an adhesive primer layer containing vinyl acetate and corresponding to a dry matter basis weight ranging from 20 to 70 g/m², the quantity of expandable graphite deposited varies from 80 to 140 g/m². The dry deposition of the expandable graphite is preferably carried out until physical saturation of the surface of the adhesive primer layer. The excess of expandable graphite is then eliminated by blowing. On the sheet, there thus remain only the particles of expandable graphite in contact with the adhesive primer layer.

The deposition of the layer of paint is carried out through spray deposition, through coating using further a roll or a brush, or through any other mode known by the one skilled in the art, the preferred mode being spray deposition. This spray deposition is implemented, for example, by means of sweeping nozzles such as those conventionally used by the one skilled in the art for the deposition of a layer of paint on a covering sheet. The layer of paint corresponds to a dry matter basis weight generally ranging from 50 to 300 g/m², and preferably from 100 to 200 g/m².

The present invention has also for object a bitumen-impregnated cellulose fiber sheet obtainable by the method according to the invention.

The present invention has also for object the use of a bitumen-impregnated cellulose fiber sheet as defined in the present invention as a roof covering material. Generally, the bitumen-impregnated cellulose fiber sheets of the present invention can be used in the building industry, in the construction or renovation of roofs. The sheets according to the invention can be used, for example, as roof accessories, such as, without being limited thereto, ridge tiles, border tiles and skylight frames.

The examples hereinafter illustrate the present invention without limiting the latter.

EXAMPLES

A) Bitumen-impregnated Cellulose Fiber Sheets Used for the Deposition of the Adhesive Primer and that of the Fireproof Coating

a. Materials

Examples of sheets are Onduline CLASSIC®, Onduline ONDUTOIT®, Onduline ONDUVILLA® or Onduline DURO235® sheets, manufactured by the Onduline Company. All these sheets have a basis weight higher than 2.6 kg/m², except the ONDUTOIT® sheets, which have a basis weight of 2.2 kg/m². The onduline CLASSIC® sheets are corrugated sheets having a weight of 6.4 kg, a length of 200 cm, a width of 95 cm, a thickness of 3 mm, and corrugations with a height of 38 mm.

The Onduline ONDUTOIT® sheets are corrugated sheets ideal for covering small storage facilities (industrial and agricultural), ancillary and leisure facilities. These are single-layer bitumen sheets, pigmented in depth, with a thermostetting resin. The sheets have a length of 200 cm, a width of 95 cm, a thickness of 2.60 mm, a wave depth of 38 mm, a wave pitch of 95 mm, a wave number of 9 to 10, and a mass of 5.60 kg. Their bursting resistance when in dry-state is 17 bars.

B) Onduline ONUVILLA® sheets are corrugated tiles having a thickness of 3 mm, a wave depth of 40 mm, a length of 40 cm and a width of 106 cm. Also included in the sheet examples are the sheets having the same thickness and the same wave depths than the Onduline ONDUVILLA® tiles, but having a length of 200 cm and a width of 106 cm.

C) Onduline DURO 235® sheets are corrugated sheets ideal for covering small storage facilities (industrial and agricultural), ancillary and leisure facilities. These are single-layer bitumen sheets, pigmented in depth, with a thermostetting resin. The sheets have a length of 200 cm, a width of 95 cm, a thickness of 3.00 mm, a wave depth of 38 mm, a wave pitch of 95 mm, a wave number of 10, and a mass of 6.75 kg. Their bursting resistance when in dry-state is 19 bars.

The Onduline CLASSIC®, Onduline ONDUTOIT®, Onduline ONDUVILLA® and Onduline DURO 235® sheets contain 44 wt. % of cellulose fibers, 8 wt. % of mineral fillers, 46 wt. % of bitumen, 1 wt. % of thermostetting resin and 1 wt. % of pigment.

b. Manufacturing Method

A method of manufacturing said sheets comprises the following steps, which are well known by the one skilled in the art:

1. Manufacturing a paper pulp from old papers, from which all foreign scraps, such as plastic for example, have been removed;
2. Applying the paper pulp on a flat table for a natural draining of the pulp;
3. Sucking and pressing the paper pulp in order to obtain cardboard sheet;
4. Roll-coating, on one of the faces of the cardboard sheet, a thermostetting resin containing pigments such as iron oxide or chromium oxide;
5. Mechanically corrugating the cardboard sheet;
6. Drying and cutting the cardboard sheet;
7. Deeply impregnating the cardboard sheet with hot bitumen.

b) Polymers Used for the Adhesive Primer

Examples of adhesive primer compositions used in the present invention are 40% vinyl acetate aqueous emulsion. The vinyl acetate is, for example, Axilat AOD 515, marketed by the Hexion Company, or Movilith LDM 1851 marketed by the Celanese Company. Axilat AOD 515, which is generally used for paint formulations, is marketed in the form of a 50% aqueous emulsion. In the present invention, it is thus diluted to 40% before application.

