Sept. 25, 1973 H. FRANZ 3,761,305

SQUEEGEE/SHIELD

Filed July 6, 1971 4 Sheets-Sheet 1

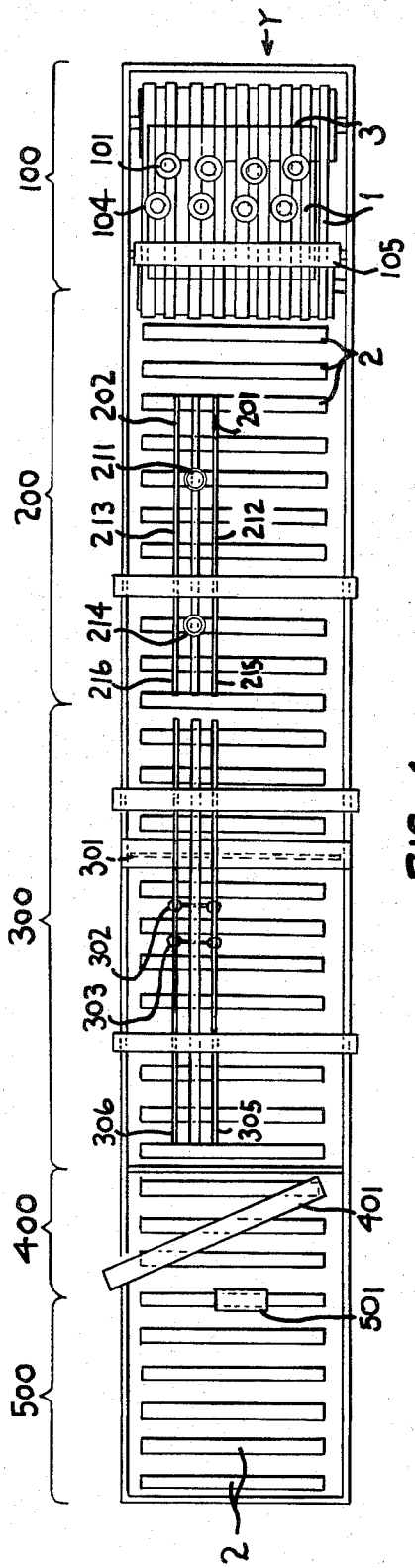


FIG. 1

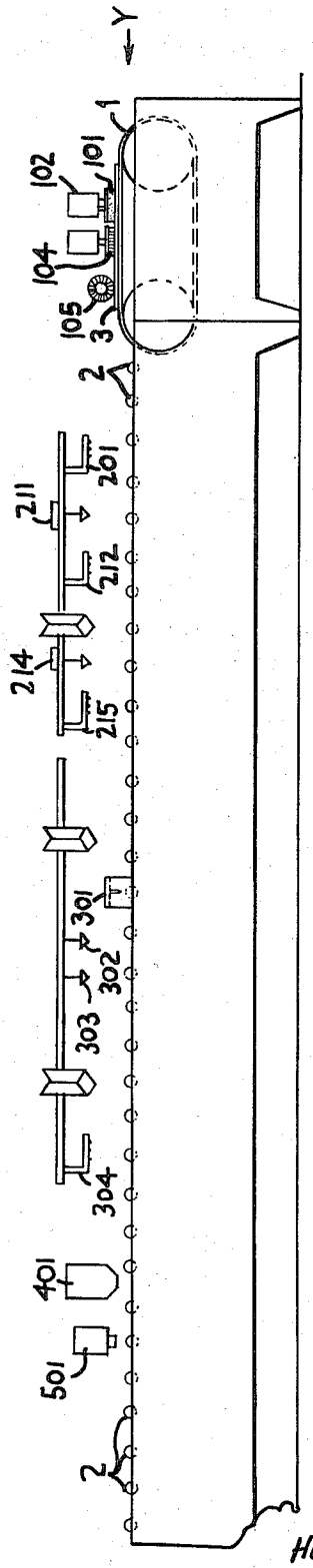


FIG. 2

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SQUEEGEE/SHIELD

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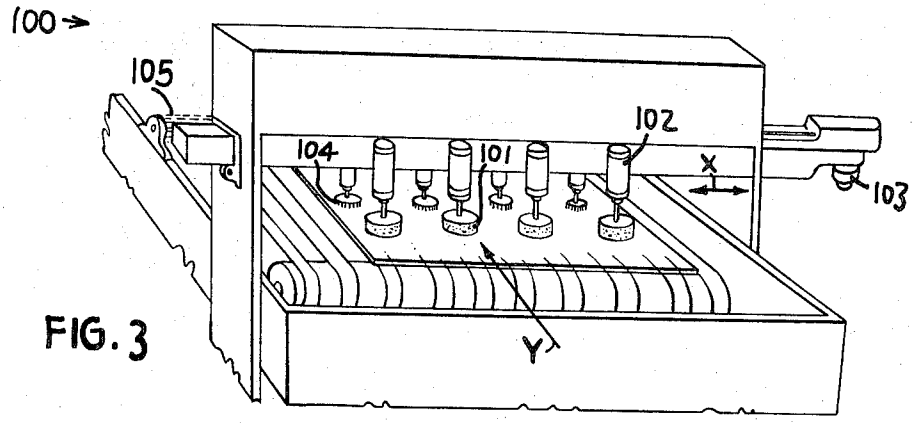


