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DECLARATION FOR A PATENT APPLICATION

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(a) Insert "Convention" if applicable
(b) Insert FULL name(s) of applicant(s)

In support of the (a) Convention application made by
(b) LIBBEY-OWENS-FORD CO.

(c) Insert "of addition" if applicable
(d) Insert TITLE of invention

(hereinafter called "applicant(s)" for a patent (c) for an
invention entitled (d)

GLASS COATING METHOD AND RESULTING ARTICLE

(e) Insert FULL name(s) AND address(es) of declarant(s)
(See headnote*)

I/We (e) Alan J. Miller, Vice President, General Counsel & Secretary of
Libbey-Owens-Ford Co., 811 Madison Avenue, Toledo, Ohio 43695

do solemnly and sincerely declare as follows:

1. ~~I am/We are the applicant(s)~~

(or, in the case of an application by a body corporate)

1. I am/We are authorized to make this declaration on behalf of the applicant(s).

2. ~~I am/We are the actual inventor(s) of the invention.~~

(or, where the applicant(s) is/are not the actual inventor(s))

(f) Insert FULL name(s) AND address(es) of actual inventor(s)

2. (f) Gerald A. Callies Eberhard A. Albach John F. Conour
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Richard A. Herrington, 300 Meadow Lane, Walbridge, Ohio

All respectively of the United States of America
is/are the actual inventor(s) of the invention and the facts upon which the applicant(s)
is/are entitled to make the application are as follows:

(g) by virtue of an Assignment dated October 3, 1985,
the applicant is the assignee of the invention from
the actual inventors.

(Note: Paragraphs 3 and 4 apply only to Convention applications)

(h) Insert country, filing date, and basic applicant(s) for the/or EACH basic application

3. The basic application(s) for patent or similar protection on which the application is based
is/are identified by country, filing date, and basic applicant(s) as follows:

(h) U.S. Patent Application Serial No. 784,976 filed October 7, 1985
UNITED STATES OF AMERICA Gerald A. Callies,
Eberhard A. Albach, John F. Conour and Richard A. Herrington.

4. The basic application(s) referred to in paragraph 3 hereof was/were the first application(s)
made in a Convention country in respect of the invention the subject of the application.

(k) Insert PLACE of signing

Declared at (k) Toledo, Ohio

(l) Insert DATE of signing

Dated (l) 22 MAY 1987

(m) Signature(s) of declarant(s)

(m) LIBBEY-OWENS-FORD CO.

By Alan J. Miller
Alan J. Miller, Vice President, General
Counsel & Secretary

To: The Commissioner of Patents

(12) PATENT ABRIDGMENT (11) Document No. AU-B-65214/86
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 593852

(54) Title
CONTINUOUS VAPOR DEPOSITION METHOD FOR PRODUCING A COATED GLASS ARTICLE

(51)⁴ International Patent Classification(s)
B05D 003/04 B05D 005/06 B32B 017/06 B32B 019/00
C03C 017/34

(21) Application No. : 65214/86 (22) Application Date : 06.10.86

(87) WIPO Number : WO87/01970

(30) Priority Data

(31) Number (32) Date (33) Country
784976 07.10.85 US UNITED STATES OF AMERICA

(43) Publication Date : 24.04.87

(44) Publication Date of Accepted Application : 22.02.90

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(56) Prior Art Documents
US 4100330
US 3378396
US 4188444

(57) Claim

1. A method for producing a coated glass article, said method comprising the steps of continuously advancing the article, while hot, past first and second successive treating stations, at least the first of which is in a closed zone, maintaining a non-oxidizing atmosphere in the closed zone in which the first treating station is situated, maintaining an oxidizing atmosphere around the second treating station and the adjacent glass, directing a non-oxidizing medium which contains a silane from the first treating station against a surface of the article to form a silicon coating on that surface, directing an oxidizing medium which includes a metal compound from the second treating station against the coated surface of the glass article, controlling the

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(10) 593852

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temperature of the glass article, the residence time in the oxidizing atmosphere around the second treating station, the composition of the non-oxidizing medium from the first treating station and the composition of the oxidizing medium from the second station so that the silane-containing medium forms a reflective silicon coating on the glass surface, the oxidizing medium which includes a metal forms a coating of an oxide of the metal, and oxidation before the article reaches the second treating station forms a silicon oxide layer on the silicon which is of sufficient thickness that the metal oxide layer is substantially free of pinholing.

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International BureauAU-AI 65214/86
593852

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁴ : B05D 1/02, 1/36, 3/02 B05D 3/04, 5/00, 5/06 C03C 17/00, 25/02, C23C 16/24 C23C 16/40, B32B 9/00, 9/04 B32B 17/06, 19/00	A1	(11) International Publication Number: WO 87/ 01970	
		(43) International Publication Date: 9 April 1987 (09.04.87)	
(21) International Application Number: PCT/US86/02055 (22) International Filing Date: 6 October 1986 (06.10.86) (31) Priority Application Number: 784,976 (32) Priority Date: 7 October 1985 (07.10.85) (33) Priority Country: US (71) Applicant: LIBBEY-OWENS-FORD COMPANY [US/US]; 811 Madison Avenue, Toledo, OH 43695 (US). (72) Inventors: CALLIES, Gerald, A. ; 2728 Oxbridge Drive, Toledo, OH 43614 (US). ALBACH, Eberhard, R. ; 4223 Shade Tree Drive, Toledo, OH 43615 (US). CO-NOUR, John, F. ; 909 Phillips, Maumee, OH 43537 (US). HERRINGTON, Richard, A. ; 300 Meadow Lane, Walbridge, OH 43465 (US).		(74) Agents: OBERLIN, Phillip, S. et al.; Marshall & Melhorn, Four SeaGate, Eighth Floor, Toledo, OH 43604 (US). (81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), FI, FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent), SU. Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> A.D.J.P. 28 MAY 1987 AUSTRALIAN 24 APR 1987 PATENT OFFICE	

This document contains the amendments made under Section 49 and is correct for printing.

