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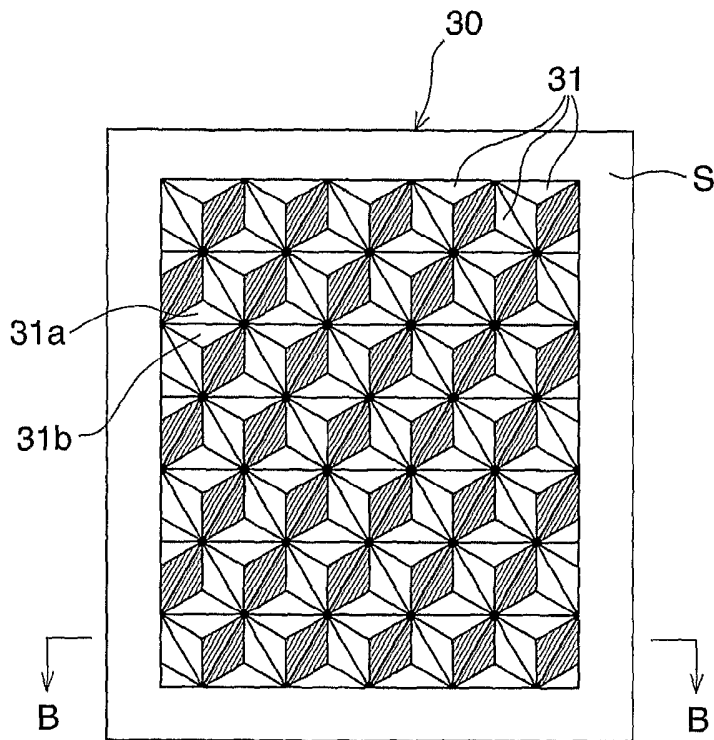
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[Continued on next page]

(54) Title: RETROREFLECTIVE ELEMENT INCLUDING CUBE CORNERS AND INCLUDING OPPOSED FRONT AND REAR SURFACES WHICH ARE BOTH RETROREFLECTIVE



(57) Abstract: A retroreflective element (10) including cube corners (31) and including opposed major front and rear surfaces that are both retroreflective. The retroreflective element (10) may be combined with a light transmissive resin to form a retroreflective resin composition that can be applied to articles to increase their retroreflectivity or molded to form retroreflective articles. The retroreflective element and articles that include the retroreflective element display excellent retroreflectivity and retroreflective efficiency.

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## RETROREFLECTIVE ELEMENT INCLUDING CUBE CORNERS AND INCLUDING OPPOSED FRONT AND REAR SURFACES WHICH ARE BOTH RETROREFLECTIVE

**Technical Field**

The present invention relates to retroreflective elements, methods of making retroreflective elements, and uses for the retroreflective elements, and, more specifically, to a retroreflective element that has a retroreflective front surface and a retroreflective rear surface; to a retroreflective material that supplies retroreflectivity to an article on which it is placed; and to a retroreflective body including the material that supplies retroreflectivity.

**Background**

Retroreflectors have the ability to redirect incident light back towards the light source. Retroreflectors are commonly used in signs, such as signposts and construction signs; in automobile and motorcycle tape; on or in clothing; on or in safety materials, such as, for example, life-saving devices; in signboard marking; as a reflecting plate for visible and laser light; and for infrared light reflecting-type sensors. There are two major types of retroreflectors: beaded articles and cube corner articles. Beaded articles commonly include glass or ceramic microspheres, such as, for example, microglass beads, that retroreflect incident light. Cube corner articles typically employ cube corner elements to retroreflect incident light. Cube corner articles may exhibit excellent retroreflective efficiency as compared to the beaded articles. This excellent retroreflective efficiency may be one reason why use of cube corner articles is increasing.

Japanese Patent Kohyo Publication 2002-538485 describes a retroreflective article having cube corner elements. Fig. 1 is a plan view showing a rear surface of a retroreflective element 10 of Japanese Patent Kohyo Publication 2002-538485. Retroreflective element 10 includes multiple cube corner elements in the form of trigonal pyramids 11. Trigonal pyramids 11 are formed on a common base surface S and are directly adjacent to one another. Adjacent trigonal pyramids 11a and 11b are both convex to the base surface of retroreflective element 10.

