



(86) Date de dépôt PCT/PCT Filing Date: 2000/09/08
(87) Date publication PCT/PCT Publication Date: 2001/03/15
(85) Entrée phase nationale/National Entry: 2001/05/07
(86) N° demande PCT/PCT Application No.: EP 00/08943
(87) N° publication PCT/PCT Publication No.: WO 01/18881
(30) Priorités/Priorities: 1999/09/09 (1013011) NL;
1999/12/02 (1013730) NL

(51) Cl.Int.⁷/Int.Cl.⁷ H01L 31/058, E04D 13/18, H01L 31/048
(71) Demandeur/Applicant:
AKZO NOBEL N.V., NL
(72) Inventeurs/Inventors:
ANDEL VAN, ELEONOR, NL;
MIDDELMAN, ERIK, NL
(74) Agent: SWABEY OGILVY RENAULT

(54) Titre : ELEMENT DE COUVERTURE HYBRIDE
(54) Title: HYBRID ROOF COVERING ELEMENT

(57) **Abrégé/Abstract:**

The invention pertains to a hybrid roof covering element comprising a flexible thin film solar cell sheet having a heat capacity of less than 3,5 kJ/m²K, preferably less than 600 J/m²K. Preferably, the flexible thin film solar cell sheet has a response speed, defined as the change in temperature per unit of time per change in net flux, of more than 5,7*10⁻⁴ K/W, preferably more than 11*10⁻⁴ K/W. The use of a thin film solar cell sheet having such a low heat capacity makes it possible to obtain a hybrid roof covering element with a high response speed. Thin film solar cell sheets manufactured by means of a roll-to-roll process, more particularly a roll-to-roll process in which a temporary substrate is employed, are preferred for use in the hybrid roof covering element according to the invention.



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

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
15 March 2001 (15.03.2001)

PCT

(10) International Publication Number
WO 01/18881 A1(51) International Patent Classification⁷: H01L 31/058,
31/048, E04D 13/18(74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel
N.V., Intellectual Property Dept. (Dept. AIP), P.O. Box
9300, NL-6800 SB Arnhem (NL).

(21) International Application Number: PCT/EP00/08943

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ,
DE, DK, DM, DZ, 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, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,
TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.(22) International Filing Date:
8 September 2000 (08.09.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
1013011 9 September 1999 (09.09.1999) NL
1013730 2 December 1999 (02.12.1999) NL(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), OAPI patent (BF, BJ, CF, CG,
CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).(71) Applicant (*for all designated States except US*): AKZO
NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arn-
hem (NL).**Published:**

- With international search report.
- Before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments.

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): MIDDELMAN,
Erik [NL/NL]; Cattepoelseweg 237, NL-6815 CC Arnhem
(NL). ANDEL VAN, Eleonoor [NL/NL]; Strootmanweg
12, NL-7548 RB Enschede (NL).For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

WO 01/18881 A1

(54) Title: HYBRID ROOF COVERING ELEMENT

(57) Abstract: The invention pertains to a hybrid roof covering element comprising a flexible thin film solar cell sheet having a heat capacity of less than 3,5 kJ/m²K, preferably less than 600 J/m²K. Preferably, the flexible thin film solar cell sheet has a response speed, defined as the change in temperature per unit of time per change in net flux, of more than 5,7*10⁻⁴ K/W, preferably more than 11*10⁻⁴ K/W. The use of a thin film solar cell sheet having such a low heat capacity makes it possible to obtain a hybrid roof covering element with a high response speed. Thin film solar cell sheets manufactured by means of a roll-to-roll process, more particularly a roll-to-roll process in which a temporary substrate is employed, are preferred for use in the hybrid roof covering element according to the invention.

HYBRID ROOF COVERING ELEMENT

The invention pertains to a hybrid roof covering element comprising a thin film solar cell sheet. Hybrid roof covering elements are elements which can
5 suitably be mounted on or in roof structures or otherwise integrated into buildings or, if so desired, in stand-alone systems, in which solar energy is employed in two ways. On the one hand, solar energy is converted into electricity by a thin film solar cell sheet. On the other hand, solar energy is used to heat a gaseous and/or liquid medium, such as air and/or water.

10

Hybrid roof covering elements comprising a thin film solar cell sheet are known. They are described, e.g., in US 5,589,006 and EP 0 820 105.

