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(54) **Transparent neutron screening material**

Durchsichtiger Neutronschutzstoff

Matériau transparent de blindage contre les neutrons

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(56) References cited:
EP-A- 0 127 241 **FR-A- 2 729 783**

- **DATABASE WPI Section Ch, Week 9419 Derwent Publications Ltd., London, GB; Class A17, AN 94-156772 XP002014656 & JP-A-06 100 743 (MITSUI PETROCHEM IND CO LTD) , 12 April 1994**
- **DATABASE WPI Section Ch, Week 8530 Derwent Publications Ltd., London, GB; Class K07, AN 85-181745 XP002014657 & JP-A-60 111 192 (TOPPAN PRINTING KK) , 17 June 1985**
- **DATABASE WPI Section Ch, Week 9319 Derwent Publications Ltd., London, GB; Class A97, AN 86-289472 XP002014658 & JP-B-05 028 359 (KOBE STEEL KK) , 26 April 1993**
- **DATABASE WPI Section Ch, Week 9329 Derwent Publications Ltd., London, GB; Class A17, AN 93-232497 XP002014659 & JP-A-05 156 100 (MITSUI PETROCHEM IND CO LTD) , 22 June 1993**

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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] This invention relates to a transparent neutron screening material used in gloved boxes and the like for handling plutonium fuel obtained by reprocessing spent nuclear fuel from a nuclear power plant.

2. Description of the Prior Art

[0002] Plutonium, like uranium, emits alpha-rays while decaying and at the same time, also emits gamma-rays and generates neutrons. While further, at the same time, daughter nuclides generated as a result of decay exist during processing and also emit beta-rays and gamma-rays. The half life of ^{239}Pu is 2.4×10^4 years, for ^{240}Pu it is 6.6×10^3 years and for ^{241}Pu it is 14 years. This means that the half life of plutonium is shorter than the half life of ^{238}U , at 4.5×10^9 years and of ^{235}U , at 7×10^8 years. Therefore, the specific radioactivity of such plutonium is about 10^5 times higher than that of uranium. But, on the other hand, plutonium has high toxicity and, in consideration of its effects on the human body its permissible concentration of radioactivity is about 1/30 that of uranium.

[0003] Accordingly, in comparison with uranium fuel production facilities, restrictive conditions resulting from the characteristics of plutonium are imposed on plutonium fuel processing and its associated facilities. These restrictive conditions are, for example, (1) the alpha-specific radioactivity is extremely high, as described above; and (2) gamma-ray intensity and neutron emissions are considerably high.

[0004] This means that sufficient consideration must be given to the handling and management of plutonium fuel. As for restrictive condition (1), for example, containment management for containing the plutonium fuel in a gloved box, etc., becomes necessary in order to avoid inhalation by operators. In other words, the process or shaping plutonium must be carried out in a completely sealed gloved box under many restrictions, including restrictions concerning the maintenance and inspection of all machinery and tools used in the shaping process. Therefore, to produce a MOX (Mixed-Oxide Fuel) pellet for future use simplification and automation of the production process are more strongly needed than in the case of uranium processing plants.

[0005] In regard to restrictive condition (2), plutonium obtained from the spent fuel of a light-water reactor contains large amounts of ^{240}Pu , ^{241}Pu and the like, and the amount of gamma-rays emitted therefrom also increases. Therefore, to reduce external exposure of the operators, screens of lead, acrylic resins, etc. must be used.

[0006] Conventional lead glass used in gloved box panels and the like is directed at screening gamma-rays and is produced according to JIS R-3701 standards. This lead glass has a chemical composition of, for example, 1 wt% of B, 25 wt% of O, 2 wt% of Na, 16 wt% of Si, 4 wt% of Ba and 51 wt% of Pb.

[0007] Acrylic plate has also been used as a transparent neutron screening material. Acrylic plate has a chemical composition consisting of, for example, 8.0 wt% (corresponding to 0.0952 g/cm^3) of H, 60.0 wt% of C and 32.0 wt% of O.

[0008] Further, lead-containing acrylic resin has been used to screen gamma-rays and neutrons. Such lead-containing acrylic resin has a chemical composition consisting of, for example, 5.8 wt% of H, 43.8 wt% of C, 20.4 wt% of O and 30.0 wt% of Pb. The properties of such lead-containing acrylic resin are somewhat inferior, and its reliability is lower than that of acrylic.

