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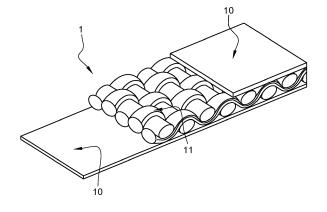
# (54) FLEXIBLE, FLAME-RETARDANT COMPOSITE MATERIAL

- (57) The invention relates to a flexible, flame-retardant composite material comprising:
- a fabric layer; and
- at least one impregnated or coated Polyvinyl Butyral (PVB) coating layer, which is integral with said fabric layer; the PVB coating layer containing 20 to 60% by weight of PVB, at least one plasticizer in an amount of 5 to 40% by weight of the coating layer, and a mixture of antimony trioxide  $\rm Sb_2O_3$  and at least one halogenated organic

compound as flame retardant in a total amount of 5 to 45% by weight with respect to the coating layer, and in a ratio of 0.1 to 5 part of antimony trioxide  $\mathrm{Sb}_2\mathrm{O}_3$  per part of halogenated organic compound.

The invention also relates to the manufacturing method thereof, comprising an impregnation or coating of a water-based dispersion of PVB onto the fabric layer, and a further curing.

Fig. 1



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## Description

#### **TECHNICAL FIELD OF THE INVENTION**

[0001] The present invention relates to a flexible, flame-retardant material of multilayered structure formed of at least one fabric layer and of at least one Polyvinyl butyral (PVB) coating layer, and its manufacturing method. In particular, the present invention relates to the field of flexible construction materials (such as facade elements) insofar as they can, for example, be used to form a digital printing media, typically for outdoor and indoor advertising, and/or a solar protection material. The digital printing medium can be a facade element, a temporary shelter, a billboard, a building wrap, a wallcovering, a display or a suspended ceiling.

## **PRIOR ART**

**[0002]** Digital printing is a method of printing from a digital-based image directly to a variety of media. Digital printing allows for on-demand printing, short turnaround time, and even a modification of the image (variable data) used for each impression. The savings in labor and the ever-increasing capability of digital presses leads to the fact that digital printing has many advantages over traditional methods.

**[0003]** Digital printing is often used in advertising, usually for indoor and outdoor banners and event signage, in trade shows, and in the retail sector at point of sale or point of purchase. It is also used in architecture where the media is a flexible composite material, which conforms to a variety of surfaces. It enables interior and exterior spaces (such as facades) to be transformed, and optionally functions as solar protection. These materials are to fulfil the requirements of more and more strict environmental standards.

**[0004]** Traditionally, these flexible materials comprise coatings made of polyvinyl chloride (PVC). However, nowadays the industry tends to avoid using PVC mainly because of its high chlorine content. There is a need of coatings made of eco-friendly polymers for the environment and for the health of the persons in contact with them.

**[0005]** Polyurethane (PU) and acrylic polymers have been envisaged, but they appear too costly for the majority of applications or do not meet all the performance criteria needed for their respective end use.

**[0006]** Therefore, when looking for a composition for coating a flexible material, it is difficult to combine eco-friendly requirements and to respond to technical requirements such as flexibility, flame retardancy, weldability, good printability, good adhesion and abrasion resistance for mechanical performances, as well as cost efficiency.

**[0007]** The technical problem which the invention intends to solve is therefore to propose a flexible, flame-retardant composite material generally of multilayered structure free of PVC, which renders it capable of being used in applications such as digital printing media, solar protection media or replace traditional PVC- or PU-coated fabrics in automotive applications.

# **DISCLOSURE OF THE INVENTION**

**[0008]** The present invention proposes solving the technical problems described above in relation with the prior art by means of a flexible, flame-retardant composite material comprising:

- a fabric layer; and
- at least one impregnated or coated Polyvinyl Butyral (PVB) coating layer, which is integral with said fabric layer; the PVB coating layer containing 20 to 60% by weight of PVB, at least one plasticizer in an amount of 5 to 40%, preferably 5 to 25%, by weight of the coating layer, and a mixture of antimony trioxide Sb<sub>2</sub>O<sub>3</sub> and at least one halogenated organic compound as flame retardant in a total amount of 5 to 45%, preferably 10 to 40%, by weight with respect to the coating layer, and in a ratio of 0.1 to 5, preferably 0.2 to 3, e.g. 0.33, part of antimony trioxide Sb<sub>2</sub>O<sub>3</sub> per part of halogenated organic compound.