C) Expandable Graphite Used for the Fireproof Coating

Non-limitative examples of expandable graphite particles used in the present invention are the expandable graphite PX200 or PX85, marketed by the Alphamin Company, or the expandable graphite S90 or S7, marketed by the Netexium Company. By way of example, the PX85 particles comprise 95 wt. % of carbon, 4 wt. % of ash, 0.5 wt. % of free acids and 6.8 wt. % of sulfates. These particles have a pH of 3 to 7. They have an expansion coefficient of 200 cm³/g and 80% of them have a nominal size of 180 μm.

Typical examples of particles that can be used for the present invention are particles of grades 160-80, 160-50,
220-80 or 220-50. The first number indicates the temperature in degrees Celsius at which the graphite expansion starts, and the second number corresponds to the size of the particles, in Mesh.

[0089] D) Paint Used for the Layer of Paint

[0090] An example of preferred paint used in the present invention is the paint ISOLA manufactured by Onduline. Other examples of paint are all aqueous-phase outdoor paints for wood.

[0091] E) Methods of Manufacturing a Bitumen-Impregnated Cellulose Fiber Sheet Including an Adhesive Primer Layer, a Fireproof Coating and a Layer of Paint

[0092] A bitumen-impregnated cellulose fiber sheet of the Onduline CLASSIC®, Onduline ONDUITOT®, Onduline ONDUVILLA® or Onduline DURO235® type, manufactured by the ONDULINE Company and as described hereinabove, is placed on a automated conveyor belt, in such a manner that the exposed surface is the surface having the layer of pigmented thermostetting resin.

[0093] The conveyor belt carries the sheet into a first stainless-steel chamber, equipped with sweeping nozzles containing the adhesive primer. In the present example, the adhesive primer is a 40% vinyl acetate aqueous emulsion, of the Axilat AOD 515 type. The emulsion is sprayed over the exposed surface of the sheet, i.e. on the surface having the layer of pigmented thermostetting resin. The sweeping nozzles are oriented in such a manner that the adhesive primer layer is the most homogeneous possible. The adhesive primer layer corresponds to a dry matter basis weight of 50 g/m².

[0094] After the deposition of the adhesive primer, the conveyor belt carries the sheet outside the first chamber so that the one skilled in the art checks the deposited layer.

[0095] Before the adhesive primer layer dries, the conveyor belt carries the sheet into a second chamber for performing the deposition of the fireproof coating. The expandable graphite used is, for example, PX200 of PX85, marketed by Alphamin, or SX90 or S7, marketed by Netexium.

[0096] In the case of hopper deposition, the chamber comprises a hopper equipped, at the lower end, with a knurled roll, whose speed may be varied and which serves to distribute the graphite as a function of the required quantities and of the speed of advance of the sheet. For example, to deposit on a sheet 100 g/m² of dry expandable graphite, at a rate of 500 sheets per hour, the linear speed of the conveyor belt is adjusted between 15 m/min and 20 m/min, preferably 18 m/min, the speed of the 85 mm diameter knurled roll being adjusted from 20 rpm to 30 rpm, preferably 26 rpm, and the relative position of the knurled roll with respect to the hopper wall is adjusted so as to obtain a lip opening of 0 mm to 1 mm, preferably 0.1 mm.

[0097] In the case of fluidized bed spray deposition, the chamber is equipped with 8 nozzles having each an opening of 51.17 mm². The nozzles are connected to a fluidized bed container containing the expandable graphite and a system for creating a flow of air.

[0098] The dry particles of expandable graphite placed in the fluidized bed container are put in suspension in an air flow swirl before being sprayed by the nozzles over the surface of the covering sheet having the non-dried adhesive primer layer. The flow of air is injected under the particles of expandable graphite so as to propel them in the gaseous flow swirl and to form a cloud of particles in suspension in the gaseous flow. The flow of air is of 2.5 Bar and allows a flow rate of dry particles of expandable graphite of 455 g/min per nozzle; i.e. a total flow rate of dry particles of expandable graphite of 3640 g/min for 8 nozzles. The layer of expandable graphite in the final product corresponds to a dry matter basis weight of at least 80 g/m² in any point of the sheet having a developed surface ranging from 1 cm² to 2 cm².

[0099] After the deposition of the fireproof coating comprising the expandable graphite, the conveyor belt carries the sheet out of the second chamber so that the one skilled in the art checks the deposited layer.