[0009] The intensity of the radiation source described above depends on the isotope composition of plutonium, and that of isotopes of higher order tends to gradually increase. In conventional gloved boxes using lead glass or plastic materials, exposure of the operators is considerably high, and further improvements in screening for the gloved boxes is currently required. In particular, the existing law stipulates that the dosage rate should be below 1 mSv/week (below $20 \mu\text{Sv/hour}$) in areas easily accessed by people (10 cm from the surface of the gloved box). Therefore, a transparent neutron screening material having a thickness equal to that of the conventional acrylic resins, lead, lead-containing acrylic resins and the like, but having higher neutron screening performance, is required for the application described above.

[0010] It is therefore an object of the present invention to provide a transparent neutron screening material which can reduce radiation exposure in gloved box operations handling plutonium fuel, which has high transparency and which can be used for a gloved box, etc.

[0011] It is another object of the present invention to provide a transparent neutron screening material which can reduce radiation exposure in gloved box operations handling plutonium fuel, which has high transparency and high surface wear resistance and which can be used for a gloved box, etc.

SUMMARY OF THE INVENTION

[0012] A transparent neutron screening material according to the present invention is set forth in claim 1.

BRIEF DESCRIPTION OF THE DRAWING

[0013] Fig. 1 is a graph showing the relation between the thickness of the transparent neutron screening plate according to the present invention and a conventional acrylic plate (thickness: mm) for a ^{252}Cf radiation source plotted against the neutron damping ratio.

DETAILED DESCRIPTION OF THE INVENTION

[0014] The transparent neutron screening material according to the present invention provides a transparent resin plate made of a cyclic olefin copolymer. This transparent resin has a greater hydrogen content, which affects neutron screening capability, than conventional acrylic resin and the like, and can provide excellent neutron screening capacity.

[0015] Also, the cyclic olefin copolymer has a bulky alicyclic structure in its main skeletal structure, is amorphous, has a high glass transition temperature (T_g) and has both polyolefin resin properties as well as amorphous resin properties.

[0016] Being amorphous, the cyclic olefin copolymer is colorless and transparent, has excellent optical characteristics such as birefringence, exhibits the lowest moisture permeation coefficient among transparent resins, has low water absorbing power but has extremely high steam resistance, acid/alkali resistance and resistance to polar solvents. Further, the bending elastic modulus temperature dependence is extremely low, it maintains high rigidity even at high temperatures, has small molding shrinkage, a low coefficient of linear expansion, excellent dimensional stability and moldability, and can be molded by various molding methods such as injection molding, injection blow molding, extrusion molding, vacuum molding, etc.

[0017] Such a cyclic olefin copolymer is disclosed, for example, in Japanese Patent Publication No. 4-14685, and is commercially available under the trade name "APEL" (APL-6509, APL-6011, APL-6013, and APL-6015) from Mitsui Petrochemical Industries, Ltd.

[0018] As described above, the transparent resin plate made of the cyclic olefin copolymer used in the present invention has a high hydrogen content, has excellent neutron screening capacity and further has excellent moldability. Therefore, it can be suitably used as a transparent neutron screening material for a gloved box, etc. However, the resin plate made of the cyclic olefin copolymer used in the present invention still has the problem of insufficient wear resistance on the surface thereof, and is not free from the drawback that the surface of the resin plate is likely to be damaged if it is used as a transparent neutron screening material.

[0019] Therefore, the present invention improves the wear resistance of the surface of the transparent neutron screening material by employing a three-layered structure wherein the transparent resin plate made of the cyclic olefin copolymer is used as a core material, and surface protective layers capable of imparting higher wear resistance to the surface of the transparent plate are deposited on the surface thereof.

[0020] This surface protective layer can be deposited by bonding a film to the surface of the transparent resin plate. Materials for the surface protective layer are not particularly limited so long as they have higher wear resistance than the transparent resin plate comprising the core and have radiation resistance. Suitable examples include an acrylic resin film such as an MMA resin film and hard-coated PET films. The thickness of the surface protective layer is also not particularly limited, and a suitable thickness can be selected in accordance with the application of the transparent neutron screening material. A primer, or the like, can be used for bonding the films.