**[0009]** Thus, the fabric layer is coated or impregnated with a PVB coating layer on at least one side. Typically, the fabric layer is coated on only one side or on its two sides. In the last case, the PVB coating layers on both sides of the fabric layer can be similar or different (different composition and/or color and/or thickness...).

**[0010]** In a preferred embodiment, the flexible, flame-retardant composite material consists essentially of, preferably consists of the fabric layer and one PVB coating layer.

**[0011]** In a preferred embodiment, the flexible, flame-retardant composite material consists essentially of, preferably consists of the fabric layer and two PVB coating layers (similar or different).

**[0012]** The invention also relates to a manufacturing method for forming the flexible, flame retardant composite material according to the invention, wherein said method comprises:

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- Providing a fabric layer;

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- Providing at least one water-based dispersion of PVB containing the PVB, the plasticizer, at least one crosslinker, and the mixture of antimony trioxide and halogenated organic compound;
- Impregnating or coating at least one side of the fabric layer with the water-based dispersion of PVB;
- Curing the thus impregnated or coated fabric layer at a temperature of 100 to 180°C, preferably 120 to 180°C.

**[0013]** The manufacturing process is surprisingly efficient since, as it is known to the skilled person, providing a coating is much more difficult technically using a water-based product than using an organic solvent-based product.

## DETAILED DESCRIPTION OF THE INVENTION

[0014] A first object of the invention is the flexible, flame-retardant composite material, which comprises at least on impregnated or coated PVB coating layer. This layer is generally a not a laminated product, which is a different composite material as can be seen easily on the composition material. Actually, laminates having a polymer layer on the outside usually have a plastic or oil-like look and touch. In these different cases, the manufacturing method is different. The impregnation or coating of the coating layer is made from a liquid composition applied onto the fabric layer or onto an intermediate layer on which thermal treatment for drying and curing is carried out. The laminated product is made from the lamination of a solid product composition like a film or foil applied onto the fabric layer or onto an intermediate layer.

[0015] Advantageously, the impregnation or coating manufacturing method according to the invention is more cost-efficient than lamination and the mechanical resistance of a coating layer manufactured by impregnation or coating is more efficient than the one of a coating layer manufactured by lamination.

**[0016]** Polyvinyl butyral (or PVB) is a resin mostly used for applications that require strong binding, optical clarity, adhesion to many surfaces, toughness and flexibility. The major application of PVB is laminated safety glass for automobile windshields in which a protective foil made of polyvinyl butyral acting is bonded between two panels of glass. This results in a large amount of PVB foils to be recycled worldwide. However, this recycling is not an easy task since the waste material to be recycled comprises a plasticizer (roughly one fourth to one third of a plasticizer which is typically TEG-EH (Triethylene Glycol Bis (2-Ethyl Hexanoate) of CAS number 94-28-0 in the case of automotive applications) as well as traces of impurities such as glass, silicone and/or rubber, depending on its grade.

[0017] According to the invention, "A and/or B" means A, or B, or A and B.

[0018] The use of PVB coatings in the art is always limited to the use of solvent-based system or foils obtained by lamination, which is costly, complicated, and not environmental-friendly.

**[0019]** Advantageously, the flexible, flame-retardant composite material of the invention comprises an eco-friendly PVB coating layer which is a water-based coating obtained by an impregnation or coating manufacturing method.

**[0020]** According to the invention, "multilayer" means at least two layers according to the invention. At least one intermediate layer (i.e. present between the PVB coating layer and the fabric layer), preferably a polymer-based intermediate layer, can be present. The layer in contact with the outside is preferably the PVB coating layer, but at least one top-coat layer can be optionally present between the PVB coating layer and the outdoor atmosphere. In any case, the layers are adapted to the need in terms of adhesion strength and flame retardancy, in as much as the layers of the composite material are mechanically and/or chemically joined.

**[0021]** According to the invention, the top-coat layer if present is for example a clear coat for improving the UV resistance and/or the abrasion resistance. This top-coat layer is typically necessary in applications like artificial leather (e.g. for car interior or furniture) or in applications where PVB would replace a PVC coated fabric in a mechanically challenging application where it sees more wear and tear (e.g. for truck tarpaulins or tents). This top-coat layer is typically made of another coating layer which can be a clear coat. This could also be a PVB or acrylic or polyurethane coating layer or a coating comprised by a mix of multiple of these polymers on top of the PVB coating layer of the composite material according to the invention. According to the invention, "integral with said fabric layer" means that the layers are mechanically and/or chemically joined. This is for example the case when there is no intermediate layer between the fabric layer and the PVB coating layer. But this is also the case when there is a primer or another intermediate layer between the fabric layer and the PVB coating layer, in as much as the primer or PVB coating layer is mechanically and/or chemically joined to both the fabric layer and the PVB coating layer. Accordingly, any such intermediate layer can be present in the composite material.