FIG. 3

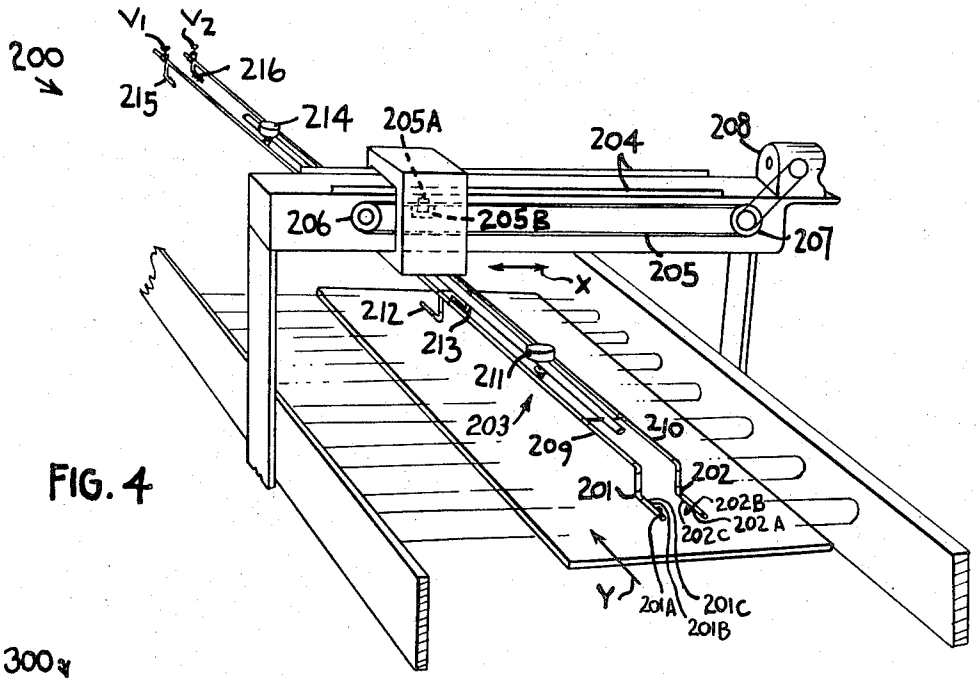


FIG. 4

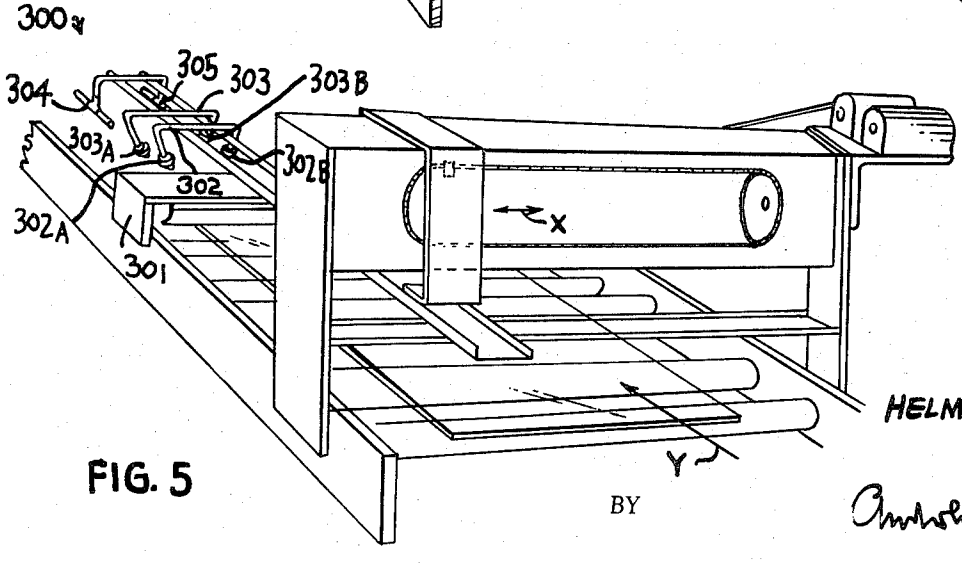


FIG. 5

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SQUEEGEE/SHIELD

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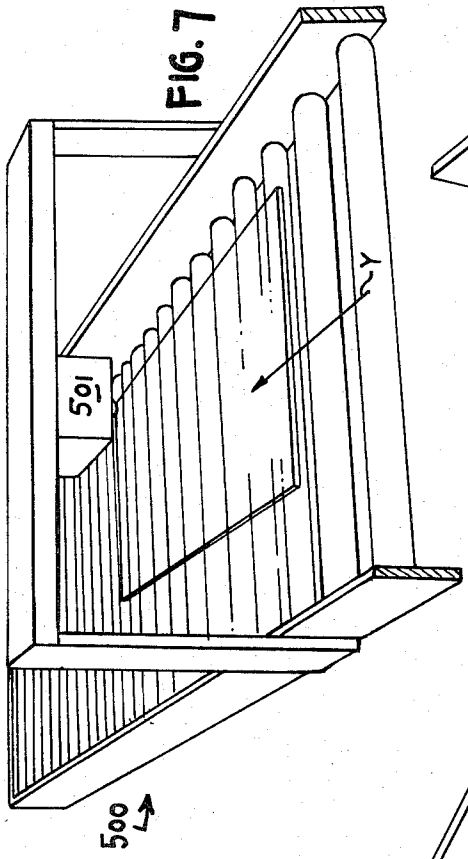