US 5,849,006 describes a hybrid roof covering element comprising, from top to bottom, a top layer composed of, preferably, a transparent coating, a
15 thin film solar cell sheet cast in a filler, a back insulating member, a filler layer, and a roofing sheet. Air is passed underneath the roofing sheet.

EP 0 820 105 describes a system where a thin film solar cell sheet is provided on a back plate of high load bearing capacity and high processability, so that the plate can be freely bent into any desired shape,
20 more specifically into a trapezoidal shape. The air is passed underneath the back plate and over the thin film solar cell sheet.

Although these hybrid roof covering elements function adequately, they are open to improvement, especially as regards heat generation efficiency.

25

It has now been found that an improvement can easily be effected in this field by directly contacting a thin film solar cell sheet with low heat capacity with the medium to be heated. This will result in higher efficiency on the part of the roof covering element, as less energy is required to heat the thin
30 film solar cell sheet itself, leaving more energy for useful processing. This leads to a higher response speed on the part of the hybrid roof covering element.

The invention thus pertains to a hybrid roof covering element comprising a thin film solar cell sheet which is characterized in that it has a heat capacity of less than $3,5 \text{ kJ/m}^2\text{K}$, preferably less than $600 \text{ J/m}^2\text{K}$.

- 5 The thin film solar cell sheet used in the hybrid roof covering element according to the invention is a flexible thin film solar cell sheet. The flexibility of the film is attractive for a number of reasons. First of all, said flexibility makes it possible to transport the thin film solar cell sheet in rolled-up form to the place where the roof covering elements are assembled.
- 10 Secondly, it is easier to divide flexible thin film solar cells up into sections of the desired size than rigid thin film solar cells on, say, a glass carrier. Thirdly, the flexibility of the thin film solar cell sheet makes it possible for the film to be integrated into the roof covering element in different ways if so desired, as a result of which the position of the film vis-à-vis the sun can be
- 15 optimized and any desired aesthetic effects may be obtained. Thus a flexible thin film solar cell sheet can not only be made into a flat sheet as is most common, but also bent into, say, a trapezoidal or some other desired shape. Thin film solar cell sheets manufactured by means of a roll-to-roll process are particularly attractive, as they very fully satisfy the desired
- 20 properties of easy transportation and easy dividing up into sections of the desired size.

The thin film solar cell sheet used in the hybrid roof covering element according to the invention generally is composed of a flexible carrier, a

25 back electrode, a photovoltaic layer, and a transparent front electrode. If so desired, the thin film solar cell sheet may be provided with one or more protective layers or other top layers. The heat capacity of such a thin film solar cell sheet is determined principally by the nature of the carrier and any protective and top layers present. In selecting these materials care has to

30 be taken to ensure that the desired properties as regards heat capacity are obtained.

The thin film solar cell sheet employed in the hybrid roof covering element according to the invention preferably has an overall thickness of less than 1000 μm , more preferably of less than 500 μm , most preferably of less than 300 μm . Generally speaking, the thinner the thin film solar cell sheet, the lower its heat capacity will be.

The thin film solar cell sheet employed in the hybrid roof covering element according to the invention preferably has a weight per surface area of less than 1400 g/m^2 , more preferably of less than 700 g/m^2 . Generally speaking, the lighter the thin film solar cell sheet, the lower its heat capacity will be. Furthermore, lighter sheets may result in simpler and less costly transportation and processing.

Suitable materials for the carrier layer of the thin film solar cell sheet include thermoplastic or thermosetting polymer films, combinations thereof, and, optionally, fibre-reinforced variations thereon. Suitable thermosetting materials include polyimides, unsaturated polyesters, vinyl esters, SI, etc. The thermoplastic materials may be amorphous as well as semi-crystalline. Examples of suitable amorphous thermoplastics are PEI, PSU, PC, PPO, PES, PMMA, SI, PVC, PVDC, FEP, and various other fluorine-containing polymers. Examples of suitable semi-crystalline materials are PET, PEN, PEEK, PEKK, PP, and PTFE. Examples of suitable liquid-crystalline materials are PPTA (Twaron, Aramica, Kevlar (all trade marks)). Use may be made of melt-extruded films as well as solution-, emulsion- or suspension-cast films. Biaxially drawn films as a rule will have superior mechanical properties. Metal films on which an insulating (dielectric) top layer has been provided, or compositions of polymer and fiber reinforcement like glass fiber reinforced epoxy-may also serve as a carrier layer if so desired.

Polymeric "co-extruded" films provided with a thermoplastic adhesive layer with a softening point below that of the carrier itself are preferred.