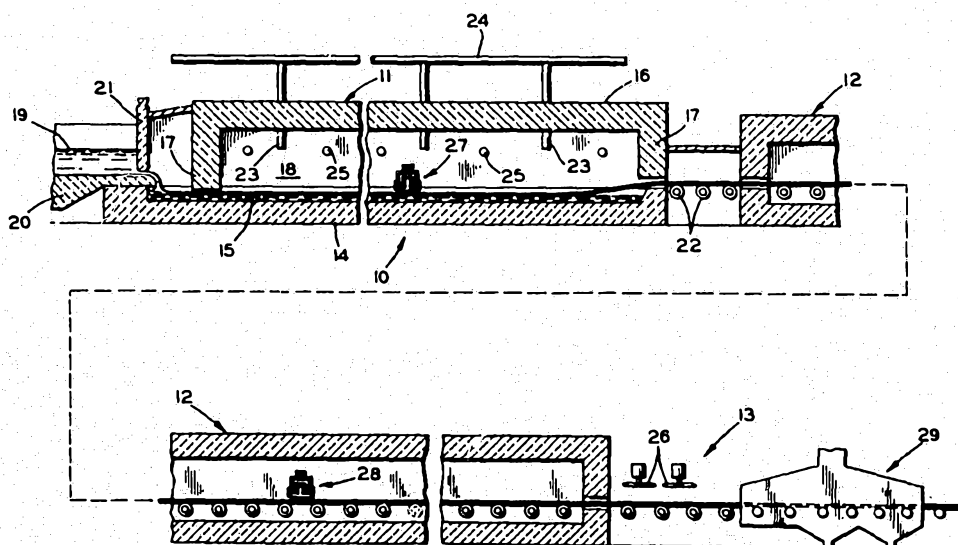
A.D.J.P. 28 MAY 1987

AUSTRALIAN

24 APR 1987

PATENT OFFICE

(54) Title: CONTINUOUS VAPOR DEPOSITION METHOD FOR PRODUCING A COATED GLASS ARTICLE

**(57) Abstract**

A continuous method for producing multi-layer coated sheet glass. Molten glass (19) is cast onto a hearth (20) and flows onto the surface of the tin bath (15), from which it is picked up by rolls (22) and conveyed through the lehr (12) and the cooling section (13). A non-oxidizing atmosphere is maintained in zone (18) by introducing a gas thereinto from the conduits (23) to maintain a positive pressure. Nothing is done to control the atmosphere in the lehr; as a consequence, the oxidizing atmosphere therein is air. The glass is treated as it travels under the distributor (27) with a gas containing silane to produce a silicon coating and as it travels under the distributor (28) with an oxidizing gas containing metal compound to form a metal oxide coating. Before the silicon coated glass reach distributor (28) a silicon oxide layer is formed.

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Description

"CONTINUOUS VAPOR DEPOSITION METHOD
FOR PRODUCING A COATED GLASS ARTICLE"

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Technical Field

This invention relates to a continuous method for producing a coated glass article, particularly, coated architectural glass, and to the coated article so produced. In a specific embodiment, the invention relates to a chemical vapor deposition method for producing a glass article coated with a layer of silicon formed by treatment with a non-oxidizing gas comprising mono-silane (SiH_4), a silicon oxide layer formed by oxidation of the surface of the silicon layer, and, on the silicon oxide layer, a layer of tin oxide formed by treatment with an oxidizing gas comprising tetramethyl tin. The invention also includes the step of washing the coated glass article with dilute hydrofluoric acid to prevent the formation of a film over the coating during subsequent tempering.

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20Background

The production of architectural glass coated with silicon formed by continuous chemical treatment with a non-oxidizing gas comprising mono-silane is disclosed in U.S. Patent 4,019,887, "Kirkbride et al.". The method disclosed by Kirkbride et al. is suitable for carrying out one step of the method of the instant invention, namely, that of forming a layer of a silicon coating on a glass article.

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The addition of ethylene to the Kirkbride et al. non-oxidizing gas comprising mono-silane is disclosed in U.S. Patent 4,188,444, "Landau", as is the benefit derived from such use of ethylene that the silicon coating has
5 significantly improved resistance to alkali.

The use of tetramethyl tin and other organo tin compounds to produce tin oxide coatings on glass by chemical vapor deposition is disclosed in U.S. Patent 4,187,336, "Gordon".

The production of a glass article having a surface
10 coated with a layer of silicon produced by the method of Kirkbride et al. and additionally coated with a layer of a metal oxide, deposited on the silicon, is disclosed by U.S. Patent 4,100,330, "Donley". The metal oxide layer, Donley discloses, can be formed by spraying the glass article to
15 which the Kirkbride et al. silicon coating has been applied with a solution in a suitable solvent of nickel acetylacetonate, of titanium diisopropyldiacetylacetonate, of dibutyl tin diacetate, or of two or more of cobalt acetylacetonate, iron acetylacetonate, chromium
20 acetylacetonate and nickel acetylacetonate. According to test data in Donley, the Kirkbride et al. silicon coating is removed by both cerium oxide and pumice used according to twenty stroke abrasion tests and by a thirty second immersion in a hot sodium hydroxide solution, while the metal oxide
25 coatings, sometimes applied directly to a glass surface and sometimes over the Kirkbride et al. silicon coatings thereon, are not removed by the procedures of the abrasion tests or by immersion in the hot sodium hydroxide solution.