The retroreflective elements shown in Fig. 1 retroreflect light that is directed toward the flat, front surface of the retroreflective elements. This retroreflection is shown

in Fig. 2, which is a sectional view of retroreflective element 10 of Fig. 1 taken along line A-A. Light I is incident on a front surface of the retroreflective element 10, is retroreflected within a cavity 21 of a trigonal pyramid 11, and propagates through the front surface as reflected light R. In this instance, cavity 21 refers to a structure that forms a portion of trigonal pyramids 11 of Fig. 1.

The retroreflective element shown in Figs 1 and 2 does not retroreflect light directed to the rear surface (*i.e.*, the structured, as opposed to flat, surface) of the retroreflective element because light propagating through the rear surface is not incident on any cavities, trigonal pyramids, or cube corner elements capable of retroreflecting the light. One prior art attempt at making the rear surface reflective involved applying a light reflective layer to the rear surface. However, no one has successfully made the rear surface retroreflective.

Retroreflectors may be manufactured as a sheet having a surface in/on/from which the retroreflective element is formed. The retroreflective sheeting may be attached to a substrate, such as, for example, a sign or article of clothing, by means of known attachment processes, including, for example, adhesion and suturing. Retroreflective sheeting may be difficult to apply to complex surfaces, such as, for example, non-flat or three-dimensional surfaces.

One method of increasing the ease with which an article having a complex structure may be made retroreflective involves applying a retroreflective composition to the article or molding a retroreflective material to form the desired article. In order to supply retroreflectivity to a resin composition, retroreflective materials may be formed as "flakes" that can be added to the resin composition to supply retroreflectivity to the resin. However, resin compositions including these flakes have been found to have poor reflective efficiency due, at least in part, to the structure of the cube corner elements conventionally used to form the resin compositions.

Specifically, Japanese Patent Kokai Publication H5 No. 1993-209142 describes a coating material that is able to provide a retroreflective film. The coating material is in the form of flakes. However, the process of forming the substrate is undesirably complicated. Specifically, the procedure involves using a die to press a metal flake onto both the front and rear surfaces of the substrate. Further, the retroreflective article formed by this method

exhibits poor retroreflective efficiency, deformation or imprecision in shape, and low structural density.

### Summary

5 The inventors of the present invention have formed a retroreflective element having cube corners and exhibiting retroreflectivity on both the front and rear surfaces of the retroreflective element. The inventors have also created a novel method of making the retroreflective element and a novel method of incorporating the retroreflective element into a resin composition. A resin composition including the retroreflective element may be applied to or molded to form a retroreflective body that exhibits excellent retroreflective  
10 efficiency.

An exemplary retroreflective element includes a substrate formed of a light transmissive material. The substrate has opposed major first (front) and second (rear) surfaces. The front surface is substantially flat, and the rear surface includes a cube corner retroreflective structure that includes multiple cube corner trigonal pyramids that are  
15 arranged adjacent to one another on a common base surface. At least some of the trigonal pyramids are concave to the rear surface and some are convex to the rear surface. A light reflective layer is preferably applied to the rear surface of the substrate. The retroreflective element can be formed in a variety of shapes, including as a sheet or in flake form.

A method of producing a retroreflective article involves (1) combining the  
20 retroreflective element described above with a light transmissible resin to form a retroreflective resin composition; and (2) applying the retroreflective resin composition to an article or molding the retroreflective resin to form a retroreflective article. The resulting dual-side retroreflective article has excellent retroreflective efficiency and excels at retroreflecting incident light with a high incidence angle. Further, the method permits  
25 complicated, three-dimensional shapes, that were previously difficult if not impossible to apply a sheet of retroreflective material to, to be highly retroreflective.