[0022] The weight ratio PVB on antimony trioxide is generally from 2:1 to 10:1, preferably from 3:1 to 7:1.

**[0023]** The weight ratio PVB on (antimony trioxide + halogenated organic compound) is generally from 0.1:1 to 4:1, preferably from 0.5:1 to 2:1.

[0024] PVB is a polymer of formula  $(C_8H_{14}O_2)_n$  or

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wherein n is an integer generally of more than 20. It is usually prepared from polyvinyl alcohol by reaction with butyral-dehyde. Its CAS number is 915977-69-4.

[0025] The PVB originates from original PVB or from recycled PVB.

**[0026]** Preferably, the PVB originates from recycled PVB waste, such as the commercial products Shark Dispersion (from various grades e.g. SX1, XS, FX2, WX2...).. This corresponds advantageously to an eco-responsible approach. The impurities which can be present in the recycled PVB waste are less than 1% by weight. This ability to recycle the waste stream as such is a surprising advantage of the invention, since it is often very difficult to integrate and/or to adapt waste stream from the recycling of goods into the current production cycle of products.

**[0027]** The PVB can also originates from original PVB (which means originating from recycling) such as the commercial products Aquarez PVB (from various grades, e.g. 501, 605, DPS48-36...) o.

**[0028]** Antimony trioxide or antimony oxide (III) (IUPAC name) (or antimonious oxide or antimony sesquioxide) of formula  $Sb_2O_3$  is an inorganic compound. Its CAS number is 1309-64-4.

**[0029]** The halogenated organic compound is preferably a polyhalogenated organic compound (such as decabromodiphenyl ether or 1,1'-oxybis(2,3,4,5,6-pentabromobenzene) of CAS number 1163-19-5). This compound is mixed with antimony as antimony trioxide. The halogen is chosen from chlorine, bromine, fluorine, iodine, and their mixtures, preferably the halogen is bromine.

**[0030]** The fabric according to the invention is a textile material of any type, such as woven materials, knitted materials, warp-knitted materials, non-woven materials, and their mixtures. In a preferred embodiment, the fabric is a rollable fabric. Preferably the fabric is a sheet stocked as a roll, that is to say a structure of low thickness with respect to the other two dimensions of the material. As an example, the thickness can be limited to about. 0.1 to 5 mm, for rolls of about 1 m to 6 m width and a weight from about 30 g/m² to about 800 m². The rolls are assembled when constructing the façade elements typically by welding them along their lengths in particular by High Frequency (HF) welding.

**[0031]** In any case, the fabric can be a mesh fabric or a plain fabric, depending mainly on its final use. The mesh fabric is particularly suitable for a use in outer advertising, for example as building wrap of reduced load.

**[0032]** According to an embodiment, the fabric is a textile-based substrate comprising fibers chosen from the group consisting of polyester, polyamide, polyacrylic, polyethylene, polypropylene, glass, wool, cotton, rayon, linen, bamboo, carbon, steel, copper, and aramide fibers and their mixtures. For example, the polyester can be polyether-terephthalate.

**[0033]** According to the invention, the term "fiber" includes both staple fibers and filaments. According to one embodiment, the fabric originates from recycled grades (such as recycled polyester from bottle chips) or from renewable resources (such as bamboo, cotton...).

**[0034]** According to a preferred embodiment, the PVB coating layer further comprises at least one mineral flame retardant, the mineral flame retardant being present in an amount of 0 to 40%, preferably 20 to 40%, by weight with respect to the coating layer. The flame retardant is preferably chosen from aluminum trihydrate, magnesium hydroxide, zinc borate, and their mixtures. More preferably, the mineral flame retardant is aluminum trihydrate.

**[0035]** The CAS number of aluminum trihydrate (or ATH) (or hydrated alumina or aluminum (III) hydroxide or aluminum trihydroxide) is 21645-51-2.

[0036] The CAS number of magnesium hydroxide (or magnesium hydroxide or milk of magnesia) is 1309-42-8.

[0037] The CAS number of zinc borate differs according to the zinc/boron ratio and the water content. The usual zinc borate has CAS number 12767-90-7. All the variants of zinc borate are also encompassed according to the invention.

**[0038]** According to a preferred embodiment, the plasticizer of the PVB coating layer is present in an amount of 5 to 25% by weight of the coating layer.