EXAMPLES

Example 1

[0021] A cyclic olefin copolymer ("APL-6509": a product of Mitsui Petrochemical Industries, Ltd.) measuring 1,000mm × 1,000mm × 10mm was used as the transparent neutron screening material for a gloved box panel. This product, APL-6509, had a chemical composition consisting of 12 wt% of H (corresponding to 0.1224 g/cm³) and 88 wt% of C.

[0022] The various properties of the resulting transparent neutron screening material were as follows.

Mechanical properties:	
Tensile yield strength (ASTM D638)	600 kg/cm ²
Tensile breaking strength (ASTM D638)	450 kg/cm ²

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Mechanical properties:	
Tensile elongation at break (ASTM D638)	30%
Bending elastic modulus (ASTM D790)	25,000 kg/cm ²
Bending strength (ASTM D790)	950 kg/cm ²
Izod impact strength:	
with notch (ASTM D256)	3.5 kg.cm/cm
without notch (ASTM D265)	20 kg.cm/cm
Rockwell hardness (ASTM D785)	120 (R scale)

Thermal properties:		
Thermal deformation temperature (ASTM D648)	18.6 kg/cm ²	70°C
	4.6 kg/cm ²	80°C
Thermal expansion coefficient (ASTM D649)		
Longitudinal		7×10 ⁻⁵
Transversal		6×10 ⁻⁵
Molding shrinkage:		
Longitudinal		0.6%
Transversal		0.5%

Optical properties:	
Light transmission (ASTM D1003: 2 mmt)	91
Haze (ASTM D1003: 2 mmt)	2

Neutron screening capacity:

[0023] Neutron screening capacity was examined for the transparent neutron screening material according to the present invention (APL-6509; hydrogen content per unit volume = 0.1224 g/cm³) and for the conventional acrylic plate (hydrogen content per unit volume = 0.0952 g/cm³).

Testing conditions:

Radiation source: ²⁵²Cf

Thickness of screening material: 10 mm

Measurement time: 30 min.

Results:	
	Damping Ratio
Inventive Product	0.773
Acrylic Plate	0.841

[0024] The results are shown in the graph of Fig.1.

[0025] It can be understood from above that because the transparent neutron screening material according to the present invention has a hydrogen content of about 30% higher than that of the conventional transparent neutron screening material made of acrylic resin, it also has a neutron damping ratio of about 30% higher and a higher neutron screening capacity.

Example 2

[0026] The transparent neutron screening material of the present invention (Embodiment 2 Product) having a three-layered structure was obtained by bonding 50 μm -thick MMA resin films to both surfaces of the transparent neutron screening material of Example 1 by using a modified polyolefin resin ("UNISTROL"; a product of Mitsui Petrochemical Industries, Ltd.) as a primer so as to provide surface protective layers.

[0027] A radiation resistance test and a surface wear resistance test were carried out for the resulting Embodiment 2 Product.

Radiation Resistance Test:

Radiation source:

Japan Atomic Energy Research Institute Tokai Research Establishment Reactor JRR-2 Pneumatic Tube highest maximum speed of neutron flux ($\text{n}/\text{cm}^2\cdot\text{sec.}$)	2.5×10^{12}
maximum thermal neutron flux ($\text{n}/\text{cm}^2\cdot\text{sec.}$)	6.5×10^{13}
gamma-rays ratio (Sv/h)	1×10^6

Test results:

	Transparency	Shape	Condition of Surface Protective Layer
Before irradiation	Fair		
10 sec. after irradiation	Fair	No Change	No Change
60 sec. after irradiation	Fair	No Change	No Change

Surface Wear Resistance Test:

[0028] The surface wear resistance test was carried out in the following way.

(a) The haze of the screening material sample obtained in the manner described above was measured in accordance with ASTM D1003.

(b) A 100 mm $\times$ 100 mm screening material sample was cut and a hole having a diameter of 6 mm was opened at the center.

(c) The screening material sample was conditioned for 48 hours at a temperature of 23°C and a humidity of 50%.

(d) The screening material sample was kept in contact with an abrasive wheel (CS10F, load: 250g $\times$ 2 = 500g), while the abrasive wheel was rotated 500 times by an abrasion tester ["Rotary Abrasion Tester", a product of Toyoseiki Seisakusho Co., Ltd.]. The surface condition of the abrasive wheel was adjusted in advance by contacting the wheel with sand paper.