Optionally, the coextruded film is provided with an anti-diffusion layer of, e.g., aluminium or SiOx.

At present, preference is given to biaxially drawn polyesters, preferably ones provided with an inorganic anti-diffusion coating.

- 5 The thickness of the carrier preferably is 75 μm to 1 mm. Preferred ranges are 100 μm to 600 μm and 150 μm to 300 μm . As indicated above, the use of a thin film solar cell sheet manufactured by means of a roll-to-roll process is attractive. An attractive roll-to-roll process for the manufacture of a flexible thin film solar cell sheet comprises the following steps:
- 10 a. providing a temporary substrate
 - b. applying the transparent conductive electrode onto said substrate
 - c. applying the photovoltaic layer
 - d. applying the back electrode
 - e. applying a permanent carrier onto the back electrode
 - 15 f. removing the temporary substrate.
 - g. optionally applying a transparent protective layer

The reason why this process is so attractive for manufacturing thin film solar cell sheets for use in hybrid roof covering elements is that the use of

20 the temporary substrate makes it possible for the front electrode of the transparent conductive oxide, the photovoltaic layer, and the back electrode to be applied under such conditions as will produce a solar cell of good quality. The permanent carrier which is applied onto the thin film solar cell sheet at a later stage can be selected such that it will readily satisfy the

25 conditions imposed by specific use in a hybrid roof covering element. However, there is no need for the permanent substrate to be resistant to the conditions, e.g., the high temperature conditions, prevailing during the application of the front electrode, the photovoltaic layer, and the back electrode, as a result of which there is greater freedom of choice when it

30 comes to selecting the permanent carrier.

For that reason the invention also pertains to a hybrid roof covering element comprising a thin film solar cell sheet manufactured by a process comprising the aforesaid steps a-g. Examples of suitable processes are those described in WO 98/13882 and WO 99/49483.

5

The nature of the back electrode, the PV layer, and the transparent front electrode are not crucial to the present invention.

The transparent front electrode as a rule will be a transparent conductive oxide (TCO). Examples of suitable transparent conductive oxides are
10 indium tin oxide, zinc oxide, zinc oxide doped with aluminium, fluor, or boron, cadmium sulphide, cadmium oxide, tin oxide, and, most preferably, F-doped SnO_2 . Said last-mentioned transparent electrode material is preferred, because it can form a desired crystalline surface with a columnar crystal structure when applied at a temperature above 400°C , preferably in
15 the range of 500 to 600°C . In addition, it is more resistant to chemicals than the much-used indium tin oxide. Also, it is far less costly.

In the present description the term "PV layer" or "photovoltaic layer" encompasses the entire system of layers needed to absorb light and generate electricity. Suitable layer configurations are known, as are
20 methods to apply them. For general prior art in this field reference may be made to Yukinoro Kuwano, "Photovoltaic Cells," Ullmann's Encyclopedia, Vol.A20 (1992), 161, and "Solar Technology," Ullmann's Encyclopedia, Vol.A24 (1993), 369.

Various thin-film semi-conductors can be utilized in the manufacture of the
25 PV layer. Examples are amorphous silicon (a-Si:H), microcrystalline silicon, polycrystalline amorphous silicon carbide (a-SiC), amorphous silicon germanium (a-SiGe), and a-SiGe:H. In addition, the PV layer in the thin film solar cell sheet according to the invention may comprise, e.g., CIS (copper indium diselenide, CuInSe_2) PV cells, cadmium telluride cells, Cu(In,Ga)Se
30 cells, ZnSe/CIS cells, ZnO/CIS cells, Mo/CIS/CdS/ZnO cells, and dye-sensitised cells. Stacked cells may also be applied.

Preferably, the PV layer is an amorphous silicon layer when the TCO comprises a fluorine-doped tin oxide. In that case the PV layer as a rule will comprise a set, or a plurality of sets of p-doped, intrinsic, and n-doped amorphous silicon layers, with the p-doped layers being arranged on the
5 side receiving the incident light.

The back electrode in the thin film solar cell sheet according to the invention preferably serves both as reflector and as electrode. The back electrode may comprise any suitable material having light reflecting properties, preferably aluminium, silver, or a combination of layers of both.
10 In the case of silver, it is preferred to first apply an adhesion promoter layer. TiO_2 and ZnO are examples of suitable materials for an adhesion promoter layer and have the advantage of also possessing reflecting properties when applied in a suitable thickness, e.g., of about 80 nm.