**[0039]** The plasticizer can be present in the PVB as raw material, if the PVB originates from recycled PVB waste. In this case, preferably, the plasticizer originates from recycled PVB waste. Actually, recycled PVB waste typically comprises around one third to one fourth of plasticizer.

[0040] The plasticizer can be chosen from phosphate-based compounds such as triarylphosphates.

[0041] More generally, the plasticizer is preferably chosen from triethylene glycol (CAS number 112-27-6), triethylene

glycol di(2-ethylhexoate) (also known as triethylene glycol bis (2-ethyl hexanoate or 2,2'-ethylenedioxydiethyl bis(2-ethylhexanoate, CAS number 94-28-0), alkyl phthalate (such as di-2-ethylhexyl phthalate, CAS number 117-81-7), dibutyl maleate (CAS 105-76-0), dibutyl adipate (CAS number 105-99-7), dibutyl sebacate (CAS number 109-43-3), tris(2-ethylhexyl) phosphate (CAS number 78-42-2), 2-ethylhexyl diphenyl phosphate (CAS 1241-94-7), triphenyl phosphate (CAS number 115-86-6), and their mixtures.

[0042] The weight ratio (PVB + plasticizer) on antimony trioxide is generally from 2:1 to 10:1, preferably from 3:1 to 9:1. [0043] The weight ratio (PVB + plasticizer) on (antimony trioxide + halogenated organic compound) is generally from 0.5:1 to 5:1, preferably from 0.8:1 to 4:1.

**[0044]** According to a particularly preferred embodiment, the PVB of the PVB coating layer is partially crosslinked, which means that it still has remaining thermoplastic properties. The skilled person is capable to adapt the crosslinking ratio according to the needs thereof. Typically, this crosslinking has been obtained when a crosslinker, preferably chosen from blocked isocyanate water-compatible compounds, was present in the compositions before its manufacture e.g. by curing. Generally, the crosslinker is no more present in the PVB coating layer.

**[0045]** Generally, when the composite material is to be used outdoor, the PVB coating layer preferably further comprises at least one compound chosen from UV filters, UV absorbers, UV stabilizers and their mixtures. The UV filters can be chosen from liquid cyanoacrylates UV absorbers, 2-ethylhexyl 2-cyano-3,3-diphenylacrylates (such as one of the commercial products Uvinul 3039, UV-3039 and Omnistab UV 3039) and their mixtures. The UV absorbers can be chosen from benzotriazoles like the one of CAS number 3896-11-5 (such as one of the commercial products Comax UV-126, Riasorb UV-326, MPI UV-absorber 326 and Tinuvin 326). The UV stabilizers can be chosen from benzophenones like the one of CAS number 1843-05-6 (such as one of the commercial products Comax UV-181, Riasorb UV-531 and MPI UV-81 (531)).

**[0046]** The composite material is generally compatible with usual pigments and inks used in digital and screen printing, including water based inks such as latex-inks or sublimations inks, solvent-based or mild-solvent based inks as well as UV-curable inks.

[0047] The flame retardancy is measured according to the standard DIN 4102-1 May 1998. The composite material of the invention must at least pass the level B2, preferable the level B1.

**[0048]** The flexibility is measured by the standard DIN EN ISO 32100. This standard describes the bally-flex test including a detailed description of the equipment to be used. For the examples, a Bally flexometer for 20000 cycles was used.

30 **[0049]** The adhesion is measured according to the standard DIN 53357.

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**[0050]** The weldability is not measured according to a standard, as known to the skilled person, since the measurement depends on the machine which is used. The skilled person is capable to determine the conditions of use so that to know is the composite material can be considered weldable.

**[0051]** The abrasion resistance is measured by a Martindale test. This test and the equipment is described in standard DIN EN ISO 12947.

**[0052]** A second object of the invention is the manufacturing method of the flexible, flame-retardant composite material of the invention.

**[0053]** The impregnation is usually carried out by coating the fabric with the water-based dispersion. The coating is usually carried out by deposit of a water-based dispersion on the fabric layer using for example knife coating or roller coating or padding technique. As already explained, the use of a water-based dispersion helps to use eco-responsible compounds. The water-based dispersion preferably does not comprise any halogen except from the one(s) in relation to the antimony trioxide.

[0054] Preferably, the PVB originates from recycled PVB waste.