Most architectural glass is produced by the "Float
30 Glass Process", a part of which is shown in the drawings of Kirkbride et al. This process involves casting glass onto a molten tin bath which is suitably enclosed, transferring the

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glass, after it cools sufficiently, to rolls that are aligned with the bath, and cooling the glass as it is advanced on the rolls, first through a lehr and, finally, while exposed to ambient conditions. A non-oxidizing atmosphere is maintained in the float portion of the process, in contact with the tin bath, to prevent oxidation, while an air atmosphere is maintained in the lehr.

It will be appreciated that it would be advantageous, when it is desired to coat glass first with silicon and second with tin or another oxide, to do so in conjunction with the production thereof by the Float Glass Process. The glass is at a suitable temperature, as is disclosed by Kirkbride et al., in the float portion of the process for treatment to apply a silicon coating; it is also at a suitable temperature in some parts of the lehr, which contains air, for treatment of a surface thereof with an oxidizing gas comprising tetramethyl tin to form a tin oxide coating on the silicon. However, when gas distributors were installed in a float glass line to treat glass first when it was at a temperature of about 1170°F. (632°C.) and in a non-oxidizing atmosphere, and second when it was at a temperature of about 1125°F. (607°C.) and in air, and glass on the line was treated first with a gas composed of 86 percent by volume of nitrogen, 4 percent by volume of ethylene and 10 percent by volume of mono-silane and second with a gas composed of 99 percent by volume of air and 1 percent by volume of tetramethyl tin, successive silicon and tin oxide coatings were formed on the glass, but the appearance of the coated glass was aesthetically unacceptable because of defects which have been called "pinholes". Overall, the coated glass had a bronze transmitted color and a silver reflective color, but there were numerous, generally circular areas, pinholes, which had a lighter transmitted color.

Accordingly, the present invention provides a method for producing a coated glass article, said method comprising the steps of continuously advancing the article, while hot, past first and second successive treating stations, at least the first of which is in a closed zone, maintaining a non-oxidizing atmosphere in the closed zone in which the first treating station is situated, maintaining an oxidizing atmosphere around the second treating station and the adjacent glass, directing a non-oxidizing medium which contains a silane from the first treating station against a surface of the article to form a silicon coating on that surface, directing an oxidizing medium which includes a metal compound from the second treating station against the coated surface of the glass article, controlling the temperature of the glass article, the residence time in the oxidizing atmosphere around the second treating station, the composition of the non-oxidizing medium from the first treating station and the composition of the oxidizing medium from the second station so that the silane-containing medium forms a reflective silicon coating on the glass surface, the oxidizing medium which includes a metal forms a coating of an oxide of the metal, and oxidation before the article reaches the second treating station forms a silicon oxide layer on the silicon which is of sufficient thickness that the metal oxide layer is substantially free of pinholing.

Disclosure of Invention

The present invention is based upon the discovery that glass being produced by the Float Glass Process can be coated immediately after it has been cast, first with silicon and second with tin or another oxide, provided that the treatment which forms the tin or other oxide coating is applied after the previously applied silicon coating has oxidized to a sufficient extent.



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Disclosure of Invention

The present invention is based upon the discovery that glass being produced by the Float Glass Process can be coated immediately after it has been cast, first with silicon and second with tin or another oxide, provided that the treatment which forms the tin or other oxide coating is applied after the previously applied silicon coating has oxidized to a sufficient extent.

10 Brief Description of the Drawing

The single Figure drawing is a somewhat schematic view in vertical section of apparatus for practicing the Float Glass Process which additionally includes two gas distributors suitably positioned to enable the practicing of the method of the instant invention.

Modes for Carrying Out the Invention

Referring to the drawing, apparatus for practicing the Float Glass Process, indicated generally at 10, comprises a float section 11, a Lehr 12 and a cooling section 13. The float section 11 has a bottom 14 which contains a tin bath 15, a top 16, sidewalls (not illustrated) and walls 17 which form seals so that there is an enclosed zone 18 within which a non-oxidizing atmosphere is maintained, as subsequently described in more detail, to prevent oxidation of the tin bath 15.

In operation of the apparatus 10, molten glass, as indicated at 19, is cast onto a hearth 20, and flows therefrom under a metering wall 21 and downwardly onto the surface of the tin bath 15, from which it is picked up by rolls 22 and conveyed through the Lehr 12 and the cooling section 13.

A non-oxidizing atmosphere is maintained in the float section 11 by introducing a suitable gas, for example one composed of 99 percent by volume of nitrogen and 1 percent

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by volume of hydrogen, into the zone 18 through conduits 23 which are operably connected to a manifold 24. The gas is introduced into the zone 18 from the conduits 23 at a rate sufficient to make up for losses (some of the atmosphere leaves the zone 18 by flowing under the walls 17) and to maintain a slight positive pressure, say 0.001 to 0.01 atmosphere above ambient. The metal bath 15 and the enclosed zone 18 are heated by radiant heat directed downwardly from heaters 25. The atmosphere in the Lehr 12 is air, while the cooling section is not enclosed, ambient air being blown onto the glass by fans 26.

The apparatus 10 also includes a gas distributor 27 in the float zone 11 and a gas distributor 28 in the Lehr 12.

