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(54) Title: PROCESS OF FORMING FIBER REINFORCED MOLDED PLASTIC ARTICLES AND PREFORMS THEREFOR USING A PHOTOSETTING BINDER

(57) Abstract

The invention relates to a method of making fiber reinforced molded articles and preforms for use in the manufacture of such molded articles which includes the steps of applying a layer of reinforcing fibers, preferably glass fibers, on a preform mold surface which has a configuration corresponding to at least a portion of the final molded article, coating the fibers with an ultraviolet light curable composition which contains a photohardenable material polymerizable under UV light and a polymerization photoinitiator, exposing the coated fibers to UV light to cure the composition, and removing the resulting preform from the preform mold surface. The preform is subsequently used by placing it and a deformable plastic material in a mold, where an article containing the plastic reinforced by the fibers is formed.

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PROCESS OF FORMING FIBER REINFORCED MOLDED PLASTIC ARTICLES AND PREFORMS THEREFORE USING A PHOTOSETTING BINDER

Cross Reference to Related Applications, If Any:

This application is a continuation in part of co-pending application Serial No. 07/463,388 filed January 11, 1990.

BACKGROUND OF THE INVENTION

Field of the Invention

The invention relates to the art of making fiber reinforced molded articles. Specifically, the invention relates to an improved process for forming fiber preforms for use in molding such articles in which an ultraviolet light, polymerizable, photohardenable composition is employed as a preform binder.

The use of preforms formed of glass or other fibers is a proven method of incorporating reinforcing fibers into complex shaped molds. Such preforms have been used for a number of years in the art of forming molded articles

utilizing matched die compression molds. When glass fibers are used as the reinforcing material, it has been common practice to chop glass fiber roving into shorter lengths. The fibers were then deposited onto preform molds which often were in the shape of a specially designed screen having a size, shape and configuration conforming to that of the part to be molded. Even distribution of the chopped glass fibers on the preform mold has been achieved by use of a vacuum behind the screen. The placement of holes and baffling the screen have also been utilized to control such distribution.

Heretofore, the binders used to bond the fibers together into a preform which can be handled have been of a heat curable type. Typically, such binder compositions are based on unsaturated polyester resins dispersed or dissolved in water. Commonly, such resins are diluted to a 5 to 7% solids concentration. This composition is sprayed on fibers and the binder composition is subsequently cured at elevated temperatures. Typically, a forced air oven is required for curing in which temperatures in the 350° to 500 °F (175°C to 260°C) range are utilized. The length of the curing cycle typically ranges between 20 seconds and several minutes, depending on the thickness of the preform and the air flow through the preform in the oven. Various manual and automated

methods have been used for this purpose. After curing, the preforms are moved from the screen, allowed to cool to ambient temperature, and then stored until they are used for molding.

There are a number of disadvantages to these conventional methods of manufacturing preforms. Firstly, the procedures are relatively slow, in that typically the preform requires 1 to 3 minutes in the oven to cure, and up to an additional 30 seconds to cool down sufficiently for removal from the screen. Secondly, the heating required often bakes the over sprayed binder to a point that makes it very difficult to clean the preform screens and associated equipment. However, more importantly, the process is very energy intensive. Large motors are required to produce sufficient vacuum behind the screen and, thus, the airflow to and through the screen requires a large amount of energy. The high temperatures required to cure the binder and the high air flow required within the oven to remove the water and cure the binder is also highly energy intensive. In addition, the oven must have a relatively large exhaust stack to vent out the water vapor laden air. While it is possible to introduce heat exchangers to reduce some of the energy losses, this is not commonly done and, in any event, creates the need for additional equipment to deal with the condensed water

vapor. In addition to water vapor present in the exhaust air, there are often volatile organic compounds also present which are vaporized or atomized from the glass and binders in the oven. Because the legally allowable limits for such emissions are constantly being reduced, the installation of expensive scrubbing equipment or, alternatively, the development of new preform binders and/or glass fiber sizing technology, is required.