FIG. 7

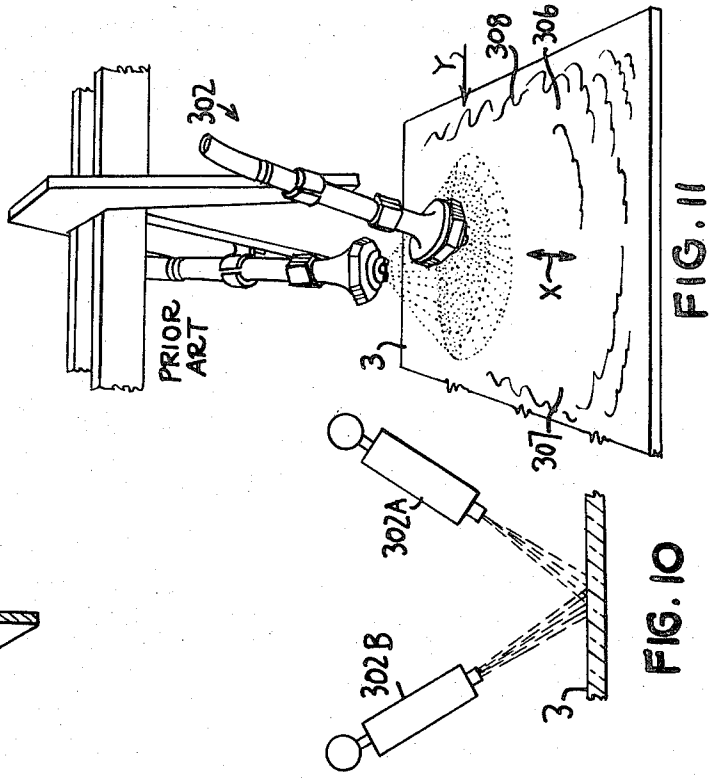


FIG. 11

FIG. 10

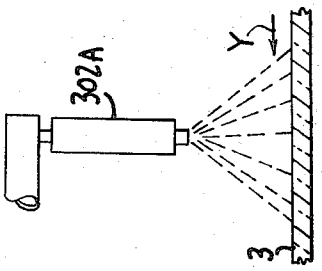


FIG. 9

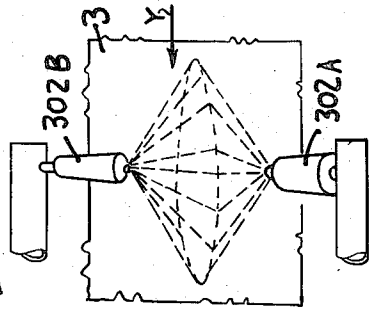


FIG. 8

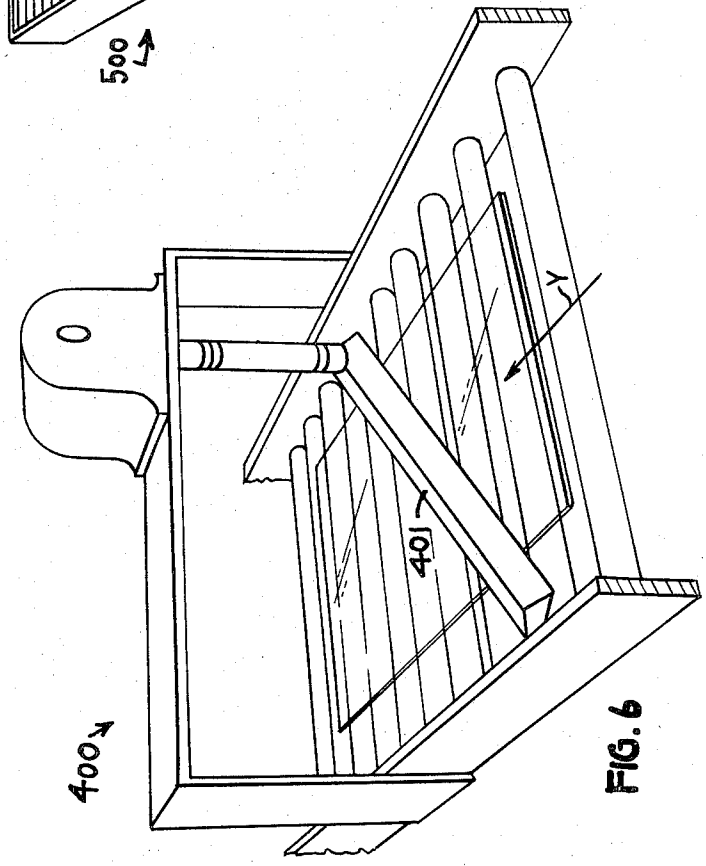


FIG. 6

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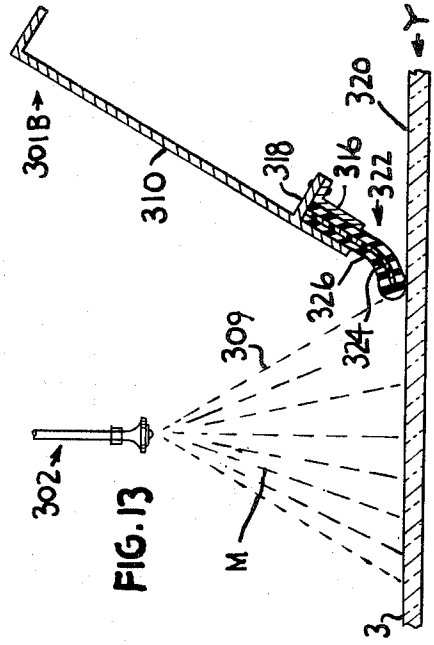