The following Example, which constitutes the best mode presently contemplated by the inventors, is presented solely for the purpose of further illustrating and disclosing, and is not to be construed as a limitation on, the invention:

Example

The apparatus 10 was used to practice the method of the instant invention by producing coated sheet glass. Heat absorbing, bronze colored glass containing about 14 percent by weight of Na_2O , 73 percent by weight of SiO_2 , 8.5 percent by weight of CaO , 0.32 percent by weight of Fe_2O_3 , 0.19 percent by weight of Al_2O_3 , 0.01 percent by weight of TiO_2 , 4 percent by weight MgO , 0.003 percent by weight of Co_3O_4 , and 0.0015 percent by weight of Se was charged onto the hearth 20 and caused to flow onto the tin bath 15 as a sheet twelve feet (3.6 meters) wide and 1/4 inch (6.4 mm.) thick. The sheet was advanced through the apparatus 10 at a speed of about 25 feet (7.6 meters) per minute. The glass temperature was 2000°F. (1093°C.) on the hearth 20. A non-oxidizing atmosphere was maintained in the zone 18 by

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introducing a gas thereinto from the conduits 23 to maintain a positive pressure above ambient of 0.006 atmosphere; the gas was composed of 99 percent by volume of nitrogen and 1 percent by volume of hydrogen. Nothing was done to control the atmosphere in thelehr; as a consequence, the oxidizing atmosphere therein was air. The glass was treated as it traveled under the distributor 27 by a gas composed of 86 volume percent of nitrogen, 10 volume percent of mono-silane and 4 volume percent of ethylene and, as it traveled under the distributor 28, by a gas composed of 99 volume percent of air and 1 volume percent of tetramethyl tin. After the glass cooled to about 100°F. (38°C.) in the cooling section 13, it was washed in an acid washer, shown schematically at 29, for about ten seconds with 4 percent by weight hydrofluoric acid. The nitrogen gas flowed from the distributor 27 at a rate of 2.3 standard cubic feet (0.065 standard cubic meter) per minute, while the air-tetramethyl tin gas flowed from the distributor 28 at a rate of 10 standard cubic feet (0.28 standard cubic meter) per minute. The glass advanced from the distributor 27 to the discharge end of the float zone 11 in from about 90 to 120 seconds, from the distributor 27 to the distributor 28 in about 8 minutes. The glass temperature was $1175 \pm 20^\circ\text{F}$. ($635 \pm 11^\circ\text{C}$.) under the distributor 27; $970 \pm 20^\circ\text{F}$. ($521 \pm 11^\circ\text{C}$.) under the distributor 28.

The glass produced as described in the foregoing Example carried a multi-layer reflective coating. The reflective coating was silicon, 300A thick, on the glass; there was a silicon oxide film 20 to 50A thick on the silicon, and a tin oxide film 200A thick on the silicon oxide. The coated glass had a shading coefficient of 0.45 to 0.55, daylight reflectance of 45 percent, daylight transmittance of 25 percent, solar transmittance of 30 percent. The transmitted color was a warm bronze, the reflective color silver.

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The coated glass was post temperable; it has been found to be compatible with most insulated glass and glazing sealants, to have excellent durability, and to have sufficiently low absorption that it requires no heat treating. The coated glass, when the step of washing with hydrofluoric acid was omitted, required washing after it was tempered to remove a film which formed during tempering.

The procedure described in the foregoing Example has also been used to coat gray, heat-absorbing glass composed approximately of 73 percent by weight of silica, 14 percent by weight of Na_2O , 8.6 percent by weight of CaO , 4 percent by weight of MgO , 0.19 percent by weight of Al_2O_3 , 0.29 percent by weight of Fe_2O_3 , 0.008 percent by weight of CO_3O_4 , 0.001 percent by weight of Se , 0.0086 percent by weight of NiO , and 0.01 percent by weight of TiO_2 . The transmitted color of the final product was gray, the reflective color silver; the shading coefficient was 0.45, the daylight reflectance 45 percent, daylight transmittance 20 percent and solar transmittance 29 percent. The film is sufficiently low absorbing that it does not require heat treating; it was post-temperable, had excellent durability, and was compatible with most insulated glass and glazing sealants. When the procedure was repeated except that the step of washing with hydrofluoric acid was omitted, the coated glass, after tempering, showed a slight haze which could be removed by washing. The step of washing with hydrofluoric acid prevented formation of the haze.

It will be appreciated that various changes and modifications can be made from the specific details of the invention as incorporated in the foregoing Example without departing from the spirit and scope thereof as defined in the appended claims. In its essential details, the invention is a continuous chemical vapor deposition method for producing

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a coated glass article. The method comprises the steps of continuously advancing the article, while hot, past first and second successive treating stations. The first treating station is in a closed zone in which a non-oxidizing atmosphere is maintained. An oxidizing atmosphere is maintained in the vicinity of the second treating station. In the foregoing Example, the non-oxidizing atmosphere in the enclosed zone in which the first treating station is positioned was maintained by introducing thereinto a gas composed of 99 percent by volume of nitrogen and 1 percent by volume of hydrogen. As is apparent from the results achieved by practicing the process of the Example, such an atmosphere is entirely suitable. However, other inert gases could be substituted for the nitrogen, and the proportion of hydrogen could be increased or decreased, so long as the necessary result is achieved, namely, oxidation of the tin bath is prevented and a silicon coating is applied to the glass. Similarly, in the method of the Example, air was used to provide an oxidizing atmosphere in the Lehr 12, but other oxidizing atmospheres can also be employed, for example, air enriched with either oxygen or nitrogen, or even one containing an inert gas other than nitrogen, so long as the required result of deposition of a tin or other oxide coating is achieved without undue detriment to the Lehr itself.