### Brief Description of the Drawings

30 Fig. 1 is a plan view showing a rear surface of a prior art cube corner type retroreflective element.

Fig. 2 is a sectional view of the prior art retroreflective element of Fig. 1 taken along line A-A.

Fig. 3 is a plan view showing a rear surface of a cube corner type retroreflective element that is retroreflective on both major opposed surfaces.

5 Fig. 4 is a sectional view of the retroreflective element of Fig. 3 taken along line B-B.

### Detailed Description

10 The term "retroreflective element" refers to an optical element that is able to alter orientation of an incident light beam such that at least a part of the incident light beam is reflected from the optical element in the same direction as the light beam was initially propagating.

15 A cube corner-type retroreflective element of the present invention includes a substrate formed of a light transmissive material. The light transmissive material may be, for example, a light transmissive polymer of the type that is commonly known for use in making a retroreflective, cube corner element. The light transmissive polymer preferably transmits at least 70% of the intensity of an incident light beam at a given wavelength. Thus the light transmissiveness of the light transmissible polymer is preferably greater than 70%. The light transmissive polymer more preferably transmits at least 80%, and  
20 most preferably at least 90%, of the intensity of an incident light beam at a given wavelength

The substrate is preferably in a sheet form having opposed major first (front) and second (rear) surfaces. The front surface is preferably substantially flat, but may be convex or concave provided that the front surface provides adequate light incidence. The  
25 rear surface preferably includes multiple cube corner elements that are arranged adjacent to one another. Fig. 3 is a plan view of one exemplary rear surface in which the cube corners are in the form of multiple trigonal pyramids 31 that are arranged adjacent to one another on a common base surface S. As shown in Fig. 3, some of trigonal pyramids 31a, 31b are concave to the common base surface S and some are convex to the common base surface S. In one preferred embodiment, the first of two directly adjacent trigonal pyramids 31 is  
30 concave and the second is convex to the common base surface S.

Fig. 4 is a sectional view of the exemplary rear surface shown in Fig. 3 taken along line B-B. Because directly adjacent trigonal pyramids 31a and 31b are in the relationship of concave-convex on the common base surface S, a cavity 41 is formed for incidence of light propagating through the front surface, and a cavity 42 is formed for incidence of light propagating through the rear surface. More specifically, light I propagates through the front surface, is retroreflected by cavity 41, and is retroreflected from the front surface as reflected light R. Also, light I' propagates through the rear surface, is retroreflected by cavity 42, and is retroreflected from the front surface as reflected light R'. Consequently, the retroreflective element is retroreflective on both its front and rear surfaces.

Trigonal pyramids 31 are in the form of trihedral prisms having three exposed planes. Adjacent planes are substantially perpendicular to one another at an angle point. The trihedral prisms generally have a vertical angle of about  $90^\circ$ , but this is not necessary.

In one preferred embodiment, one trigonal pyramid and three trigonal pyramids adjacent thereto form a full cube corner. The term "full cube corner" refers to a cube corner element in which three planes that form a corner also form a hexahedron shape. The exemplary cube corners shown in Fig. 3 are full cube corners.

The trigonal pyramid size is variable, as is known to those of skill in the art. An exemplary trigonal pyramid has a ridge line that is between about 50 microns and about 5 millimeters, preferably between about 100 microns and 2.5 millimeters, and more preferably between about 250 microns and about 1 millimeter. At this time, formation of a trigonal pyramid having a side that is less than 50 microns is difficult. Also, the formation of a trigonal pyramid having a side that is longer than 5 millimeters may undesirably result in the formation of large flakes that are difficult to treat and manipulate.

The shape of the cube corner element may vary, as is known to those of skill in the art. One exemplary cube corner shape is described in U.S. Patent No. 4,775,219 in which the trigonal pyramid has a vertical angle departing from  $90^\circ$ . Another exemplary cube corner shape is described in U.S. Patent No. 4,588,258 in which an angular point of the trigonal pyramid may be placed aslant to the center of the trigonal pyramid. Additional exemplary shaped cube corner elements are described in U.S. Patent Nos. 4,938,563; 4,775,219; 4,243,618; 4,202,600; 3,712,706; and 4,588,258. The shape of the cube corner

elements can be chosen to obtain a preferred retroreflectiveness when a wide angle over multiple visible planes is involved.