FIG. 13

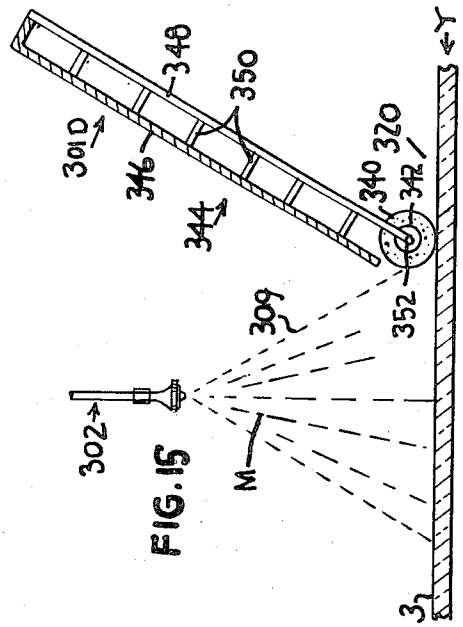


FIG. 15

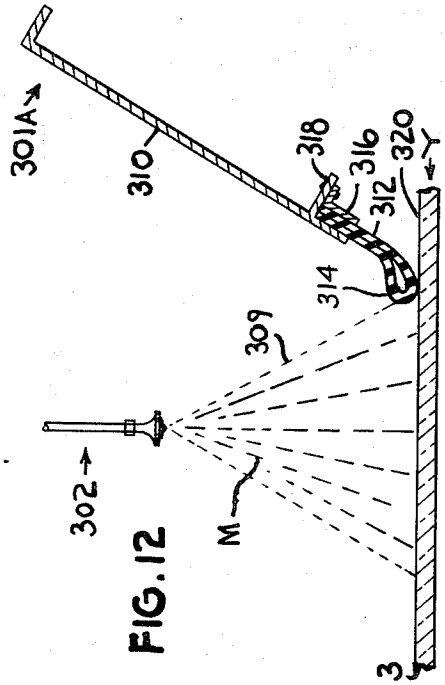


FIG. 12

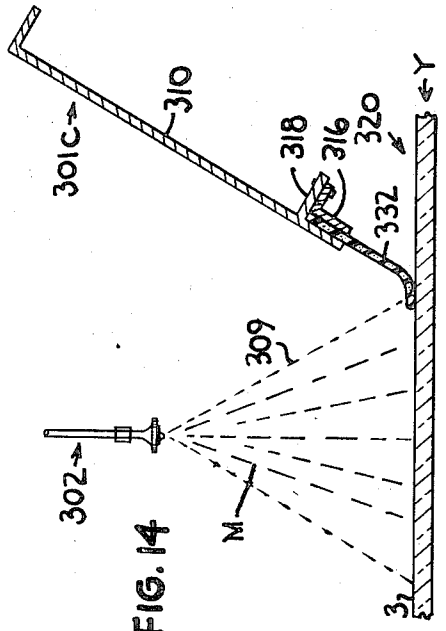


FIG. 14

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United States Patent Office 3,761,305 Patented Sept. 25, 1973

3,761,305

SQUEEGEE/SHIELD

Helmut Franz, Pittsburgh, Pa., assignor to PPG Industries, Inc., Pittsburgh, Pa.

Filed July 6, 1971, Ser. No. 159,747
Int. Cl. B44d 1/08
U.S. Cl. 117—105.3 6 Claims

ABSTRACT OF THE DISCLOSURE

A transparent substrate to be spray coated passes beneath a squeegee/shield apparatus to avoid formation of finger-like fronts or puddles in the spray area and to prevent splashing of the spray medium onto the substrate surface.

CROSS REFERENCES TO RELATED APPLICATIONS

This application is related to U.S. patent application Ser. No. 829,705, filed in the names of Richard G. Miller et al. on June 2, 1969, and entitled "Electroless Process for Forming Thin Metal Films," now U.S. Pat. No. 3,671,291. This application is also related to U.S. patent application Ser. No. 829,755, filed on June 2, 1969, in the name of Richard G. Miller, and entitled "Electroless Process for Forming Thin Metal Films," now U.S. Pat. No. 3,672,939. This application is also related to U.S. patent applications Ser. Nos. 57,451, 57,575, which is now abandoned, and 57,754, filed on July 23, 1970, in the name of Richard G. Miller, and entitled "Wet Chemical Method for Producing Transparent Metal Films," now U.S. Pat. No. 3,675,517, "Transparent Metal-Boron Coated Glass Articles" and "Solution for Depositing Transparent Metal Films," respectively, and U.S. patent application Ser. No. 57,527 of Charles B. Greenberg et al., filed on July 23, 1970, for "Wet Chemical Method for Producing Transparent Metal Films." This application is also related to U.S. patent application Ser. No. 11,904, filed on Feb. 2, 1971, in the name of Helmut Franz et al. and entitled "Chemical Filming Solution and Process for Plating Therewith." This application is also related to U.S. patent application Ser. No. 130,468, filed on Apr. 1, 1971, in the name of Helmut Franz, and entitled "Removal of Metal Containing Deposits from Non-Metallic Substrates."

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to a method and an apparatus for providing non-conductive transparent substrates with transparent coatings having optical properties of good uniformity, and particularly relates to a squeegee/shield apparatus that avoids sources of non-uniformity of said optical properties.

(2) Description of the prior art

In the past, transparent metal coated glass articles have been produced by various vapor deposition techniques which generally involve the deposition, from the vapor phase, of substantially pure metals, such as nickel or chromium on a prepared glass substrate. However, while such techniques are generally capable of providing metal films of acceptably uniform thickness and specified visual transparency, commercial films of this type have been observed to possess an undesirably high number of visible pin-holes. Further, this process is expensive and complex. Metal coated metallic and non-metallic articles have been produced by various well-known electroless or chemical plating techniques. These techniques generally involve the immersion of a metallic article or a

sensitized non-metallic article into a suitable electroless plating bath comprising an aqueous medium having dissolved therein a metal salt and an appropriate reducing agent, whereupon a metal film is deposited upon the immersed article by an autocatalytic mechanism.