In practicing the instant invention, a non-oxidizing gas which contains a silane is directed against a surface of the article to form a silicon coating on that surface. In the foregoing Example, the silane was mono-silane (SiH_4). However, the treating gas can contain other silanes, in addition to mono-silane, or in place thereof. Examples of other silanes that can be used include monochlorosilane (ClSiH_3), dichlorosilane (Cl_2SiH_2), other halosilanes, alkoxysilanes and di-tri- and higher silanes. Organosilanes, e.g., methyltrichlorosilane, are less desirable reactants

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than the silanes mentioned above, because it is difficult to break the silicon to carbon bond to form the desired silicon coating. Mono-silane is the presently preferred treating agent for reasons of cost and availability and because the
5 by-product of its use (hydrogen) does not constitute an ecological problem (contrast the chlorosilanes mentioned above, where the by-product is hydrogen chloride).

The procedure of the foregoing Example involved the treatment of the glass with a gas composed of 99 volume
10 percent of air and 1 volume percent of tetramethyl tin, directed onto the glass from the distributor 28. The purpose of this treatment was to form a tin oxide coating over the silicon/silicon oxide layers that previously had been formed. An oxidizing atmosphere is required to enable
15 tetramethyl tin to deposit a tin oxide coating. Air is a convenient oxidizing gas to use for this purpose, but air enriched with either oxygen or nitrogen or even another inert gas could be substituted for the air. A mixture of more than about 1½ volume percent of tetramethyl tin in air
20 is flammable and, therefore, should be avoided. Other tin compounds can be substituted for tetramethyl tin, for example stannic chloride and various organo tin compounds that are available. The use of dibutyl tin diacetate to form a tin oxide coating on glass has been suggested (see
25 Donley, identified above); this compound, however, because of its low vapor pressure, has been used as an organic solvent solution. The use of tetramethyl tin or of another tin or other metal compound which can be vaporized in air is strongly preferred for ecological and safety reasons.
30 Indeed, titanium oxide coatings can be applied over the silicon and silicon oxide layers, for example using titanium tetrachloride, alumina coatings for example using diethyl aluminum chloride, silica coatings, for example using monochlorosilane or methylidisilane, or combined titanium
35 oxide/boron oxide/aluminum oxide coatings from mixtures of

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titanium tetrachloride, boron hydride and diethyl aluminum chloride.

In the foregoing Example, the glass temperature at the distributor 27 was $1175 \pm 20^\circ\text{F}$. ($635 \pm 11^\circ\text{C}$) and $790 \pm 20^\circ\text{F}$. (521 $\pm 11^\circ\text{C}$) under the gas distributor 28; the residence time of the glass in the oxidizing atmosphere (air) of the lehr 12, before it was treated with the air-tetramethyl tin gas from the distributor 28, was about 6 minutes; the non-oxidizing gas from the distributor 27 was composed of 86 volume percent of nitrogen, 10 volume percent of mono-silane and 4 volume percent of ethylene; and the oxidizing gas from the distributor 28 was composed of 99 volume percent of air and 1 volume percent of tetramethyl tin. These temperatures and gas compositions are all important variables in practicing the method of the instant invention. In general, the glass must be at a sufficiently high temperature that a silicon coating is formed by the gas from the distributor 27 and a metal oxide coating is formed by the gas from the distributor 28. The upper limit of temperature is determined by the physical properties of the glass; it must be sufficiently low that the viscosity of the glass is high enough to withstanding the necessary manipulations. In general, both the rate at which the silicon coating is formed and the rate at which the metal oxide coating is formed vary as direct functions of temperature. Accordingly, if lower temperatures are used, the silicon and metal oxide coatings form at slower rates and, if excessively low temperatures are used, multiple distributors are required to form these coatings at adequate thicknesses. The rate of coating formation also varies with the identity of the treating chemicals used; for example, chlorosilanes form silicon coatings at lower temperatures than does mono-silane, other factors being equal. As has been indicated above, the preferred treating compounds for use in practicing the method of the instant

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invention are mono-silane and tetramethyl tin. It is preferred that the glass surface be at a temperature of at least 1100°F. (593°C.) when treated with mono-silane and that the glass be at a temperature of at least 750°F. (398°C.) when the treatment with tetramethyl tin is carried out.

Finally, the reflective silicon coating must oxidize sufficiently, before the metal compound is used to form a metal oxide coating, that pinholing does not occur to such an extent that the result is aesthetically unacceptable.

The time required for the requisite degree of oxidation can be shortened by increasing the temperature or by increasing the oxygen partial pressure or, conversely, can be increased by reducing the temperature or by decreasing the oxygen partial pressure. It has been found that the extent of

oxidation required to avoid pinholing depends upon the temperature at which the treatment with tin tetrachloride or the like is carried out. For instance, in the procedure of the foregoing Example the glass was at a temperature of $970 \pm 20^\circ\text{F}$. ($521 \pm 11^\circ\text{C}$) when the tetramethyl tin treatment was carried out, and there was a silicon oxide film from 20 to 50A thick on the silicon. It has been found, however, that, with a silicon oxide film of this thickness, pinholing occurs if the tetramethyl tin treatment is carried out while the glass is at a temperature of 1170°F. (632°C.), but that tetramethyl tin treatment at this temperature can be carried out without pinholing if the silicon oxide coating is from 60 to 90A thick.

The procedure of the foregoing Example included the step of washing the coated glass with dilute hydrofluoric acid, specifically washing for ten seconds with 4 percent by weight hydrofluoric acid. As has been explained above, if this washing step is omitted, a film or haze forms on the coated glass article during tempering. While the film,

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generally a bluish-white splotchy defect, can be washed from the article after tempering has been completed, it is greatly advantageous to produce an article which is not subject to the formation of a film during tempering or other processing subsequent to the original production of the article.