[0100] The sheet is then possibly carried into a third stainless-steel chamber for the deposition of a layer of paint. The third chamber is equipped with sweeping nozzles conventionally used by the one skilled in the art for the deposition of paint on the covering sheets. The paint used is the paint ISOLA from ONDULINE. It is sprayed through the nozzles over the previously deposited layer of fireproof coating. The layer of paint corresponds to a dry matter basis weight ranging from 140 to 150 g/m².


[0102] The European Standard EN 13 501-5 allows for a fire classification of the construction products and building elements as a function of their fire resistance. The test methods used to test the roofs exposed to an external fire are defined in the Standard XP ENV 1187: This Standard contains four types of tests:

[0103] Test 1 is performed with inflamed firebrands (baskets). It is based on the German Standard DIN 4102-7;

[0104] Test 2 is performed with inflamed firebrands in the presence of wind. It is based on the Scandinavian Standard Nordtest NT Fire 006;

[0105] Test 3 is performed with inflamed firebrands in the presence of wind and radiating heat. It is based on the order of Sep. 10, 1970, of the French Ministry of Interior. It defines the classes and index T30/1;

[0106] Test 4 is performed in two steps with inflamed firebrands in the presence of wind and radiating heat. It is based on the British Standard BS 476/3.

[0107] Each test is independent. There exists no predetermined order to perform them. Each test defines the criteria that must be met by the sheets subjected to an external fire as well as the conditions in which the sheets are tested.

[0108] Only Tests 1 and 3 are detailed hereinafter. However, the sheets according to the invention have responded positively to Tests 2 and 4.

[0109] a) Tests 1

[0110] Tests 1 have been carried out with corrugated sheets having a length of 1.8 m, a width of 0.8 m, a thickness of 3 mm, and corrugations with a height of 38 to 40 mm. The sheets contain 44 wt. % of cellulose fibers, 8 wt. % of mineral fillers, 46 wt. % of bitumen, 1 wt. % of thermostetting resin and 1 wt. % of pigment. Some sheets have been tested as such, i.e. with no adhesive primer layer and no fireproof coating; they are called hereinafter "sheets without fireproof coating". They constitute the test specimens of Tests 1 and 3. Sheets according to the invention, called hereinafter "sheets with fireproof coating", have been tested with the following coatings:

[0111] an adhesive primer layer comprising vinyl acetate (Axilat AOD 515), having a dry matter basis weight of 30 to 50 g/m²;

[0112] a fireproof coating comprising expandable graphite of the PX85 type, having a local dry matter basis
weight of about 100 g/m² in any point having a developed surface ranging from 1 cm² to 2 cm²,

[0113] a layer of vinyl paint of the ISOL A type, having a dry mat basis weight of 140 g/m² to 150 g/m².

[0114] The conditions of Test 1 are the following:

[0115] the slope of the roof is 15° or 45°,

[0116] the firebrand is a basket of 300 mm x 300 mm x 200 mm with 600 g of pine straw,

[0117] the test is stopped after the fire is totally stopped.

[0118] The sheets responding positively to the test are classified B_roof and those responding negatively to the test are classified F_roof.

[0119] The following Table presents the results of Test 1.

<table>
<thead>
<tr>
<th>Main Criteria</th>
<th>Criteria of Classification</th>
<th>Sheets without fireproof coating</th>
<th>Sheets with fireproof coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upward external fire propagation</td>
<td>&lt;0.7 m</td>
<td>&gt;0.7 m (fire)</td>
<td>&lt;0.7 m</td>
</tr>
<tr>
<td>Maximum burned length</td>
<td>&lt;0.8 m</td>
<td>&gt;0.8 m (fire)</td>
<td>&lt;0.8 m</td>
</tr>
<tr>
<td>Incandescent points penetrating the roof</td>
<td>None</td>
<td>Fire under the sheet</td>
<td>Non</td>
</tr>
<tr>
<td>Fire Classification</td>
<td>B_roof</td>
<td>F_roof</td>
<td>B_roof</td>
</tr>
</tbody>
</table>

b. Tests 3

[0120] Tests 3 have been carried out with sheets similar to those used for Test 1. The only criteria that change are the length of the sheets, which is then of 2 m instead of 1.8 m, and the width of the sheets, which is of 1.2 m instead of 0.8 m.

[0121] The conditions of Test 3 are the following:

[0122] the slope of the roof is fixed to 30°,

[0123] the firebrand is a wood-fiber basket of 55 mm x 55 mm x 32 mm, impregnated with n-heptane,

[0124] the wind is applied at a speed of 3 m/s,

[0125] the radiating panel providing the radiant heat has a power of 12.5 kW/m².

[0126] the test is stopped after the fire is totally stopped.