The electroless process is an old and established one. For example, Brenner and Riddell disclosed in 1944 that an opaque coating of nickel could be autocatalytically deposited upon metallic substrates by immersing the substrate into a nickel salt solution containing sodium hypophosphite. U.S. Pat. Nos. 2,532,283 and 2,532,284 were issued to Brenner and Riddell upon their discoveries. The use of sodium hypophosphite as the reducing agent results in deposits which are not pure metal, but which contain about 2 to 10 percent elemental phosphorus by weight. In this connection, it is known that the presence of phosphorous in a deposited nickel film affects certain of the film characteristics, including its dominant wave lengths, infrared absorption characteristics, excitation purity and electroconductivity. In addition, and for reasons not wholly understood, it has been found that the uniformity of deposited nickel-phosphorous films generally decreases rapidly with increased thickness when the thickness of the coated glass substrates is greater than about 3/16 of an inch.

Other electroless immersion plating processes involve the use of boron-containing reducing agents which are effective at room temperature. U.S. Pat. Nos. 2,968,578, 3,140,188, 3,096,182 and 3,045,334 are representative of improved electroless plating processes of this type. U.S. Pat. No. 2,956,600, issued to Carlson et al., describes a spraying process wherein two separate solutions are sprayed upon substrates to form nickel coatings. This process uses sodium hydrosulfite and sodium hypophosphite as a reducing agent.

To a large extent the prior art has been concerned with production of opaque coatings by electroless coating, although it is understood that the assignee of U.S. Pat. No. 2,702,253 produces a glass plate having a transparent nickel coating possibly by the process therein disclosed. The problem of producing transparent glass or like articles is much more difficult because relatively minute variations in thickness are readily visible to the naked eye as unsightly defects. Other variations in such coatings can provide streaks with a glass region appearing almost opaque due to reflection of light in an otherwise transparent glass plate.

Many solutions suggested by the prior art develop a coating of gradually increasing thickness well beyond thicknesses which are opaque. The production of uniform transparent films with such solutions is especially difficult.

U.S. application Ser. No. 57,451, filed on July 23, 1970, in the name of Richard G. Miller, teaches a method whereby transparent substrates such as glass are provided with a uniform transparent coating by contacting the glass simultaneously with a mixture of a reducible metal salt in a solution and a reducing agent, which mixture becomes rapidly depleted of its film forming capacity before the resulting coating becomes opaque. This produces a uniform coating at a rate which is relatively rapid and then relatively slower and which effectively ceases to produce coating while the coating remains transparent. According to said application, it has been found that by using such mixtures and discontinuing the contact therewith after the rate of deposition of coating has reached the slower rate, transparent films of improved uniformity with few pin-holes can be achieved. The application further states that coatings of the best uniformity may be obtained even with large plates having four or more square feet of surface when the coating is applied by

separately spraying a solution of reducing agent and a solution of the reducible metal salt on the glass plate preferably while the major surfaces thereof are in a horizontal or substantially horizontal plane. The process has been found to be effective over a broad temperature range for coating any of the so-called catalytic metal substrates or non-catalytic substrates sensitized in a conventional manner to promote deposition of continuous, adherent transparent metal films. An advantage of the process is that it will deposit highly uniform transparent films when performed at about room temperature, i.e., from about 20° C. to about 30° C. The application further states that in order to insure that each of a plurality of substrates is provided with a coating that exhibits substantially the same physical and chemical characteristics, it is advantageous that the process temperature be held constant to within about ±1° C., for example, over 100 substrates or over 1000 square feet of substrates, or the like. Best uniformity and appearance of transparent films is achieved when films are deposited to a thickness having a luminous transmission of about 35 to 40 percent or less, and when the films comprise nickel-boron, cobalt-boron, iron-boron, and the like. Films comprising mixtures of boron and nickel, cobalt and/or iron may also be provided. In all such films, the boron is present in a minor amount (rarely exceeding about 15 percent by weight and normally between about 2 and 7 percent by weight) while the metal (nickel, cobalt and/or iron) is present in preponderant amounts (rarely less than 85 percent by weight and normally between about 93 and 98 percent by weight).

The transparent substrates obtained in accordance with the last-mentioned process may be employed, for example, as transparent windows or outside walls in a building such as a skyscraper or other multistory structure. These substrates may be especially advantageously employed as one of the plates which make up multiglazed units as described in the previously mentioned U.S. patent application Ser. No. 57,575, now abandoned. It will be understood that uniformity of coating in such uses is especially important because otherwise the reflected color of portions of the building differs sharply from that of other portions, thus distracting from its appearance.

To generalize, the prior art teaches a process whereby glass plates are conveyed along an article movement path through a sequence of rinse and spray stations. After a plate leaves a rinse station, it is normally covered with a layer of water. When the plate enters a spray station, this layer of water is normally pushed toward the trailing edge of the plate and tends to accumulate toward the trailing edge. As more water accumulates at the trailing edge, the water tends to flow back into the spray zone. The problem is especially severe at the trailing edge where water is retained by the edge of the plate. After reaching equilibrium thickness at the trailing edge, some of the water flows back into the spraying zone so that the glass plate is sprayed while it is covered with a thin film of water of non-uniform thickness. As a result, there is an uneven dilution of the sprayed-on solutions in the sensitizing and coating stations, and this causes the coating on the plate to vary in thickness, in absorption and in reflectance. This is extremely pronounced adjacent to the trailing edge of the plate.

In addition, finger-like waves of sprayed-on solution form immediately downstream and immediately upstream of each spray station. The deposition of solution begins prematurely in those areas of the sensitized surface which are in contact with the rear wave, causing streaks in the final coating in the direction of travel of the plate. In addition, splashing of the spray medium onto the sensitized area causes streaks and mottle in the final coating. The prior art recognized the existence of the problem of non-uniformity of coating, but failed to recognize the cause and therefore the solution.