[0055] The water-based dispersion comprises at least one crosslinker generally chosen from blocked isocyanates (such as one of the commercial products Imprafix 2794XP, Trixene Bl2021 and Trixene Bl201), isocyanates (such as one of the commercial products Desmodur DN and Easaqua XD 401),carbodiimides (such as one of the commercial products Desmodur XP 2802, Picassian XL-732, Picassian XL-702 and Picassian XL-725), and their mixtures, preferably blocked isocyanate. The amount of crosslinker in the water based dispersion is preferably from more than 0% and up to 20%, by weight based on the weight of the PVB polymer in the water based dispersion.

**[0056]** According to a preferred embodiment, a drying step is carried out after the impregnation step and before the curing step. In practice, the curing step is generally carried out in an oven or the like, and the temperature rise in the oven to reach the curing temperature is carried out in the oven, which constitutes the drying step. The drying step is carried out as known to the skilled person, for example at 100°C in an oven.

**[0057]** The invention and the benefits that flow from it will be clearer upon reading the following figures and examples, given to illustrate the invention and not to limit it in any way.

#### **BRIEF DESCRIPTION OF THE FIGURES**

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**[0058]** The way of carrying out the invention as well as the advantages thereof will become apparent from the following description, made by way of non-limiting indication and with the aid of the accompanying drawings, in which:

Figure 1 is a perspective view of a flexible sheet constituting a first embodiment of the invention.

Figure 2 is a perspective view of a flexible sheet constituting a second embodiment of the invention.

Figure 3 is a cross section of a first apparatus for the manufacture of a flexible sheet according to the invention.

Figure 4 is a cross section of a second apparatus for the manufacture of a flexible sheet according to the invention.

Figure 5 is a cross section of a third apparatus for the manufacture of a flexible sheet according to the invention.

## **DETAILED DESCRIPTION OF THE FIGURES**

[0059] Identical numbers denote identical parts.

[0060] Figure 1 is a perspective view of a flexible sheet 1 constituting a first embodiment of the invention. The flexible sheet 1 comprises a fabric layer 11 coated on both sides by a PVB coating layer 10.

**[0061]** Figure 2 is a perspective view of a flexible sheet **2** constituting a second embodiment of the invention. The flexible sheet **2** comprises a fabric layer **11** coated on both sides by a PVB coating layer **10**, the side to be in contact with the outdoor atmosphere being further coated by a top-coat layer **12**. This top-coat layer **12** is a clear coat.

[0062] Figure 3 is a cross section of a first apparatus 3 for the manufacture of a flexible sheet 39 according to the invention. The apparatus 3 can typically be used for both mesh fabrics and plain fabrics, especially fabrics of large width. The arrows indicate the direction of circulation of the sheet. A fabric 29 is unwound from a roll 28, and further guided by rolls 33. The fabric is impregnated in a bath 30 of liquid PVB present in a container 31. Two scrapers 22 remove excess 32 of PVB which fall down in the bath. The coated fabric 36 is then guided, optionally passed next to a nozzle 20 which blows air by micro jets to clean the holes in the coated fabric 36 if necessary (for example in the case of a mesh fabric if the holes of the mesh fabric are of dimension less than 5 mm), to an oven 25 which allows the drying and crosslinking and thus leads to obtaining the flexible sheet 29.

[0063] Figure 4 is a cross section of a second apparatus 4 for the manufacture of a flexible sheet 40 according to the invention. The apparatus 4 can typically be used for mesh fabrics. The arrows indicate the direction of circulation of the sheet. The fabric 29 is unwound from the roll 28, further impregnated in the bath 30 of liquid PVB present in the container 31 and guided by the transfer roll 42 which transfers the coating onto the mesh fabric 29. The following rollers 34 transfers the liquid coating between both sides of the mesh fabric back and forth and ensure an equal, uniform coating of both sides and the inner surface of the mesh fabric. The coated fabric 37 is then guided optionally passed next to a nozzle 21 which blows air by micro jets to clean the holes in the coated fabric 37 if necessary (for example if the holes of the mesh fabric are of dimension less than 3 mm), to an oven 26 which allows the drying and crosslinking and thus leads to obtaining the flexible sheet 40.

[0064] Figure 5 is a cross section of a third apparatus 5 for the manufacture of a flexible sheet 41 according to the invention. The apparatus 5 can typically be used for plain fabrics. The arrow indicates the direction of circulation of the sheet. The fabric 29 is unwound from the roll 28, and the liquid PVB 30 is spread onto the fabric 29 using a doctor blade 24. During the knife coating step, the fabric 38 is stabilized by a support roll 35. Afterwards it enters an oven 27 which allows the drying and crosslinking and thus leads to obtaining the flexible sheet 41.