The retroreflective element of the present invention includes a light reflective layer applied on the rear surface (not shown in the Fig.s). This light reflective layer reflects light directed to the rear surface of the retroreflective element. Without a light reflective layer, much of the light may propagate through the retroreflective element. One preferred light reflective layer is a mirror-type reflective layer. Preferred reflective layers have a thickness that maximizes the retroreflectivity of the element, and is preferably greater than 200 angstrom, and more preferably greater than 400 angstrom.

The light reflective layer may include a metal, such as, for example, aluminum; silver; platinum; nickel; tin; copper; rhodium; chromium; lead; palladium; molybdenum; tungsten; gold; and combinations thereof. The light reflective layer may also include a metal oxide, such as, for example, SnO<sub>2</sub>; ZnO; In<sub>2</sub>O<sub>3</sub>; and combinations thereof or a doped metal oxide, such as, for example, SnO<sub>2</sub>:F; SnO<sub>2</sub>:Sb; ITO; ZnO:Al; ZnO:Ga; and combinations thereof.

The light reflective layer may also include non-metals, such as multilayered dielectric laminates in which layers of Na<sub>2</sub>AlF<sub>6</sub>; MgF<sub>2</sub>; SiO<sub>2</sub>; SiO; Al<sub>2</sub>O<sub>3</sub>; CeF<sub>3</sub>; PbF<sub>2</sub>; Nd<sub>2</sub>O<sub>3</sub>; ZrO<sub>2</sub>; TiO<sub>2</sub>; CeO<sub>2</sub>; ZnS; ZnSe; CdTe; Si; Ge; PbTe; and combinations thereof are layered. The layers may be bound physically or chemically, as is known to those of skill in the art, by processes such as, for example, vacuum evaporation, sputtering, chemical vapor deposition (CVD), plasma enforced CVD, electrodeless vapor deposition; and combinations and variations thereof. The specific process used will likely depend on the composition and properties of the desired film.

The light reflective layer may have multiple layers, such as, for example, a base layer, a barrier layer, and a layer for promoting cohesion to a protection overcoating layer. An exemplary multi-layer film suitable for a polycarbonate substrate includes a titanium dioxide layer having a thickness of about 1 nm and an atomized aluminum layer having a thickness of about 100 nm. The titanium dioxide layer serves as a barrier, promotes cohesion, and minimizes the effect of pinholes that may be present in the aluminum layer.

The light reflective layer may be formed with a light transmissible material having a refractive index higher than that of the light transmissible polymer. Alternatively, the

light reflective layer may be formed with a multi-layered reflective film that interferes with light beams.

The retroreflective element may be shaped in a flake form. In such a form, the retroreflective element can serve as a retroreflectiveness supplying material. For example, an appropriate amount of the retroreflectiveness supplying material may be added to a composition, such as a resin, to form a retroreflective resin composition. Alternatively, the retroreflectiveness supplying material may be molded to form a retroreflective article. In these instances, the substrate material of the retroreflective element preferably includes a light transmissive polymer that is solvent- and heat-resistant. Exemplary light transmissive polymers include methacrylic resin, polycarbonate resin, polystyrene resin, fluorine resin, polyimide resin, polyamide resin, polyether sulfone resin, polysulfone resin, polyurethane resin, and combinations and/or modifications thereof.

A retroreflective element may be shaped into flake form by cutting, for example, with a die; by laser-processing; and by means of other methods of cutting or forming flakes commonly known to those of skill in the art. The retroreflective flakes preferably have an average diameter that is between about 0.1 mm to about 10 mm, more preferably between about 0.5 mm and about 5 mm; and most preferably between about 0.5 mm to about 7 mm.