It is an object of the present invention to overcome these problems by providing a new process of manufacturing preforms in which the curing can be performed at ambient temperatures. More specifically, the present invention involves the use of ultraviolet light to cure a UV activated polymeric binder at or near ambient temperatures. The present invention thus eliminates the problems heretofore encountered with smoke generation and volatile organic compound emissions, reduces the difficulty of cleaning the equipment and, most importantly, greatly reduces the energy consumption of the process. A further advantage of the present invention is the achievement of an enormous increase in the speed of preform production by greatly reducing the time required to cure the preforms.

An important object of the invention is to provide a very rapid and low energy consuming method for making fiber preforms which utilizes 100% solids or very high solid content ultraviolet curable thermoset binders. A further object of the invention is to provide a low energy consuming method of rapidly bonding or attaching fiber appendages to existing preforms.

The present invention achieves the foregoing objects and advantages by providing a method of making fiber reinforced molded articles, which method may include the steps of first applying a layer of reinforcing fibers against a preform mold surface which has a configuration corresponding to that of the final molded article. The method then includes the step of coating the fibers with an ultraviolet light curable composition which contains a photohardenable material that is polymerizable under UV light and a polymerization photoinitiator. The fibers are coated to a degree sufficient to coat the individual fibers without filling the interstices among the fibers. The thus coated fibers are then exposed to ultraviolet light to cure the composition. The resulting preform has the strength to be handled and stored for later use if desired, or transported in commerce.

Alternatively, it is an object of the present invention to provide a method of making fiber reinforced

molded articles by coating the reinforcing fibers with an ultraviolet light composition, placing the coated fibers against a preform mold surface and curing them with ultraviolet light.

When used, the preform is placed in a mold with a deformable plastic material. The fiber preform and the plastic material are then molded together to form an article which consists of the plastic material containing the fibers therein as a fiber reinforcement. The fiber reinforced plastic article is then removed from the mold and processed further in accordance with conventional practice.

Any of the common UV curable resins and monomers may be used as the photohardenable material in practicing the invention. Examples of suitable materials are unsaturated polyesters, methacrylated and acrylated urethanes, methacrylated and acrylated epoxies, polyester acrylates, polyether acrylates, compositions containing allyl unsaturated and cationically polymerizable monomers and polymers in which UV radiation is used to unblock a cationic catalyst.

Application of the photohardenable composition to the fibers on the mold is accomplished by spraying, roll coat

application or transfer roll coat application, or other common coating transfer methods. In a further aspect of the invention, a number of layers of glass matt may be treated individually and subsequently stacked to form a multilayered preform. It is also possible to coat several layers simultaneously and then cure them together. The amount of photohardenable material varies somewhat with the type of photohardenable material used as well with the type of fiber employed. In the case of glass fiber preforms, the UV curable binder generally comprises between 0.2 and 15% by weight of the total glass fibers. The preferred binder content is in the 3 to 5% by weight range.

In addition to glass fibers, various other fibers, such as carbon fibers, ceramic fibers, metal fibers, and plastic fibers such as polyester, polyethylene, aramide and other nylon fibers, may be used. The speed and uniformity of UV curing is improved significantly by the use of fibers which are optically clear and, thus, capable of transmitting ultraviolet light through them.

If desired, peroxides and/or metallic dryers may be incorporated in the photohardenable composition to improve curing of any areas which may not receive sufficient UV radiation. In accordance with conventional practice, the

photohardenable binder composition can be further formulated with fillers, pigments, dyes and additives to improve rheology, adhesion to the fibers, cure rate and other process parameters.

The shape of the preform is constructed by wrapping glass fibers around a mandrel or mold of a desired shape to preconstructed matts of chopped or continuous fibers, woven or non-woven fabrics, unidirectional or bidirectional stitched matts, or matts with sandwiched construction. The reinforcing fibers may be continuous or chopped. Alternatively, continuous or chopped glass fibers may be placed in a mold formed of a screen which is preferably transparent to UV radiation. The preferred screen materials are glass or clear plastic, but other metallic or non-metallic materials may be substituted if desired. Generally, the screen or mandrel is preselected to conform to the shape of the finished article. However, in some cases it may be desirable to preform several components or sections of the finished article individually, and to later combine the sections into a final composite article.