Accordingly, the ten second washing step with 4 percent by weight hydrofluoric acid, or an equivalent washing step, is preferably used in practicing the method of the instant invention. It has been found that both the concentration of the hydrofluoric acid and the length of the washing step can be changed from those used in the procedure of the foregoing example. For example, three inch (7.6 cm.) by six inch (15.2 cm.) glass samples which had coatings produced as described in the foregoing Example, except that the washing step was omitted, were used to determine the minimum immersion time in hydrofluoric acid of three different strengths required to prevent film formation on subsequent tempering. One-half of each sample tested was dipped in hydrofluoric acid and the sample was then tempered at 1300°F. (704°C.), five minutes at temperature. It was found that film formation upon tempering was prevented by a ten second or longer immersion in 3 percent by weight hydrofluoric acid, by an eight second or longer immersion in 6 percent by weight hydrofluoric acid. Immersion of up to 15 seconds in hydrofluoric acids of these three concentrations caused no visible deterioration of either the glass or the coating. It will be appreciated from an extrapolation of the foregoing data that film formation should be prevented by immersion for as little as four seconds in 10 percent by weight hydrofluoric acid and that hydrofluoric acid as dilute as 2 percent by weight could be used to prevent film formation by increasing the immersion time to about twelve seconds; it will also be appreciated that other acid washes can be used

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provided that they are equivalents for those identified above in preventing filming during tempering without adversely affecting either the coating or the glass substrate.

Agitation of the acid during washing of the coating, for example by brushing, is advantageous because it brings fresh acid to the surface.

It will be appreciated from the foregoing discussion that the instant invention is a continuous chemical vapor deposition method for producing a coated glass article. The method comprises the steps of continuously advancing the article, while hot, past first and second successive treating stations, at least the first of which is in a closed zone. A non-oxidizing atmosphere is maintained in a portion of the closed zone which includes the first treating station, while the second treating station is in an oxidizing atmosphere. A non-oxidizing gas which contains a silane is directed from the first treating station against a surface of the article to form a silicon coating on that surface. An oxidizing gas which includes a metal compound in the vapor phase is directed from the second treating station against the coated surface of the glass article. The temperature of the glass article, the residence time in the oxidizing atmosphere, in which the second treating station is situated, the composition of the non-oxidizing gas from the first treating station and the composition of the oxidizing gas from the second station are all controlled so that the silane-containing gas forms a reflective silicon coating on the glass surface, the oxidizing gas which includes a metal forms a coating of an oxide of the metal, and oxidation before the article reaches the second treating station forms a silicon oxide layer on the silicon which is of sufficient thickness that the metal oxide layer is substantially free of pinholing.

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In the procedure described in the foregoing Example the non-oxidizing gas which was used in the distributor 27 to apply a reflective silicon coating contained ethylene in addition to mono-silane and nitrogen. The ethylene is
5 important because it changes the nature of the silicon coating on the treated glass. It has been suggested that, chemically, the change is the formation of a combined silicon/silicon carbide coating on the glass; attempts to detect silicon carbide in the coating by analytical means,
10 however, have been unsuccessful. In any event, it is clear that the coating is changed, because its resistance to alkali is significantly improved by comparison with that of the silicon coating produced when only nitrogen and mono-silane are employed. It has been found that other ethylenically
15 unsaturated aliphatic hydrocarbons, acetylenically unsaturated aliphatic hydrocarbons and even aromatic hydrocarbons provided, in each case, that they are vaporized can be used in place of ethylene. Because of their greater toxicity, however, all other unsaturated hydrocarbons are less desirable
20 than ethylene. A small amount of ethylene or other unsaturated hydrocarbon, for example from 4 to 5 volume percent with from 9 to 13 volume percent of a silane, balance nitrogen or other inert gas, is a preferred treating gas for producing the silicon coating according to the method of the instant
25 invention.

Other changes and modifications from the specific details of the invention as disclosed above will be apparent to those skilled in the art and can be made without departing from the spirit and scope thereof if within the definitions
30 of the appended claims.

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Claims

- 5 1. A method for producing a coated glass article, said
method comprising the steps of continuously advancing
the article, while hot, past first and second successive
treating stations, at least the first of which is in a
10 closed zone, maintaining a non-oxidizing atmosphere in
the closed zone in which the first treating station is
situated, maintaining an oxidizing atmosphere around
the second treating station and the adjacent glass,
directing a non-oxidizing medium which contains a silane
15 from the first treating station against a surface of
the article to form a silicon coating on that surface,
directing an oxidizing medium which includes a metal
compound from the second treating station against the
coated surface of the glass article, controlling the
20 temperature of the glass article, the residence time in
the oxidizing atmosphere around the second treating
station, the composition of the non-oxidizing medium
from the first treating station and the composition of
the oxidizing medium from the second station so that
25 the silane-containing medium forms a reflective silicon
coating on the glass surface, the oxidizing medium
which includes a metal forms a coating of an oxide of
the metal, and oxidation before the article reaches the
second treating station forms a silicon oxide layer on
30 the silicon which is of sufficient thickness that the
metal oxide layer is substantially free of pinholing.