A resin composition including retroreflective flakes may include an acrylic resin, a urethane resin, a vinyl chloride resin, an alkyd resin, a polyester resin, or combinations or modifications thereof. The resin composition may include a photocurable resin. Some photocurable resin compositions may be cured without heating, such as, for example, acrylic resins or aqueous urethane resins not containing a solvent.

Retroreflective flakes may be incorporated into the resin in a ratio that is between about 5 to about 100 parts by weight, preferably between about 10 to about 70 parts by weight, and more preferably between about 20 to about 50 parts by weight.

Exemplary uses of the retroreflective element include use in the manufacture of signs, such as, for example, pavement markings, signposts, and construction signs; tape, such as, for example, automobile or motorcycle tape; clothing; safety materials, such as, for example, life jackets or other life-saving materials; and markings on a signboard.

### Examples

The following Examples further illustrate a dual-sided retroreflective element. However, these Examples are not to be construed as limiting the present invention.

#### 5 EXAMPLE 1

A cube corner retroreflective sheet having a flat surface and full cubes (as shown in Fig. 3) was obtained. An exemplary commercially available retroreflective sheet of this kind is Reflective Board™ E39-R1 manufactured by Omron K.K. This specific commercially available retroreflective sheeting includes trigonal pyramid cube corners  
10 whose sides have a length of about 1.5 mm. Aluminum was vapor deposited on the rear surface of the retroreflective sheet to a thickness of about 100 nm. The front and rear surfaces of the retroreflective sheet were irradiated following vapor deposition, and the brightness of the reflected lights were measured with a reflectometer (Model 920 manufactured by Art-Gamma Scientific Inc.). The results are provided in Table I. As  
15 shown in Table 1, retroreflectivity was observed on the front and rear surfaces. Further (not shown in Table I), the sheet was retroreflective on both the front and rear sides when immersed in either water or fluorine resin (the specific fluorine used was Florinate™ manufactured by 3M Company).

#### 20 EXAMPLE 2

The vapor-coated and irradiated cube corner retroreflective sheet of Example 1 was cut into 5 mm squares and was combined with aqueous urethane resin (R960 manufactured by Kusumoto Kasei K.K.; 20 parts by weight of the retroreflective sheet per 100 parts by weight of the aqueous urethane resin) to form a retroreflective resin composition. The  
25 retroreflective resin composition was applied to a road surface made of uneven asphalt (a non-drainable road surface) and was allowed to dry. The surface of the dried composition was observed and it was determined that the cut piece of retroreflective sheet successfully retroreflected light on both a front surface and a rear surface.

#### 30 COMPARATIVE EXAMPLE 1

The non-vapor-coated and non-irradiated retroreflective sheet of Example 1 was irradiated and its brightness was measured as described in Example 1. The results are in Table I. As Table I shows, only the front surface of the retroreflective sheet retroreflected light.

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#### COMPARATIVE EXAMPLE 2

A cube corner retroreflective sheet having a flat surface and the cube corner structure as shown in Fig. 1 was obtained. An exemplary commercially available retroreflective sheet of this kind is reflective board manufactured by 3M Company. This specific commercially available retroreflective sheeting has trigonal pyramid cube corners whose sides have a length of about 1.5 mm. Aluminum was vapor deposited on the rear surface of the retroreflective sheet to a thickness of about 100 nm. The front and rear surfaces of the retroreflective sheet were irradiated following vapor deposition, and the brightness of the reflected lights were measured with a reflectometer (Model 920 manufactured by Art-Gamma Scientific Inc.). The result of these measurements is provided in Table I. As shown in Table I, retroreflectivity was observed on only the front surface.

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#### COMPARATIVE EXAMPLE 3

The front and rear surfaces of the non-vapor coated retroreflective sheet of Comparative Example 2 were irradiated, and the brightness of the resulting sheet was measured as described in Comparative Example 2. The results of these measurements is provided in Table I. As shown in Table I, retroreflectivity was observed only on the front surface.