#### **EXAMPLES**

[0065] 8 examples, among which 5 comparative examples and 3 examples according to the invention, were carried out. [0066] First, the components of the compositions of the 8 different PVB coating layers are summarized in Tables 1 and 1a below, and the related ratios in Table 2 below.

**[0067]** These 8 compositions were used in a manufacturing corresponding the one disclosed in Figure 3, using the same fabric layer which is made of woven PES spun yarn and has a weight per area of about 125 g/m2. The drying was carried out for 1 minute at 80 °C followed by a cueing step for 2 minutes at 150°C.

**[0068]** The properties of the thus obtained composite materials were tested according to the standard, except weldability which was measured using a stationary high frequency (HF-) welding machine manufacturesd by Forsstrom, Sweden, model type Forsstrom XP 160. Pressure: 3,0 kg/cm². Welding time: 6s. Welding current: 0,55 A. Cooling time: 8 seconds. The results are summarized in Table 3 below.

Table 1: composition (part on top of 100 parts of resin dispersion)

	Example n°	1 Comp	2 Inv	3 Comp	4 Comp	5 Comp	6 Inv	7 Comp	8 Inv		
	Aqueous PVB dispersion (Shark dispersion SX1)	100	100	100	100	100	100	100	100		
	UV filter (Univul 3039)	1	1	1	1	1	1	1	1		
)	Crosslinker : blocked isocyanate (Imprafix 2794)	0	3	8	3	3	3	3	3		
	Mineral flame retardant: ATH powder (Alfrimal 104D)	50	50	50	50	50	50	0	0		
5	Flame retardant component: comprising Br/Sb <sub>2</sub> O <sub>3</sub> , 1 part of Sb <sub>2</sub> O <sub>3</sub> per 3 parts of brominated agent (Flacavon FH 9004/123)	40	40	40	0	20	50	0	60		
)	White pigment TiO <sub>2</sub> (Tubiprint weiss K90)	15	15	15	15	15	15	15	15		
	Where Comp means comparative and Inv means Invention										

Table 1a: composition (in % in the dried coating before curing)

Example n°	1 Comp	2 Inv	3 Comp	4 Comp	5 Comp	6 Inv	7 Comp	8 Inv
PVB	27	26.8	26.5	33.3	29.7	25.5	61.8	36.8
TEG-EH	8.5	8.5	8.4	10.5	9.4	8.1	19.5	11.6
UV filter	0.7	0.7	0.7	0.9	0.8	0.7	1.7	1.0
Crosslinker : blocked isocyanate	0	0.7	1.8	0.8	0.7	0.6	1.5	0.9
Mineral flame retardant: ATH	37.3	37.1	36.7	46.1	41.1	35.4	0	0
Sb <sub>2</sub> O <sub>3</sub>	4.9	4.9	4.8	0	2.7	5.8	0	10.1
brominated agent	14.8	14.7	14.5	0	8.1	17.5	0	30.3
TiO <sub>2</sub>	6.7	6.7	6.6	8.3	7.4	6.4	15.4	9.2

**[0069]** It can be seen that examples 1 to 3 were carried out modifying only the content of crosslinker (blocked isocyanate, cells in bold), examples 3 to 6 were carried out modifying only the content of the flame retardant component (brominated organic compound + antimony trioxide, cells in bold), some ATH as mineral flame retardant being present, and examples 7 and 8 ware were carried out modifying only the content of the flame retardant component (brominated organic compound + antimony trioxide, cells in bold), no mineral flame retardant being present.

Table 2: ratios (Sb as Sb<sub>2</sub>O<sub>3</sub>, Br as the brominated organic compound)

Example n°	1 Comp	2 Inv	3 Comp	4 Comp	5 Comp	6 Inv	7 Comp	8 Inv
Ratio PVB on Sb	5.5:1	5.5: 1	5.5:1	N/A	10.9:1	5.5: 1	N/A	3.6: 1
Ratio PVB on (Sb + Br)	1.4:1	1.4: 1	1.4:1	N/A	2.7:1	1.4: 1	N/A	0.9: 1
Ratio (PVB + plasticizer) on Sb)	7.2:1	7.2: 1	7.2:1	N/A	14.4:1	7.2: 1	N/A	4.8: 1

#### (continued)

Example n°	1 Comp	2 Inv	3 Comp	4 Comp	5 Comp	6 Inv	7 Comp	8 Inv	
Ratio (PVB + plasticizer) on (Sb + Br)	1.8:1	1.8: 1	1.8:1	N/A	3.6:1	1.8: 1	N/A	1.2: 1	
Where Comp means comparative, Inv means Invention and N/A means Not Applicable or not defined (not calculable)									