SUMMARY OF THE INVENTION

It has now been discovered that the manner in which the solution contacts the sensitized glass surface is extremely critical, if a uniform coating is to be obtained. Optimum film quality is obtained when the first contact is made by fresh spray solution. The solution cannot be permitted to flow back onto the sensitized area or the glass surface will be covered non-uniformly by a mixture of fresh solution and spent solution, causing banding and streaking defects in the final coating. The solution cannot be permitted to accumulate at the trailing edge of the plate or defects will be most pronounced in this area. In addition, rinse water cannot be permitted to flow back into the spray zone in an uneven fashion or an uneven dilution of the solution (and therefore an uneven coating) will result.

According to the present invention, a squeegee/shield apparatus is installed immediately downstream of the first spray station. This apparatus prevents the formation of rear waves rearward of the apparatus and prohibits splashing of the solution onto the sensitized surface rearward of the apparatus, thereby eliminating any accumulation of solution at the trailing edge. In addition, it only permits a thin, uniform film of rinsing medium to pass beneath the spray station.

The location of the squeegee/shield apparatus relative to the surface to be coated and to the cone of dispensed rinsing medium is an important part of the present invention. The squeegee must touch the sensitized glass surface so that no dispensed solution passes rearward of the squeegee and only a thin, uniform layer of rinsing medium reaches the spray area. It must also cut off a portion of the spray fan to insure that initial contact with the glass surface is by fresh solution. Ideally, the squeegee should be placed so that it touches the tip of the spray fan, but since it is very impractical to maintain an exact relative positioning, the squeegee generally is positioned initially to overlap the spray fan by about ¼ of an inch. If there is a gap between the spray fan and the squeegee, spent solution may contact the glass surface before fresh solution in random areas, causing coating defects. If the squeegee cuts off, for example, about 2 inches of the spray fan, too much spray solution drips down onto the sensitized surface from the squeegee, instead of being sprayed onto the surface. The shield is above the squeegee to prevent splashing of the spray solution rearward onto the sensitized area before the sensitized surface reaches the dispensing station.

The squeegee may be made in the form of a lip seal of any soft, elastomeric material, such as natural rubber, neoprene, silicone rubber, and some plastic materials such as polyvinyl chloride. It is important to note that the material have a durometer of between about 50 and about 90, and preferably about 70. Certain plastics, such as polytetrafluoroethylene, have been proven to be too hard, therefore damaging the surface.

In another embodiment of the present invention, the squeegee is made in the form of a roller rather than a lip seal as previously described. The roller can be, for example, 1½ inches in diameter and driven by friction at the sensitized surface. As in the case of the lip seal, the roller can be made of any soft, elastomeric material, however, a closed cell foam rubber over a steel tube has proved very desirable.

Coated glass, made in accordance with the present invention, is capable of inhibiting transfer of radiant heat such as that from the sun's rays by the light reflectance and absorption of the film and the fact that it permits transmittance of less than 35 to 40 percent of visible light from sunlight. Panels having light transmittance of 5 to 25 percent are especially useful in warm to temperature climates such as the United States. In other climates such as Northern Europe, panels of greater transmittance are preferred.

The color of the panels is dependent upon the amount and composition of metal which is reduced. Especially attractive nickel-boron and like metal-boron coatings which have a neutral color reflecting and passing essentially white light are provided according to this invention. Cobalt coatings are blue while iron coatings are brown. Other colors can be obtained by producing mixtures of these coatings.

The nickel-boron and metal-boron compounds herein contemplated are usually electroconductive. Thus, these films may be used as heating elements. For example, in a double-glazed window comprising two-spaced glass panels enclosed by a glass, metal or organic sealing around the edge of the panel, one such panel may be coated on its interior side by the process of this invention. By applying an electromotive force across this coating, heat may be generated in the panel, thus minimizing or preventing substantial heat loss from the interior of the building in which such windows are mounted.

Coatings having one or more of the desirable properties set forth above are effectively produced according to this invention by spraying, as hereinafter disclosed in greater detail. Such a process is especially valuable in producing uniform coatings on large articles such as plates of glass or other substrates having one dimension in excess of 3 feet, with the other being in excess of 1.5 feet, for example, panels of 3 feet by 6 feet or larger.

Immersion processes have serious disadvantages. These disadvantages are especially acute where transparent coatings are desired since, for example, the composition of the plating bath changes during use, thereby requiring frequent chemical analysis and addition of materials to maintain a constant bath composition. If a constant bath composition is not maintained, the metal films formed thereon will not be uniform. In this latter connection, it should be appreciated that contamination of a bath composition, which may be caused, for example by an inadvertent admixture therewith of the solutions employed to activate the glass being coated, may necessitate a complete shut down of the process and a renewal of the bath. Furthermore, immersion processes are not especially adoptable to forming transparent films inasmuch as the rate of deposition is difficult to control. Thus, it is relatively common for a heavier coating to be deposited on that portion of the substrate which is first to enter and last to leave the plating bath.

Spraying a coating avoided the tapered coating thickness associated with dip coating in a plating bath. However, prior to the present invention, the non-uniformity of appearance of transparent coatings in some frequency made it necessary to improve the coating operation.