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Table I. Results of Reflected Light Brightness Measurement (Unit: CPL)

Example	Retroreflective Structure	Aluminum Vapor Deposition	Front Surface (Flat Side)	Rear Surface (Structured Side)
1	Full Cube	Yes	220	260
Comp. 1	Full Cube	No	500	1
Comp. 2	Concave-concave	Yes	200	0

	trigonal pyramids			
Comp. 3	Concave-concave trigonal pyramids	No	222	0

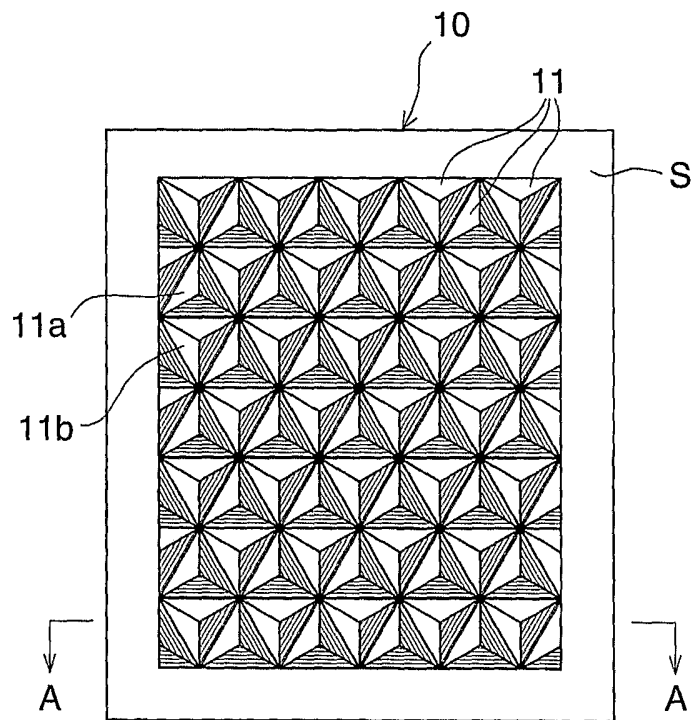
What is claimed is:

1. A retroreflective element, comprising:  
a substrate having a substantially flat front surface and a rear surface including multiple cube corner elements and at least partially coated with a light reflective layer, the substrate formed of a light transmissive material;  
wherein the cube corner elements are trigonal pyramids that are closely adjacent one another on a base surface and wherein at least some of the cube corner elements are convex to the base surface and some of the cube corner elements are concave to the base surface.
2. The retroreflective element of claim 1, wherein the light reflective layer is a specular reflective layer.
3. The retroreflective element of claim 1, wherein four adjacent cube corner elements form a full cube corner.
4. A retroreflectiveness supplying material, comprising:  
the retroreflective element of claim 1 wherein the retroreflective element is in the form of a flake.
5. A retroreflective article including the retroreflectiveness supplying material of claim 4.
6. A process for producing a retroreflective article, comprising:  
incorporating the retroreflectiveness supplying material of claim 4 in a resin composition; and  
applying the resin composition to an article.

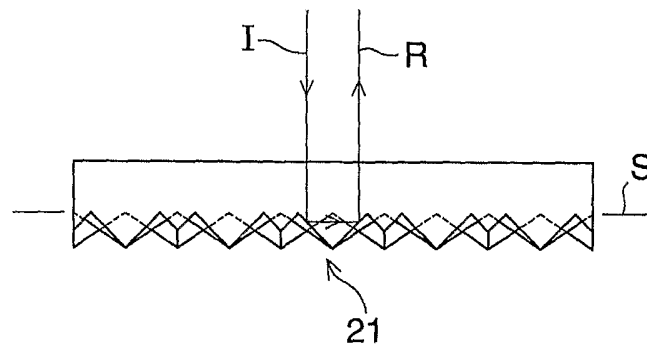
7. The process of claim 6, wherein the resin composition is a light transmissive resin.

5 8. The process of claim 6, wherein the applying the resin composition to an article involves molding the resin composition to form the article.