The composition containing the photohardenable material is preferably 100% reactive. In any event, it should be a high solid content composition which contains

a photoinitiator. The composition should be responsive to and harden when subjected to UV radiation in the range of from 200 nm (nanometers) to 500 nm. The preferred range is from 250 nm to 400 nm.

Any source of UV radiation commonly used for curing thin films may be employed. Preferred sources are those with intensities of 200 watts or greater. Examples of such radiation sources are medium and high pressure mercury vapor lamps and electrodeless mercury vapor lamps. Examples of such units are those manufactured by Ashdee Corp., (Evansville, Indiana) and Fusion Systems, Inc. (Rockville, Maryland). Particularly advantageous for complex shapes are those sources which spread their energy over a large area, such as pulse lamps with multidirectional reflectors (similar to units manufactured by IST America, Nashville, Tennessee). Especially suitable for concentrating energy when it is desired to attach a small appendage to a larger preform are sources directing energy by means of a flexible optical wand. National Engineered Fiber Optic Systems, Inc. of Buffalo, New York, and Uvex, Inc. of Mountain View, California are suppliers of optical wand UV delivery systems.

Preforms prepared in accordance with the invention can be used to make various reinforced plastic articles. The

plastic employed may either be thermoplastic or thermosetting. Examples of the finished articles are items used in the transportation, construction, furniture, recreational, marine, agricultural, and electrical industries. The finished articles are made by placing the preform together with a thermosetting or thermoplastic material in an enclosed mold zone having a shape conforming to the finished product. The materials in the mold zone are then heated and compressed to form the molded shape. If the plastic deformable material is a thermoplastic, the material can be preheated to its deformation temperature and then forced within the mold cavity containing the preform to form the molded shape and thereafter allowed to cool and solidify. If a thermosetting plastic material is used, the plastic composition can be mixed, placed in the mold and heated to cure within the mold. The mold may be heated by any available conventional means, such as microwave, hot oil, steam, radiant heaters, sonic heaters, or the like.

Thermosetting materials include but are not limited to polyester, epoxy, polyurethane, polyisocyanurate, polyurea and phenolic molding resins.

An example of a thermosetting mixture is one containing approximately 55% by weight styrene containing

polyester resin, 44% by weight calcium carbonate and 0.5% by weight of a benzoyl peroxide catalyst mixture and 0.5% for an internal mold release composition. Such mixtures can be molded at pressures of approximately 200 to 2,000 psi (14 to 140 Kg per square centimeters) in a mold cavity heated to approximately 300° F (150°C) and will cure within the mold in approximately 1-2 minutes.

The invention will further be illustrated by means of the following examples wherein all parts referred to are by weight, unless otherwise noted.

EXAMPLE 1

An ultraviolet curable binder containing 70 parts of urethane diacrylate oligomer (CHEMPOL® 19-4830, a product of Freeman Chemical Corporation), 25 parts trimethylolpropane trimethacrylate (Sartomer Co. SR 350), 2 parts 2-hydroxy-2-methyl-1-phenyl-propane-1-one (E. Merck, Darocure 1173), 3 parts N-methyldiethanolamine and 5 parts methyl ethyl ketone was applied to continuous strand glass at a concentration of approximately 3 grams binder per 33 grams glass.

Four layers of treated glass were sandwiched in an acrylic mold and exposed for 30 seconds on each side to 400 watts UV radiation from a portable Hoenle mercury vapor ultraviolet lamp having a UV output of 400 watts.

The resulting glass composite was stiff and held its shape well. No odor of uncured resin could be detected.

A small piece of woven glass was bonded (stitched) onto the composite using the same procedure.

EXAMPLE 2

An ultraviolet curable epoxy acrylate resin (CHEMPOL® 19-4837) prepared in accordance with the teaching of U.S. Patent No. 4,216,306, issued August 5, 1980, and assigned to the assigner of the present invention, and containing benzophenone photoinitiator coreacted on its backbone and having a viscosity of 4900 cps at 25°C was applied to continuous strand whirl matt glass by spraying or transferring from a thin film on polyester sheet.