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2. A continuous chemical vapor deposition method for producing a coated glass article, said method comprising the steps of continuously advancing the article, while hot, past first and second successive treating stations, at least the first of which is in a closed zone, maintaining a non-oxidizing atmosphere in the closed zone in which the first treating station is situated, maintaining an oxidizing atmosphere around the second treating station and the adjacent glass, directing a non-oxidizing gas which contains a silane from the first treating station against a surface of the article to form a silicon coating on that surface, directing an oxidizing gas which includes a metal compound in the vapor phase from the second treating station against the coated surface of the glass article, controlling the temperature of the glass article, the residence time in the oxidizing atmosphere around the second treating station, the composition of the non-oxidizing gas from the first treating station and the composition of the oxidizing gas from the second station so that the silane-containing gas forms a reflective silicon coating on the glass surface, the oxidizing gas which includes a metal forms a coating of an oxide of the metal, and oxidation before the article reaches the second treating station forms a silicon oxide layer on the silicon which is of sufficient thickness that the metal oxide layer is substantially free of pinholing.
3. A method as claimed in claim 2, wherein the non-oxidizing gas which contains a silane additionally contains an unsaturated hydrocarbon in such proportion that it imparts alkali resistance to the silicon coating.

4. A method as claimed in either of claims 2 or 3, which additionally includes the steps of washing the coating on the glass article, after it has cooled to a sufficiently low temperature, with dilute hydrofluoric acid, and controlling the temperature of the glass, when washed, the duration of the washing step and the concentration of the hydrofluoric acid so that neither the glass article nor the coating thereon is significantly deteriorated, while the formation of a film on the coated article upon subsequent tempering is prevented.
5. A method as claimed in claim 4, which additionally includes the step of agitating the hydrofluoric acid during the washing step, and wherein the duration of the washing step is from about four seconds to about twelve seconds while the concentration of the hydrofluoric acid is from 2 1/2 percent by weight to 10 percent by weight.
6. A method as claimed in any one of claims 3 to 5, wherein said non-oxidizing gas comprises approximately 4 to 5 volume percent of an unsaturated hydrocarbon, from 9 to 13 volume percent of a silane, balance nitrogen.
7. A method as claimed in claim 6, wherein said unsaturated hydrocarbon comprises ethylene.
8. A method as claimed in any one of claims 2 to 7, wherein said oxidizing gas which includes a metal compound comprises approximately 99 volume percent of air and 1 volume percent of tetramethyltin.
9. A method as claimed in any one of claims 2 to 8, wherein said glass surface is at a temperature of at least 1100°F when treated with said non-oxidizing gas containing a silane and at least 750°F when the



treatment with the oxidizing gas which contains a metal compound is carried out.

10. A method as claimed in claim 8, wherein the residence time in the oxidizing atmosphere around the second treating station is sufficient to produce a silicon oxide coating of from 20 to 50 A thickness on the silicon coating and said oxidizing gas treatment is carried out at a temperature of $970 \pm 20^{\circ}\text{F}$.
11. A method as claimed in claim 8, wherein the residence time in the oxidizing atmosphere around the second treating station is sufficient to produce a silicon oxide coating of from 60 to 90 A thickness and said oxidizing gas treatment is carried out at a temperature of approximately 1170°F .
12. A method as claimed in any one of claims 2 to 11, wherein said glass comprises a heat absorbing bronze coloured composition and the coated glass article has a shading coefficient of 0.45 to 0.55.
13. A coated article produced by the method according to any one of claims 1 to 12, said coated article comprising a glass substrate, a reflective silicon coating adhered to a surface of the substrate, a layer of silicon oxide adjacent the surface of the silicon opposite that adhered to the substrate, and a metal oxide coating adhered to the silicon oxide layer, the silicon oxide layer being sufficiently thick that the metal oxide layer is substantially free of pinholing.
14. A coated article produced by the method according to any one of claims 1 to 12, said coated article comprising a glass substrate, a reflective silicon coating adhered to a surface of the substrate, a layer of silicon oxide adjacent the surface of the



silicon opposite that adhered to the substrate, and a methal oxide coating adhered to the silicon oxide layer, the silicon oxide layer being sufficiently thick that the metal oxide layer is substantially free of pinholing, at least the coating of the article having been subjected to an acid wash to enable tempering of the article without the formation of a film thereon.

15. A method according to claim 1, substantially as herein before described with reference to the accompanying drawings.
16. A method according to claim 2, substantially as herein before described with reference to the accompanying drawings.

DATED: 29 NOVEMBER 1989

LIBBEY-OWENS-FORD CO.