1/2



*Fig. 1*



*Fig. 2*

2/2

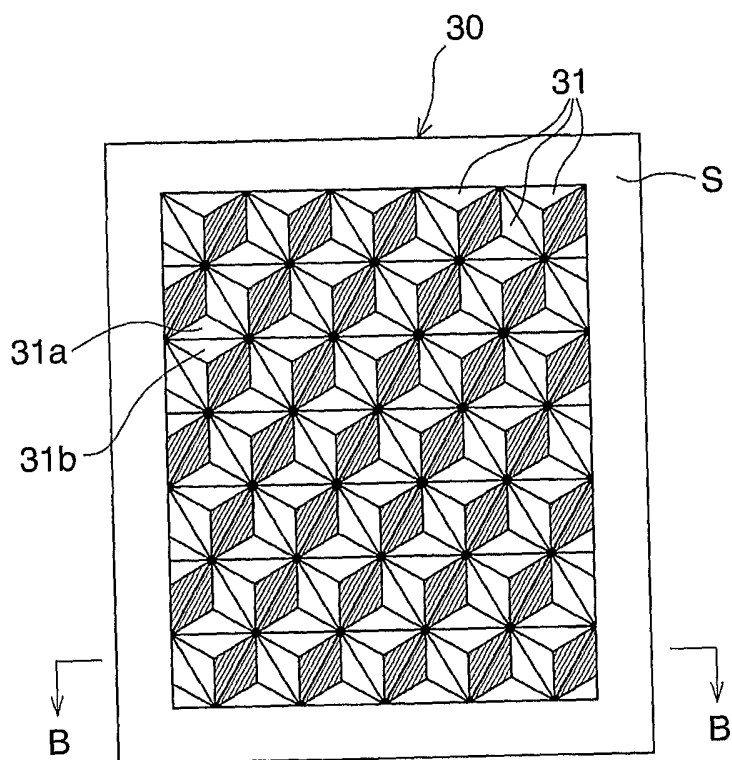


Fig. 3

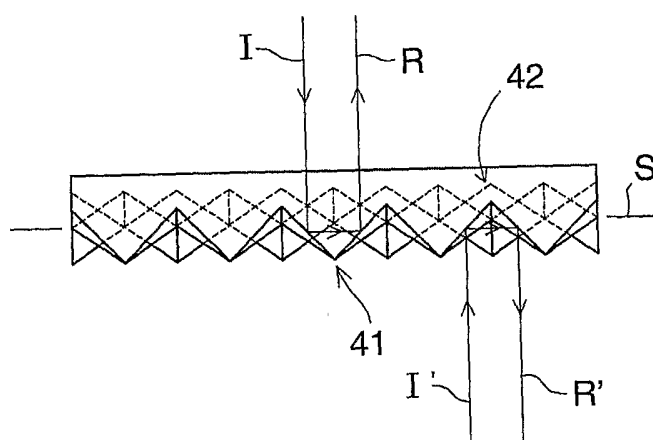


Fig. 4

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2006/003262

**A. CLASSIFICATION OF SUBJECT MATTER**  
INV. G02B5/122

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/133194 A1 (BENSON GERALD M ET AL) 17 July 2003 (2003-07-17) paragraphs [0054], [0056], [0058], [0098]; figure 4	1-3
Y	paragraph [0058]; figure 4	4-8
Y	US 2004/169928 A1 (NILSEN ROBERT B ET AL) 2 September 2004 (2004-09-02) paragraph [0102]	4-8
X	GB 918 015 A (WILLIAM GEORGE FREDERICK WESTBROOKE) 13 February 1963 (1963-02-13) figure 1	1
X	US 3 712 706 A (STAMM R,US) 23 January 1973 (1973-01-23) figure 7a	1
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Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

\*A\* document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search

30 May 2006

Date of mailing of the international search report

08/06/2006

Name and mailing address of the ISA/

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Denise, C

INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2006/003262

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 010 223 A (GUBELA, SR. ET AL) 4 January 2000 (2000-01-04) figure 4	1
X	& EP 0 844 056 A (NIPPON CARBIDE KOGYO KABUSHIKI KAISHA) 27 May 1998 (1998-05-27) figure 6  -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2006/003262

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