By weighing the glass before and after treating with resin, it was determined that the binder constituted 4.5% of the total weight of the treated glass.

Flat sheets of treated glass were exposed to ultraviolet radiation emitted by one 200 watt per inch mercury vapor lamp in an Ashdee UV cure unit. The glass matt was passed under the UV lamp at a rate of 100 feet (30.5m) per minute (approximately 0.4 second exposure). Upon exiting from the UV unit, the matt was stiff and no odor of uncured resin could be detected.

EXAMPLE 3

One layer of glass matt treated with the composition of Example 2 was wrapped around a steel cylinder of 2 inch (5.1cm) diameter and secured with clear adhesive tape. The part was rotated under the 200 watt per inch lamp for 1-2 seconds. Upon removal of the tape and cylinder, the glass matt was rigid and held its cylindrical shape.

EXAMPLE 4

The UV curable binder system of Example 2 was applied to continuous strand glass by drawing down a film onto a glass plate, placing the glass fiber onto the film and rolling the glass with a hard rubber printer's roller to distribute the binder.

The binder contents varied from 3% to 5% by weight of the total glass.

Four layers of the thusly treated glass were sandwiched in a two-part clear acrylic mold in the shape of an automotive bumper beam 24 inches (61cm) in length, three inches (7.6cm) in width and three inches (7.6cm) in height.

The molded glass was then exposed by passing through the mold ultraviolet light emitted by a 118 watt per centimeter electrodeless lamp (Fusion Systems, Inc. "H bulb"). After 15-30 seconds of exposure, the glass was rigid, non-tacky and retained its molded shape after removal of the acrylic mold.

EXAMPLE 5

The procedure of Example 4 was followed except the source of ultraviolet light is a 400 watt mercury vapor lamp with an elliptical reflector manufactured by Dr. Hoenle, West Germany. The glass was rigid, non-tacky and held its shape after removal from the mold.

EXAMPLE 6

The procedure of Example 4 was followed except the source of ultraviolet light is high pressure mercury short arc lamp with an output of 100 milliwatts/cm2 and light was delivered by a flexible optical light guide. The unit was manufactured by National Engineered Fiber Optics Systems, Inc. The glass was rigid, non-tacky and held its shape after 15-30 seconds exposure.

EXAMPLE 7

The application and curing procedures of Examples 4, 5 and 6 were repeated with a binder consisting of 70 parts epoxy acrylate oligomer (CHEMPOL® 19-6600, Freeman Chemical Corporation), 25 parts tripropylene glycol diacrylate (CL Industries, Georgetown, Illinois), 2 parts benzildimethyl ketal (Irgacure 651, Ciba Geigy Corporation), 3 parts N-methyl diethanolamine and 5 parts methyl ethyl ketone. The binder is a clear, colorless liquid with viscosity of 450 cps at 25°C.

After 15-30 seconds exposure, the glass composite was rigid, non-tacky and held the shape of the mold.

EXAMPLE 8

The application and curing procedures of Examples 4, 5 and 6 were repeated with a polymerizable resin produced from combining acrylic acid, the diglycidyl ether of 1,4 butane diol and 3,3', 4,4' benzophenone tetracarboxylic dianhydride (BTDA). The resin so prepared is a product of Freeman Chemical Corporation and is designated CHEMPOL® 19-4837.

After 30-45 seconds, the glass composite was rigid, non-tacky and held its shape after removal from the acrylic mold.

EXAMPLE 9

A 3" x 5" triangular-shaped appendage was "stitched" onto the glass composite of Example 7 by applying a band of the binder system of Example 1 to the point at which the fin-shaped appendage makes contact with the bumper beam and exposing the binder to the optical wand delivered UV radiation from a 100 milliwatt per sq. cm. high pressure mercury vapor short arc lamp (Efos unit). After 5-10 seconds exposure, the fin was tightly bonded to the bumper beam-shaped glass composite.