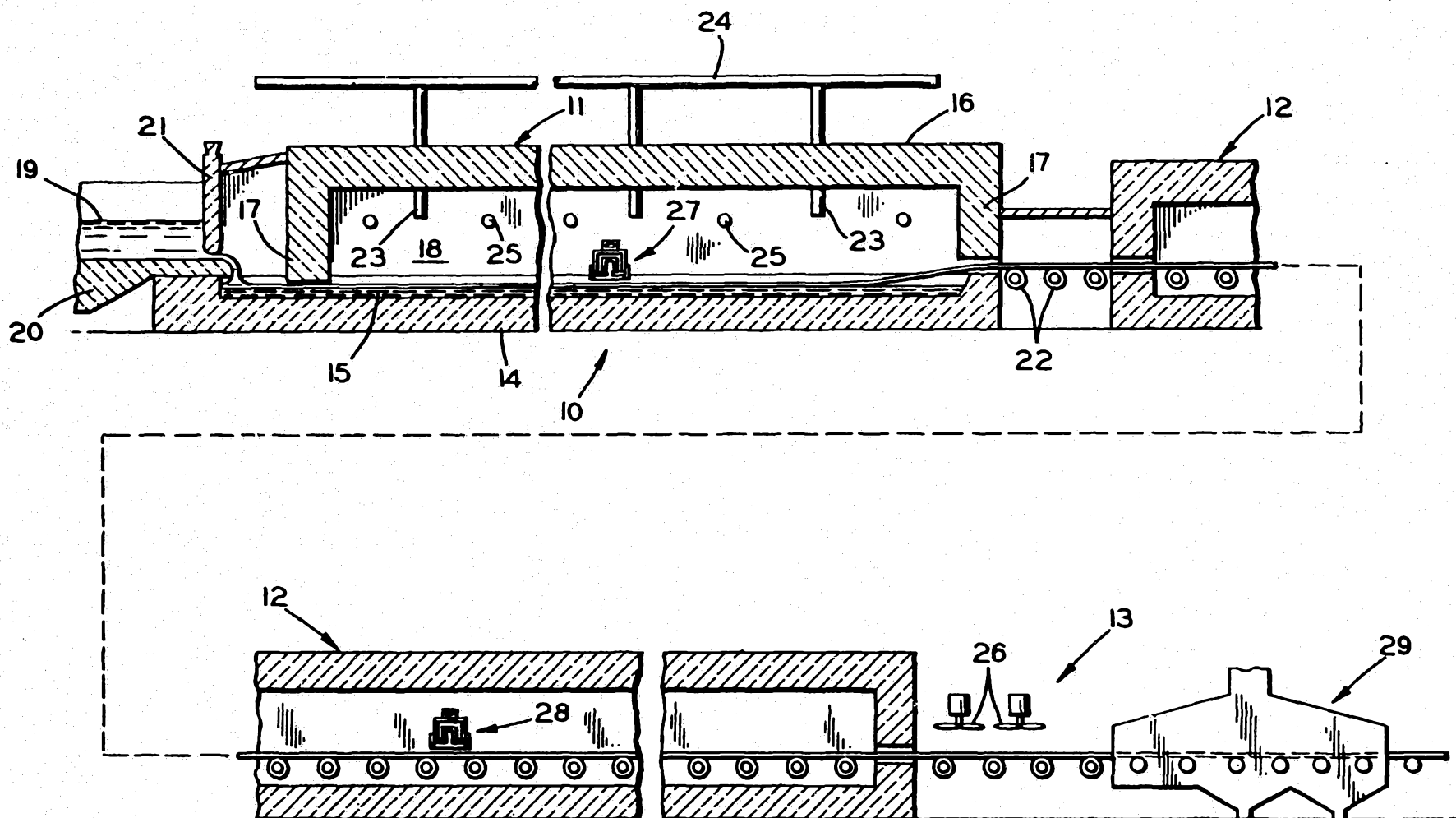
By their attorneys:

PHILLIPS ORMONDE & FITZPATRICK

David P. Fitzpatrick



1/1



INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/02055

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT CL4 See Attachment Sheet		
US CL See Attachment Sheet		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S.	65/60.2,60.5,60.51,60.52,60.53,60.8;427/166,167,226;427/248.1,255,255.3,255.7,343,376.2,377,419,2,424,427;428/426,428,432,448,702	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category ⁶	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
Y	US,A, 3,374,141 Published 19 MARCH 1968 (JUNGE). see column 3, line 47 to column 4, line 33.	4,5,14
A	US,A, 3,378,396 Published 16 APRIL 1968 (ZAROMB)	13,14
A	US,A, 4,019,887 Published 26 APRIL 1977 (KIRKBRIDE)	1-14
Y	US,A, 4,100,330 Published 11 JULY 1978 (DONLEY). See column 1, line 58 to column 2, line 40.	1-14
A	US,A, 4,187,336 Published 05 FEBRUARY 1980 (GORDON)	1-14
Y	US,A, 4,188,444 Published 12 FEBRUARY 1980 (LANDAU). See column 2, lines 29-33.	6 & 7
Y	US,A, 4,188,452 Published 12 FEBRUARY 1980 (CROTH). See column 5, lines 21-50.	2, 3, 9-14
A	US,A, 4,206,252 Published 03 JUNE 1980 (GORDON).	1-14
A	US,A, 4,230,773 Published 28 OCTOBER 1980 (BAKOS).	1-14
A	US,A, 4,259,371 Published 31 MARCH 1981 (POSTUPACK).	1-14
A	US,A, 4,397,671 Published 09 AUGUST 1983 (VONG).	1-14
<p>¹⁵ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹⁹	Date of Mailing of this International Search Report ¹	
16 DECEMBER 1986	06 FEB 1987	
International Searching Authority ¹	Signature of Authorized Officer ²⁰	
ISA/US	SADIE L. CHILDS	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

INT CL4: B05D 1/02,1/36,3/02,3/04,5/00,5/06; C03C 17/00,25/02;
C23C 16/24,16/40; B32B 9/00, 9/04,17/06,19/00.

US CL : 65/60.2,60.5,60.51,60.52,60.53,60.8;427/166,167,226,
248.1, 255,343,376.2,377,419.2,424,427;428/426,428,
432,448,702.

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE 10

This International search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers because they relate to subject matter ¹² not required to be searched by this Authority, namely:
2. ☐ Claim numbers because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING 11

This International Searching Authority found multiple inventions in this international application as follows:

- I. Claims 1-12, drawn to a method in class 427, subclass 255.
II. Claims 13 and 14, drawn to an article classified in class 428, subclass 428.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
☐ No protest accompanied the payment of additional search fees.

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

Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No ¹⁸
A	US,A, 4,431,692 Published 14 FEBRUARY 1984 (HOFFMAN)	1-14
A	US,A, 4,492,722 Published 08 JANUARY 1985 (RITTER)	1-14
A	US,A, 4,598,023 Published 01 JULY 1986 (VAN LAETHEN)	1