(e) After the screening material sample was washed with water and dried, haze was measured in the same way as described above in step (a).

$$\Delta H\% = (\text{Haze before wear test}) - (\text{Haze after wear test})$$

[0029] Further, the lower the $\Delta H\%$ value, the higher the surface wear resistance of the surface.

Test results:		
	Embodiment 2 Product	Transparent Resin Plate (core material)
$\Delta H\%$	15	70

Example 3

[0030] A transparent neutron screening material of the present invention having surface protective layers (Embodiment 3 Product) was produced by bonding a hard-coated PET film having a thickness of 100 μm to both surfaces of a transparent resin plate (thickness: 10 mm) made of a cyclic olefin copolymer (APL-6509) using "UNISTOLE" (a product of Mitsui Petrochemical Industries, Ltd.) as the primer.

[0031] A radiation resistance test and a surface wear test were carried out for the resulting Embodiment 3 Product in the same manner as in Example 2.

Radiation resistance test results:			
	Transparency	Shape	Condition of Surface Protective Layer
Before irradiation	Fair		
10 sec. after irradiation	Fair	No Change	No Change
60 sec. after irradiation	Fair	No Change	No Change

Surface wear resistance test results:		
	Embodiment 3 Product	Transparent Resin Plate (core material)
$\Delta H\%$	13	70

[0032] The transparent neutron screening material according to the first embodiment of the present invention has high neutron screening capacity and is suitable as, for example, a transparent neutron screening material for gloved box panels.

[0033] The transparent neutron screening material according to the second embodiment of the present invention has high neutron screening capacity and excellent surface wear resistance and is suitable as, for example, a transparent neutron screening material for gloved box panels.

Claims

1. A transparent neutron screening material comprising:

a transparent resin plate made of a cyclic olefin copolymer; and
 surface protective layers having higher wear resistance than said transparent resin plate and deposited on both surfaces of said transparent resin plate;
 wherein the cyclic olefin copolymer has a bulky alicyclic structure in its main skeletal structure, is amorphous, has a high glass transition temperature and has both polyolefin resin properties as well as amorphous resin properties.

2. The transparent neutron screening material according to claim 1, wherein said surface protective layer is bonded to said transparent resin plate by a primer.

3. The transparent neutron screening material according to claim 1 or 2, wherein said surface protective layer is an acrylic resin type film or a hard-coated PET film.

Patentansprüche

1. Transparentes neutronenabschirmendes Material umfassend:

eine transparente Harzplatte aus einem zyklischen Olefin-Copolymer und

auf beiden Seiten von der transparenten Harzplatte aufgebrachte oberflächenschützende Lagen mit einem größeren Abriebwiderstand als die transparente Harzplatte;

worin das zyklische Olefin-Copolymer eine voluminöse alizyklische Struktur besitzt, in seiner überwiegenden Skelettstruktur amorph ist, eine hohe Glasübergangstemperatur und sowohl Polyolefinharz-Eigenschaften als auch amorphe Harzeigenschaften besitzt.

2. Transparentes neutronenabschirmendes Material gemäß Anspruch 1, worin die oberflächenschützende Lage über eine Grundierung an die transparente Harzplatte gebunden ist.

3. Transparentes neutronenabschirmendes Material gemäß Anspruch 1 oder 2, worin die oberflächenschützende Lage ein Acrylharzfilm oder ein hartbeschichteter PET-Film ist.

5 **Revendications**

1. Matière de blindage transparente pour des neutrons comprenant:

10 une plaque de résine transparente constituée qu'un copolymère d'oléfine cyclique, et
des couches de protection superficielles dont la résistance à l'usure est supérieure à celle de ladite plaque
de résine transparente et déposées sur les deux surfaces de ladite plaque de résine transparente;
dans laquelle le copolymère d'oléfine cyclique possède une structure alicyclique volumineuse dans sa struc-
ture de squelette principale, est amorphe, possède une température de transition vitreuse élevée et possède
15 à la fois des propriétés de résine de polyoléfine et des propriétés de résine amorphe.

2. Matière de blindage transparente pour des neutrons selon la revendication 1, dans laquelle ladite couche de pro-
tection superficielle est collée à ladite plaque de résine transparente à l'aide d'une couche de fond.