15 The hybrid roof covering element according to the invention has a higher response speed than conventional hybrid roof covering elements where the thin film solar cell sheet has been cast in a filler or is present on a rigid weatherproof carrier with load bearing capacity, e.g., made of copper plate. Response speed in this context means the rate at which the temperature of
20 the matter to be heated changes when the radiation intensity changes. The response speed thus is defined as the change in temperature per unit of time per change in net flux and has the unit K/W.

In the case of the hybrid roof covering element according to the invention, it is possible to distinguish the response speed of the thin film solar cell sheet
25 itself on the one hand and the response speed of the medium to which the heat is dissipated on the other. This latter value is also referred to as the response speed of the hybrid roof covering element. The response speed of the thin film solar cell sheet itself is a first indication of the response speed of the hybrid roof covering element. The thin film solar cell sheets
30 employed in the hybrid roof covering element according to the invention

preferably have a response speed of more than $5,7 \cdot 10^{-4}$ K/W, more preferably of more than $11 \cdot 10^{-4}$ K/W.

When the medium in the hybrid roof covering element to be heated is air, the response speed of the roof covering element preferably is more than
5 $5,7 \cdot 10^{-4}$ K/W, more preferably more than $11 \cdot 10^{-4}$ K/W.

When the medium in the hybrid roof covering element to be heated is water, the response speed of the roof covering element preferably is more than $1 \cdot 10^{-4}$ K/W, more preferably more than $2 \cdot 10^{-4}$ K/W.

10 The hybrid roof covering element according to the invention can be constructed in different forms. It may be suitable for the simultaneous generation of electricity and hot water; alternatively, it may be suitable for the simultaneous generation of electricity and hot air. Depending on the individual circumstances, other gaseous or liquid media may also be
15 heated.

The hybrid roof covering element according to the invention may comprise, for example, from top to bottom, a single or multiple transparent layer, a thin film solar cell sheet, and a thermally insulating material. Between the
20 transparent layer and the thin film solar cell sheet and/or between the thin film solar cell sheet and the thermally insulating material there is a space comprising the medium to be heated, such as air. In this case the single or multiple transparent layer preferably has a transparency to visible light of more than 70% and a k-value of less than $4 \text{ W/m}^2 \cdot \text{K}$. The k-value is a
25 parameter conventionally used in the art for the isolation performance of panels.

The hybrid roof covering element according to the invention is described in greater detail below with reference to a roof covering element suitable for
30 heating air, but it will be evident to the skilled person that the heating of different media can be carried out in a corresponding manner.

In a hybrid roof covering element according to the invention which is suitable for the simultaneous generation of electricity and hot air, the thin film solar cell sheet is present in a space into which cold air is introduced on one side while hot air is discharged on the other. The air's supply and
5 discharge may result from natural draught or be brought about by a ventilating plant.

In the roof covering element the thin film solar cell sheet may be mounted such that it is suspended freely, so that air will pass over the thin film solar cell sheet on either side. If so desired, the thin film solar cell sheet may be
10 mounted on a rigid substrate with good insulating properties in the hybrid roof covering element. In said latter case, the heat capacity of the substrate should be so low that the combined heat capacity of the thin film solar cell sheet and the rigid substrate does not exceed $3000 \text{ J/m}^2\text{K}$. Preferably, the combined heat capacity of the thin film solar cell sheet and the rigid
15 substrate is less than $900 \text{ J/m}^2\text{K}$, more preferably less than $450 \text{ J/m}^2\text{K}$.

As regards energy efficiency, it is preferred to mount the thin film solar cell sheet in an air chamber, so that the thin film solar cell sheet will be in contact with the air flowing past on either side. For reasons of firmness the use of a rigid substrate may be desired. The rigid substrate is made of, e.g.,
20 (foamed) plastic or a similar material and constructed in the thinnest possible form.

The air chamber has to be insulated sufficiently also on the side receiving the incident sunlight, this in order to ensure that the heat generated is not dissipated to the outside air. This can be achieved by providing a suitable
25 insulating top layer. As described above, this top layer preferably has a transparency to visible light of more than 70% and a k-value of less than $4 \text{ W/m}^2\text{K}$. As was observed earlier, there is no need for the thin film solar cell sheet to be mounted flatly. It can also be mounted shaped in a certain way, e.g., as disclosed in EP 0 820 105, or in any other manner.

The most efficient way of obtaining hot water using a hybrid roof covering element according to the invention is to generate hot air in the hybrid roof covering element and use this to generate hot water with the aid of a heat exchanger.