DESCRIPTION OF THE DRAWINGS

A complete understanding of the invention may be obtained from the foregoing recital of the prior art and following description of an illustrative embodiment of the present invention, taken together with the appended drawings, in which:

FIG. 1 is a diagrammatic top plan view, with portions removed for the sake of clarity, of an apparatus suitable for carrying out the process of the present invention on a continual basis;

FIG. 2 is a diagrammatic front elevation of the apparatus of FIG. 1;

FIG. 3 is a diagrammatic partial perspective view of a glass loading and cleaning section of the apparatus of FIG. 1;

FIG. 4 is a diagrammatic partial perspective view of a sensitizing and activating section of the apparatus of FIG. 1;

FIG. 5 is a diagrammatic partial perspective view of a metal-boron deposition section of the apparatus of FIG. 1;

FIG. 6 is a diagrammatic partial perspective view of a drying section in the apparatus of FIG. 1.;

FIG. 7 is a diagrammatic partial perspective view of a film density measuring and unloading section included in the apparatus of FIG. 1;

FIG. 8 is a diagrammatic top plan view of a metal solution-reducing solution dispensing spray gun set of a metal-boron deposition coating of the apparatus of FIG. 1, illustrating the disposition of spray guns in said set relative to each other and to an advancing glass substrate, and illustrating a fan-shaped pattern assumed by the respective solutions beiny sprayed;

FIG. 9 is a diagrammatic side elevational view of the coating apparatus illustrated in FIG. 8;

FIG. 10 is a diagrammatic front elevational view of the apparatus illustrated in FIG. 8;

FIG. 11 is a diagrammatic perspective view of a metal-boron spray gun set without a squeegee/shield apparatus;

FIG. 12 is a diagrammatic side cross-sectional view showing the details of a squeegee/shield apparatus made in accordance with a first embodiment of the present invention together with a spray gun;

FIG. 13 is a diagrammatic side cross-sectional view showing the details of a squeegee/shield apparatus made in accordance with a second embodiment of the present invention together with a spray gun;

FIG. 14 is a diagramatic side cross-sectional view showing the details of a squeegee/shield apparatus made in accordance with a third embodiment of the present invention together with a spray gun; and

FIG. 15 is a diagrammatic side cross-sectional view showing the details of a squeegee/shield apparatus made in accordance with a fourth embodiment of the present invention together with a spray gun.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to the drawings, there are shown several embodiments of an apparatus suitable for coating a monolithic substrate, such as a glass plate, with a transparent metal and boron-containing film of superior uniformity of film appearance in accordance with the present invention. As shown, the apparatus comprises five basic units or sections, which are designated a glass loading and cleaning section (section **100**), a glass sensitizing and activating section (section **200**), a metal-boron coating composition deposition section (section **300**) , a glass drying section (section **400**) and a film density measuring and glass unloading section (section **500**). The apparatus also comprises a conveyor means including a plurality of belts **1** in section **100** and rollers **2** in sections **200**, **300**, **400** and **500** for carrying and advancing glass plates **3** (FIGS. 1 to 7) past the various sections **100** to **500** along an article movement path in the direction of the arrows Y. As explained below, the belts **1** and the rollers **2** are rotated by conventional means (not shown) so as to advance the plates **3** at a rate of from about 0.5 to about 7 feet per minute, and preferably from about 3 to about 6 feet per minute.

During continuous operation, a plurality of glass plates **3** are loaded onto the belts **1**, so that the belts advance the plates into and through section **100** of the apparatus. Referring to FIGS. 1, 2 and 3, a plurality of rotating discs or blocks **101** gently abrade the uppermost surface of each plate, preferably with a mixture of cerium oxide or red rouge and water, to loosen and remove any dirt therefrom. This blocking operation is preferably carried out with cattle hair felt blocks having a diameter of from about 4 to about 12 inches. Each of the blocks is mounted on a shaft **102** which is rotated by a suitable motor **103** and gear means (not shown) at a rate of from about 200 to about 600 revolutions per minute. In the preferred embodiment, the blocks are rotated at about 300 to about 500 revolutions per minute and are oscillated, for example, a distance of about 2 to 4 inches in a direction transverse to the direction Y of the advancing plate to insure that the entire uppermost surface of the plate is blocked.

While still in section **100**, each plate advances beneath a plurality of rotary cup brushes **104** that wash the surface of the plate with tap water. The brushes **104**, which may have nylon bristles or the like, are generally rotated at the same rate as the blocks **101**, and are preferably oscillated in the same manner as well. Each plate finally advances beneath a rotary cylinder brush **105** disposed across the advancing plate. The brush **105** may comprise nylon bristles or the like which contact the plate and complete the cleaning thereof. The brush is generally rotated at about 300 to about 400 revolutions per minute. Both the rotary cup brushes **104** and the rotary cylinder brush **105** may be driven by conventional means such as motors (not shown) that may be similar to motors **103**.

Each plate **3** then enters into and passes through section **200** of the apparatus, wherein the surface thereof is sensitized and then activated (super-sensitized). As illustrated in FIGS. 1 and 2, and more particularly in FIG. 4, the plate is subjected to a first rinse, preferably with demineralized water, as it enters section **200** to remove any traces of cerium oxide, red rouge, tap water or any other undesirable matter carried over from section **100**. The first rinse may be performed in any conventional manner. For example, the plate may be rinsed by reciprocating a single water spray apparatus transversely of the advancing plate (i.e., in the direction of arrow X) while the plate advances in the direction indicated by arrow Y. However, the rinse is preferably performed by employing a cross-fire technique.

As illustrated in FIG. 4, when employing a cross-fire technique, a mutually opposed pair of pipes **201** and **202** are supported from a carriage **203** that reciprocates along the X axis on a track **204** at a rate of between about **25** and about **70** single passes per minute, and preferably between about **45** and about **60** single passes per minute. The carriage **203** is driven by a chain or belt **205** that runs over a pair of pulleys **206** and **207** arranged at the opposite ends of the track **204**. A motor **208** drives the chain **205** while a connection **205A** between the chain and the carriage slides up and down in a vertical groove **205A** between the chain and the carriage slides up and down in a vertical groove **205B** in the carriage **203** as the connection moves around the pulleys. The drive construction is similar to that shown in Bramsen et al. U.S. Pat. No. 2,246,502.