[0127] The sheets responding positively to Test 3 are classified B_roof, C_roof, or D_roof, according to their degree of resistance, the sheets B_roof being the most performing and the sheets D_roof being the less performing. The sheets responding negatively to the test are classified F_roof.

[0128] The following Table presents the results of Test 3.

<table>
<thead>
<tr>
<th>Main Criteria</th>
<th>Criteria of Classification</th>
<th>Sheets without fireproof coating</th>
<th>Sheets with fireproof coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time of external fire propagation (TE)</td>
<td>TE &gt; 30 min</td>
<td>TE &gt; 10 min</td>
<td>TE &gt; 10 min</td>
</tr>
<tr>
<td>Time until fire penetration</td>
<td>TP &gt; 30 min</td>
<td>TP &gt; 15 min</td>
<td>TP &gt; 5 min</td>
</tr>
<tr>
<td>Fire Classification</td>
<td>B_roof</td>
<td>C_roof</td>
<td>D_roof</td>
</tr>
</tbody>
</table>

[0129] The results of Tests 1 and 3 show that the cellulose fiber sheets according to the present invention respond correctly to the different criteria of fireproof classification of the Standard EN 13501-5, contrary to the sheets having no fireproof coating.

[0130] Other tests have shown that the sheets processed according to the invention have a very good aging ability (UV exposure, frost/thaw cycles, wet abrasion).

[0131] The dry deposition of expandable graphite, and in particular fluidized bed spray deposition or hopper deposition, is thus a performing method to obtain a layer of expandable graphite that is sufficiently homogeneous to obtain the desired result, which is to improve the fire resistance.

1. A bitumen-impregnated cellulose fiber sheet, comprising on at least one of its main surfaces an adhesive primer layer, characterized in that a fireproof coating comprising expandable graphite is deposited on this adhesive primer layer.

2. The bitumen-impregnated cellulose fiber sheet according to claim 1, characterized in that it includes corrugations.

3. The bitumen-impregnated cellulose fiber sheet according to claim 1, characterized in that the expandable graphite has an expansion coefficient higher than 120 cm³/g at 600°C.

4. The bitumen-impregnated cellulose fiber sheet according to claim 1, characterized in that the expandable graphite has a trigger temperature lower than 300°C.

5. The bitumen-impregnated cellulose fiber sheet according to claim 1, characterized in that the expandable graphite has a trigger temperature ranging from 160°C to 220°C.

6. The bitumen-impregnated cellulose fiber sheet according to claim 1, characterized in that the mean dry matter basis weight of expandable graphite varies from 80 to 140 g/m².

7. The bitumen-impregnated cellulose fiber sheet according to claim 1, characterized in that the local dry matter basis weight of expandable graphite is at least 80 g/m² in any point having a developed surface ranging from 1 cm² to 900 cm².

8. The bitumen-impregnated cellulose fiber sheet according to claim 7, characterized in that the local dry matter basis weight of expandable graphite is at least 80 g/m² in any point having a developed surface ranging from 1 to 2 cm².

9. The bitumen-impregnated cellulose fiber sheet according to claim 1, characterized in that it includes a layer of paint deposited on the fireproof coating.

10. A method of manufacturing a bitumen-impregnated cellulose fiber sheet according to claim 1, comprising (a) depositing an adhesive primer on at least one of the main surfaces of the bitumen-impregnated cellulose fiber sheet, (b) depositing through dry deposition, on the adhesive primer layer, a fireproof coating comprising expandable graphite.

11. The method according to claim 10, further comprising (c) depositing a layer of paint on the fireproof coating.

12. The method according to claim 10, characterized in that the fireproof coating is deposited by fluidized bed spray deposition.

13. The method according to claim 10, characterized in that the fireproof coating is deposited by hopper deposition.

14. The method according to claim 13, characterized in that the fireproof coating is deposited through a hopper equipped, at the lower end, with a knurled roll.

15. Method of covering a roof which comprises: providing a bitumen-impregnated cellulose fiber sheet according to claim 1, and applying said sheet to the roof as a roof covering material.
16. The bitumen-impregnated cellulose fiber sheet according to claim 2, characterized in that the expandable graphite has an expansion coefficient higher than 120 cm³/g at 600°C.

17. The bitumen-impregnated cellulose fiber sheet according to claim 2, characterized in that the expandable graphite has a trigger temperature lower than 300°C.

18. The bitumen-impregnated cellulose fiber sheet according to claim 2, characterized in that the mean dry matter basis weight of expandable graphite varies from 80 to 140 g/m².

19. The bitumen-impregnated cellulose fiber sheet according to claim 2, characterized in that the local dry matter basis weight of expandable graphite is at least of 80 g/m² in any point having a developed surface ranging from 1 cm² to 900 cm².