EXAMPLE 10

The composition of Example 7 was applied to three layers of continuous strand glass matt by spraying with a low pressure spray gun manufactured by Croix Air Products, Inc. Binder content was 6% by weight. The treated glass was exposed for 8 seconds to ultraviolet radiation of a 200 watt per inch mercury vapor lamp (Ashdee Model 25H/2A UV curing unit). Next, the cured treated glass was placed into an 45.7cm x 45.7cm x 0.32cm aluminum resin transfer mold. A 2 part epoxy molding resin based on a diglycidyl ether of bisphenol A (Epon 828) and 1,2 diaminocyclohexane hardner (Shell Chemical Co.) was injected into the RTM mold under low pressure.

After maintaining the mold temperture at 66°C for 1 hour, the hardening panel was removed from the mold and post cured for 2 hours at 135°C. Physical properties were determined and compared to a control panel prepared with 3 layers of untreated glass. Results are summarized in Table I.

EXAMPLE 11

The procedure of Example 10 was followed for treating and curing of preform binder. Three layer panels of glass with binder contents of 0%, 4.6%, 6.8% and 8.4% were thusly prepared. Each of the three layers of glass were placed in the RTM mold described in Example 10.

Next, a dicyclopentadiene-based polyester molding resin, (Stypol 40-0824 from Freeman Chemical Corp.) was injected under low pressure into the mold held at 54°C. The hardened panel was removed from the mold after 60 seconds and post hardened for 2 hours at 135°C. Physical properties of treated and untreated glass reinforced polyester composites are shown in Table II.

TABLE I

PHYSICAL PROPERTIES OF GLASS REINFORCED

EPOXY MOLDING COMPOUND

	% PREFORM BINDER	
PROPERTY	0	6
Shore D Hardness	86	86
Impact Strength (Convert to Metric)		
Izod Notched (llb/in.)	10.33	8.97
Izod unnotched (llb/in.)	9.52	13.53
Flexural Strength (PSI)	1093.0	1465.8
Flexural Modulus (PSI)	52358.0	61390.4
Tensile Strength (PSI)	735.9	645.0
Tensile Modulus (PSI)	41157.2	43224.5
% Tensile Elongation	3.19	2.78
Heat Distortion Temperature (°C)	>140	>140

TABLE II

PHYSICAL PROPERTIES OF GLASS REINFORCED POLYESTER MOLDING COMPOUND

	% BINDER			
PROPERTY	0	4.6	6.8	8.4
Shore D Hardness	86	86	86	85
Impact Strength (Note must convert to metric for Foreign Filing)				
IZOD Notched (lb./in.)	11.98	14.48	14.40	14.92
IZOD Unnotched (lb./in.)	16.27	22.38	18.99	18.96
Flexural Strength (PSI)	1669.5	2395.5	1922.6	1761.9
Flexural Modulus (PSI)	75611.4	87868.3	82800.1	73958.6
Tensile Strength (PSI)	831.7	920.2	1025.0	958.7
Tensile Modulus (PSI)	61695.7	64885.0	64895.2	57074.6
% Tensile Elongation	2.45	2.45	2.87	2.87
Heat Distortion Temp. (°C)	>140	>140	>140	>140

What is claimed is:

1. A method of making fiber reinforced molded articles comprising:

a. applying a layer of reinforcing fibers on a preform mold surface which has a configuration corresponding to at least a portion of the final molded article,

b. coating at least some of said fibers with an ultraviolet light curable composition which contains a photohardenable material polymerizable under UV light and a polymerization photoinitiator, to a degree sufficient to coat said fibers without filling the interstices among said fibers,

c. exposing said coated fibers to UV light to cure said composition,

d. removing the resulting preform from said preform mold surface,

e. placing said preform and a deformable plastic material in a mold,

f. molding said preform and said plastic material together to form an article comprising said plastic with said fibers contained therewithin as a reinforcement, and,

g. removing the resulting fiber reinforced plastic article from said mold.

2. A method according to Claim 1, wherein uncoated reinforcing fibers are initially applied to the mold surface and then coated with said ultraviolet light curable composition prior to exposure to said UV light source.