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Table 3: results of the tests

Example n°	1 Comp	2 Inv	3 Comp	4 Comp	5 Comp	6 Inv	7 Comp	8 Inv
HF weldability	YES	YES	NO	YES	YES	YES	YES	YES
Flexibility	FAIL	PASS	PASS	Not tested	Not tested	PASS	PASS	PASS
Fire retardancy, B2	PASS	PASS	PASS	FAIL	FAIL	PASS	FAIL	PASS

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[0070] It can be seen that examples 2, 6 and 8 according to the invention are the only examples fulfilling all the requirements.

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**[0071]** Comp 1 shows a good weldability. However, due to the lack of crosslinker, the coating is not durable enough and shows not sufficient adhesion to the textile substrate.

**[0072]** Comp 3 gives a very durable and still flexible coating and shows very good coating adhesion due to the high level of crosslinker. Therefore, it loses some of its thermoplastic properties. As a result, it cannot be welded anymore, which is a disadvantage for a coated fabric.

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[0073] Comp 4 demonstrates that even a high load of a mineral flame retardant like ATH is not sufficient in order to get the desired flame retardancy properties. Even in combination with a moderate amount of antimony trioxide/halogen (Ratio PVB on  $Sb_2O_3$ : >10:1), a high ATH loading is not sufficient (Comp 5). If the ratio PVB on  $Sb_2O_3$  is <10:1 whilst ATH is present, the flame retardant properties are in line with the requirements (Inv 6). If the mineral flam retardant is omitted, a low ratio of PVB on  $Sb_2O_3$  is necessary to pass the flame retardancy requirements (Inv 8).

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# Claims

- 1. A flexible, flame-retardant composite material comprising:
  - a fabric layer; and
  - at least one impregnated or coated Polyvinyl Butyral (PVB) coating layer, which is integral with said fabric layer; the PVB coating layer containing 20 to 60% by weight of PVB, at least one plasticizer in an amount of 5 to 40% by weight of the coating layer, and a mixture of antimony trioxide  $Sb_2O_3$  and at least one halogenated organic compound as flame retardant in a total amount of 5 to 45% by weight with respect to the coating layer, and in a ratio of 0.1 to 5 part of antimony trioxide  $Sb_2O_3$  per part of halogenated organic compound.
- 2. The flexible, flame retardant composite material according to claim 1, wherein said material is a rollable fabric.
- 3. The flexible, flame retardant composite material according to claim 1 or claim 2, wherein the fabric is a mesh fabric or a plain fabric.
  - 4. The flexible, flame retardant composite material according to any one of claims 1 to 3, wherein the fabric is a textile-based substrate comprising fibers chosen from the group consisting of polyester, polyamide, polyacrylic, polyethylene, polypropylene, glass, wool, cotton, rayon, linen, bamboo, carbon, steel, copper, and aramid fibers and their mixtures.
- 5. The flexible, flame retardant composite material according to any one of claims 1 to 4, wherein the PVB coating layer further comprises at least one mineral flame retardant, the mineral flame retardant being present in an amount of 0 to 40% by weight with respect to the coating layer, the flame retardant being preferably chosen from aluminum trihydrate, magnesium hydroxide, zinc borate and their mixtures.

- **6.** The flexible, flame retardant composite material according to any one of claims 1 to 5, wherein the plasticizer is present in an amount of 5 to 25% with respect to the coating layer.
- 7. The flexible, flame retardant composite material according to any one of claims 1 to 6, wherein the plasticizer originates from recycled PVB waste.
  - 8. The flexible, flame retardant composite material according to any one of claims 1 to 7, wherein the plasticizer is chosen from triethylene glycol, triethylene glycol di(2-ethylhexoate), alkyl phthalate, dibutyl maleate, dibutyl adipate, dibutyl sebacate, tris(2-ethylhexyl) phosphate, 2-ethylhexyl diphenyl phosphate, triphenyl phosphate, and their mixtures.
  - 9. The flexible, flame retardant composite material according to any one of claims 1 to 8, wherein the PVB of the PVB coating layer is partially crosslinked.
- **10.** The flexible, flame retardant composite material according to any one of claims 1 to 9, wherein the PVB coating layer at least one compound chosen from UV filters, UV absorbers, UV stabilizers and their mixtures.
  - **11.** The flexible, flame retardant composite material according to any one of claims 1 to 10, wherein the fabric originates from recycled grades or from renewable resources.
  - **12.** A manufacturing method for forming the flexible, flame retardant composite material according to any one of claims 1 to 11, wherein said method comprises:
    - Providing a fabric layer,