5

Example 1

A hybrid roof covering element for the simultaneous generation of electricity and hot air is built up of the following elements, from top to bottom: a
10 sealing against the effects of the weather, a transparent insulating cavity plate of plastic underneath which air can flow, a thin film solar cell sheet on a foam plastic insulating layer, and a roofing layer. The roof covering element is provided with inlets and outlets for cold and hot air, respectively. The air is heated in the space between the thin film solar cell sheet and the
15 transparent insulating plastic plate.

The thin film solar cell sheet comprises a plastic carrier with superimposed thereon an aluminium back electrode which also acts as reflector, a photovoltaic layer of amorphous silicon, and a layer of fluorine-doped tin oxide as transparent front electrode. The film is covered with a protective
20 top layer of polymer. The thin film solar cell sheet has a heat capacity of $440 \text{ J/m}^2\text{K}$, a thickness of $250 \text{ }\mu\text{m}$, and a weight per surface area of 300g/m^2 . The thin film solar cell sheet and foam plastic plate combined have a heat capacity of $2500 \text{ J/m}^2\text{K}$.

The thin film solar cell sheet has a response speed of $2,2 \cdot 10^{-3} \text{ KW}$.

25 The roof covering element has a response speed of $6,7 \cdot 10^{-4} \text{ KW}$.

CLAIMS

1. Hybrid roof covering element suitable for simultaneously heating a medium and generating electricity which comprises a flexible thin film solar cell sheet with a heat capacity of less than 3,5 kJ/m²K, preferably less than 600 J/m²K.
5
2. The hybrid roof covering element according to claim 1 wherein the flexible thin film solar cell sheet has weight per surface area of less than 1400 grams per m², preferably less than 700 grams per m².
10
3. The hybrid roof covering element according to claim 1 or 2 wherein the flexible thin film solar cell sheet has a response speed of more than 5,7*10⁻⁴ K/W, preferably more than 11*10⁻⁴ K/W.
15
4. The hybrid roof covering element according to any one of the preceding claims wherein the thin film solar cell sheet comprises a carrier, a back electrode, a photovoltaic layer, and a transparent electrode.
20
5. The hybrid roof covering element according to any one of the preceding claims wherein the thin film solar cell sheet has a thickness of less than 1000 μm, more preferably of less than 500 μm, more preferably still of less than 250 μm.
25
6. The hybrid roof covering element according to any one of claims 4-5 wherein the carrier has a thickness of 75 μm to 1 mm, preferably of 100 μm to 600 μm, more preferably of 150 μm to 300 μm.

7. The hybrid roof covering element according to any one of the preceding claims wherein the flexible thin film solar cell sheet is manufactured by means of a roll-to-roll process.
- 5 8. The hybrid roof covering element according to claim 7 wherein the flexible thin film solar cell sheet is manufactured by means of a process comprising the following steps
- providing a temporary substrate
 - 10 • applying the transparent conductive electrode onto said substrate
 - applying the photovoltaic layer
 - applying the back electrode
 - applying a permanent carrier onto the back electrode
 - removing the temporary substrate.
 - 15 • optionally applying a transparent protective layer.
9. The hybrid roof covering element according to any of the preceding claims in which the medium to be heated is air, wherein the roof covering element has a response speed of more than $5,7 \cdot 10^{-4}$ KW, preferably more than $11 \cdot 10^{-4}$ KW.
- 20
10. The hybrid roof covering element according to any of the preceding claims 1-8 in which the medium to be heated is water, wherein the roof covering element has a response speed of more than $1 \cdot 10^{-4}$ KW, preferably more than $2 \cdot 10^{-4}$ KW.
- 25
11. The hybrid roof covering element according to any one of the preceding claims which, from top to bottom, comprises a single or multiple transparent layer, a thin film solar cell sheet, and a thermally insulating material, wherein between the transparent layer and the
- 30 thin film solar cell sheet and/or between the thin film solar cell sheet

and the thermally insulating material there is a space which comprises the medium to be heated.

- 5 12. The hybrid roof covering element according to claim 11 wherein the single or multiple transparent layer has a transparency to visible light of more than 70% and a k-value of less than $4\text{W/m}^2\cdot\text{K}$.
- 10 13. The hybrid roof covering element according to any one of claims 1-9, 11, or 12 wherein the medium to be heated is air and the energy from the air heated in the hybrid roof covering element is used to heat water with the aid of a heat exchanger.