3. A method according to Claim 1, wherein said reinforcing fibers are pre-coated with said ultraviolet light curable composition prior to being applied to said preform mold surface prior to exposure to said UV light source.

4. A method according to Claim 1, wherein said photohardenable composition is selected from the group consisting of unsaturated polyesters, methacrylated urethanes, acrylated urethanes, acrylated epoxies, methacrylated epoxies, polyether acrylate resins, polyether methacrylate resins, acrylated polyesters, methacrylated polyesters, compositions containing allyl unsaturated and cationically polymerizable compositions containing a blocked cationic catalyst which can be unblocked by UV radiation, or mixtures of the above photohardenable compositions and polyethylenically unsaturated organic monomers.

5. A method according to Claim 1, wherein said preform mold comprises a screen or a material transparent to UV radiation having a shape conforming to that of the part to be molded.

6. A method according to Claim 1, wherein said preform mold comprises a mandrel around which said fibers are deposited.

7. A method according to Claim 1, wherein said fibers are optically clear.

8. A method according to Claim 1, wherein said fibers are glass fibers, and said photohardenable composition is coated thereon in an amount of about 0.2 to 15% by weight of said fibers.

9. A method according to Claim 1, wherein said composition also contains a peroxide curable material and a peroxide catalyst.

10. A method of making fiber reinforcement preform for use in making fiber reinforced molded articles comprising:

a. applying a layer of reinforcing fibers on a preform mold surface which has a configuration corresponding to at least a portion of the final molded article,

b. coating said fibers with an ultraviolet light curable composition which contains a photohardenable material polymerizable under UV light and a polymerization photoinitiator, to a degree sufficient to coat said fibers without filling the interstices among said fibers,

c. exposing said coated fibers to UV light to cure said composition,

d. removing the resulting preform from said preform mold surface.

11. A method according to Claim 10, wherein uncoated reinforcing fibers are initially applied to the mold surface and then coated with said ultraviolet light curable composition prior to exposure to said UV light source.

12. A method according to Claim 10, wherein said reinforcing fibers are pre-coated with said ultraviolet light curable composition prior to being applied to said preform mold surface prior to exposure to said UV light source.

13. A method according to Claim 10, wherein said photohardenable composition is selected from the group consisting of unsaturated polyesters, methacrylated urethanes, acrylated urethanes, acrylated epoxies, methacrylated epoxies, polyether acrylates, polyether methacrylates, acrylated polyester resins, compositions

containing allyl unsaturation and cationically polymerizable compositions containing a blocked cationic catalyst which can be unblocked by UV radiation, or mixtures of the above photohardenable compositions and polyethylenically unsaturated organic monomers.

14. A method according to Claim 10, wherein said preform mold comprises a screen or transparent mold having a shape conforming to that of the part to be molded.

15. A method according to Claim 10, wherein said preform mold comprises a mandrel around which said fibers are deposited.

16. A method according to Claim 10, wherein said fibers are optically clear.

17. A method according to Claim 10, wherein said fibers are glass fibers, and said photohardenable composition is coated thereon in an amount of about 0.2 to 15% by weight of said fibers.

18. A method according to Claim 10, wherein said composition also contains a peroxide curable material and a peroxide catalyst.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/07528

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: B 29 B 11/16, B 29 C 65/14 43/02,35/08

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	B 29 B; B 29 C

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	US, A, 4478771 (SCHREIBER) 23 October 1984, see abstract	10,12, 13,16-18
Y		1-9,11, 14,15
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Y	US, A, 4425287 (HESSE ET AL) 10 January 1984, see abstract	1-18
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Y	US, A, 4692291 (ANGELL, JR) 8 September 1987, see column 8, line 52 - column 9, line 56; column 29, line 49 - line 50; claims 1-29	1-9, 18
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* Special categories of cited documents: [10]

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

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
19th April 1991	15 MAY 1991
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	MISS T. TAZELAAR

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

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Y	Patent Abstracts of Japan, Vol 11, No 50, M562, abstract of JP 61-215016, publ 1986-09-24 (YOSHITERU NOMOTO)	1-18
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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/US 90/07528

SA 44152

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 23/03/91
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