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- Providing at least one water-based dispersion of PVB containing the PVB, the plasticizer, at least one crosslinker, and the mixture of antimony trioxide and halogenated organic compound;
- Impregnating or coating at least one side of the fabric layer with the water-based dispersion of PVB;
- Curing the thus impregnated or coated fabric at a temperature of 100 to 180°C.
- 30 13. The manufacturing method according to claim 12, wherein the PVB originates from recycled PVB waste.
  - **14.** The manufacturing method according to claim 12 or claim 13, wherein a drying step is carried out after the impregnation step and before the curing step.
- **15.** The manufacturing method according to any one of claims 12 to 14, wherein the crosslinker is chosen from blocked isocyanates, isocyanates, carbodiimides and their mixtures, and is present in an amount from more than 0% up to 20% by weight based on the weight of the PVB polymer in the water based dispersion.

Fig. 1

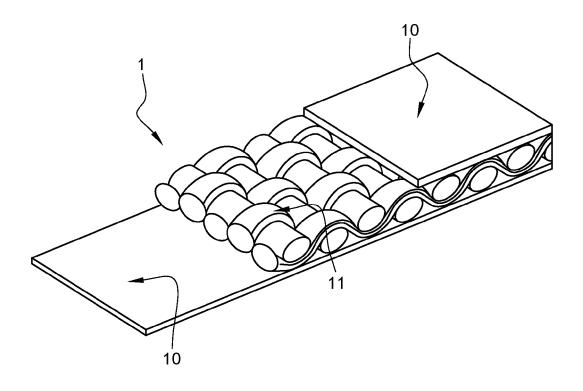


Fig. 2

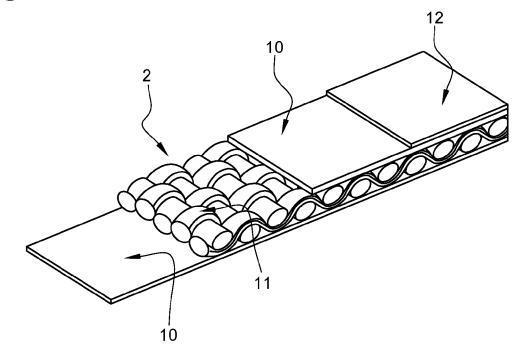


Fig. 3

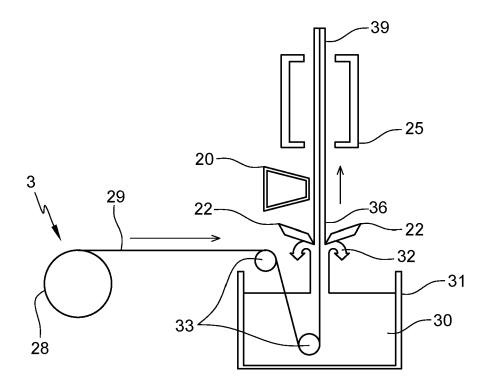


Fig. 4

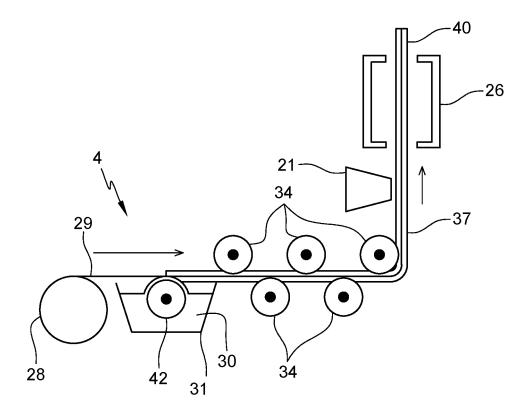
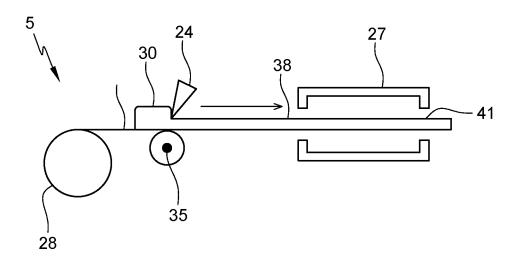


Fig. 5





# **EUROPEAN SEARCH REPORT**

**Application Number** 

EP 21 30 6185

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# ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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