3. Matière de blindage transparente pour des neutrons selon la revendication 1 ou 2, dans laquelle ladite couche de
20 protection superficielle est un film du type d'une résine acrylique ou un film PET muni d'un revêtement dur.

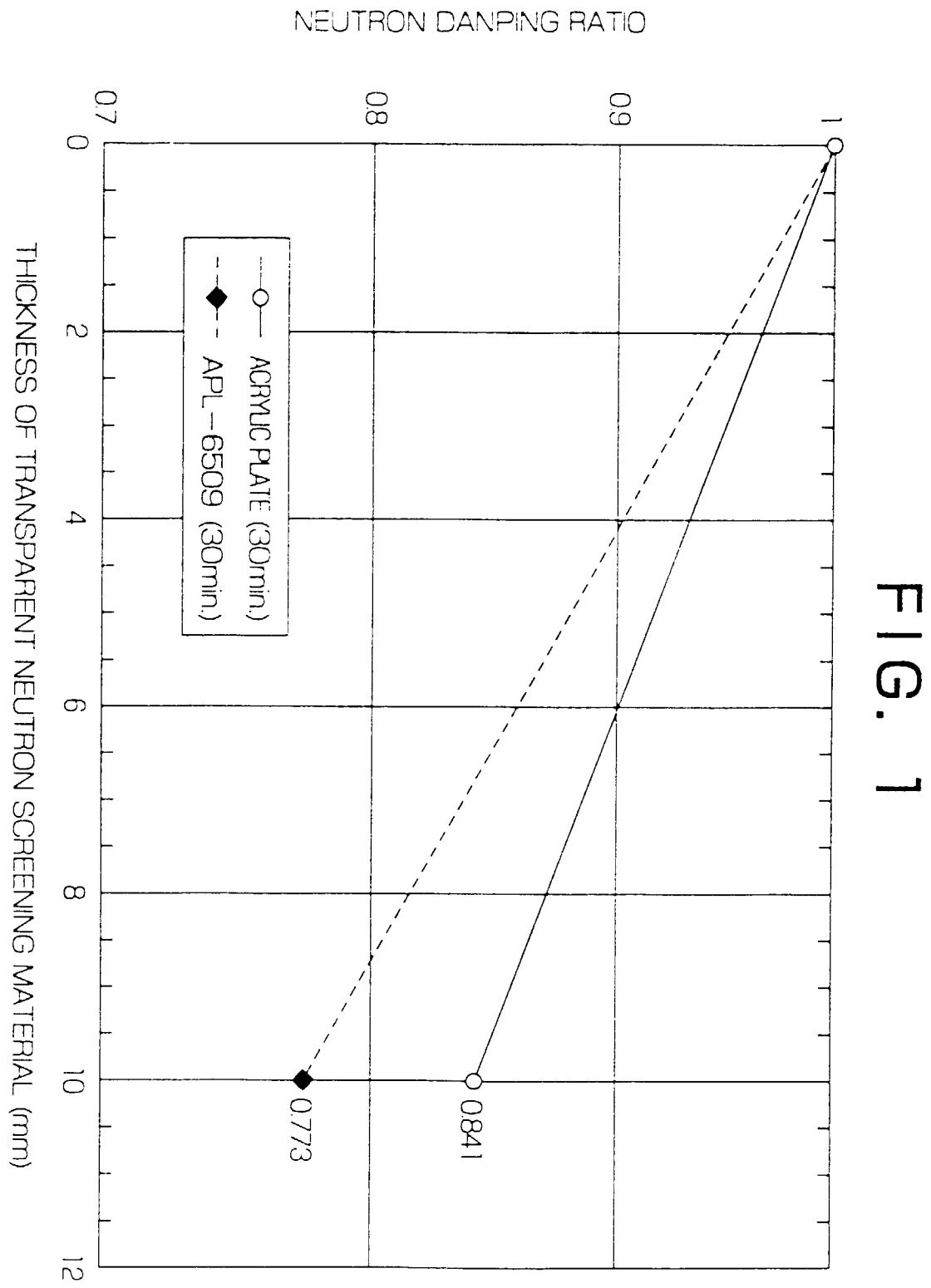


FIG. 1