During the reciprocating motion of the carriage **203**, demineralized water is fed alternately to the pipes **201** and **202** in such a program that water is sprayed only from nozzles **201A**, **201B** and **201C** when the carriage is moving from left to right in FIG. 4, and only from nozzles **202A**, **202B** and **202C** when the carriage is moving in the opposite direction. The pipes **201** and **202** are supplied with water or other rinsing composition through lines **209** and **210**, respectively, by any suitable means. The pipes are advantageously operated at pressures between about 25 and about 80 pounds per square inch, preferably between about 25 and about 45 pounds per square inch, and at flow rates of about 500 to about 600 milliliters per minute per pipe.

There are many commercially available control means to alternate the flow of rinsing medium between line **209** and line **210**. Valves V_1 and V_2 are illustrated as an example of suitable control means, either automatic or manual, that become apparent to one skilled in the art.

After undergoing the first rinse with demineralized water, the plate advances beneath a reciprocating gun **211** which sprays a dilute solution of stannous chloride on the clean surface. The stannous chloride solution may comprise any of the formulations known in the art as being capable of sensitizing non-conductive substrates to metal deposition. However, a preferred formulation comprises from about 0.02 to about 1.0 gram of stannous chloride per liter of solution, together with a small amount of hydrochloric acid. Such a solution may be prepared, for example, by mixing about 20 grams of stannous chloride and 2 to 3 milliliters of concentrated hydrochloride acid (12 N) in enough demineralized water to form one gallon of stock concentrate, and then diluting each part of the concentrate with about 19 parts of demineralized water. In a preferred embodiment, about one part of the above-described concentrate is injected into a stream comprising about 19 parts of demineralized water, whereafter the combined stream is mixed with air at about 60 to about 80 pounds per square inch, and sprayed through the gun **211** in a highly atomized state at a rate of about 500 to about 700 milliliters per minute.

As illustrated in FIG. 4, the stannous chloride composition dispensing spray gun **211** is supported from the same carriage **203** that supports the first rinse pipes **201** and **202**. In addition, a second set of rinse pipes **212** and **213**, a palladium chloride composition dispensing spray gun **214** and a third set of rinse pipes **215** and **216** may also be supported from carriage **203**.

As the plate **3** continues to advance along the article movement path Y, it passes beneath the second set of rinse pipes **212** and **213**. These pipes are operated in the same manner as pipes **201** and **202**.

The sheet **3** then passes under the gun **214** which sprays an atomized mixture of air and dilute palladium chloride on the now sensitized surface so as to activate (or supersensitize) the surface for the ensuing metal-boron deposition. As is the case with the stannous chloride solution, the palladium chloride may comprise any of the well-known formulations that are suitable for activating a previously sensitized substrate. However, a formulation comprising from about 0.005 to about 1.0 gram of palladium chloride per liter of solution, together with a small amount of hydrochloric acid, is preferred. One such formulation may be prepared by mixing about 2 grams of palladium chloride and 2 to 3 milliliters of concentrated hydrochloric acid with a sufficient amount of demineralized water to form one gallon of concentrated stock solution, and then diluting each part of the stock solution with 19 parts of demineralized water. As is the case with the stannous chloride solution, the diluted palladium chloride is preferably mixed with air at a pressure of about 60 to about 80 pounds per square inch and sprayed onto the glass at a rate of about 500 to about 700 milliliters per minute.

After passing spray gun **214** and before leaving section **200** of the apparatus, the plate **3** undergoes a third demineralized water rinse. This rinse is carried out in the same manner as the first and second rinses, and is designed to remove any excess palladium chloride from the advancing plate before it reaches the metal-boron coating composition deposition section.

The spacing between the respective guns in section **200** of the apparatus may vary within wide limits depending, for example, upon the rate at which the plate **3** is advancing, the dimensions of the fan-shaped spray pattern generated by each gun, the rate of traverse of each gun, and the like. However, it is preferred to arrange the various guns in section **200** such that the time required for the leading edge of the given plate **3** to advance from each gun or set of guns to the next successive gun or sets of guns is from about 10 to about 90 seconds.

As illustrated, the plate then passes from section **200** of the apparatus to section **300** thereof, wherein a metal and boron-containing coating, preferably nickel-boron, cobalt-boron, iron-boron or a mixture of at least two of said metal-boron coatings is deposited on the now activated surface thereof. The deposition is preferably accomplished by simultaneously spraying a metal-containing solution and a boron-containing reducing solution from separate spray nozzles and intermixing said solutions onto the activated surface such that the metal ions present in the contemplated metal solution become reduced to a transparent boron-containing metal film which tenaciously adheres to the activated surface.

It will be appreciated that the number, disposition, and the spacing of the guns which spray the metal solution and the boron-containing reducing solution, and the rate at which they are reciprocated, are determined generally by the rate at which the plate advances, the temperature, pH, and concentration of the intermixed film forming composition and the like, and primarily by the time required for the film forming composition to be substantially depleted in its film forming capacity, and the desired thickness and transparency of the deposited film. The importance of these latter two parameters will become more apparent in view of the illustrative example set forth below.

For the sake of illustration, section **300** is shown in FIGS. 1, 2 and 5 as having two reciprocating spray gun sets **302** and **303**, each comprising a first nozzle for dispensing a metal-containing solution, **302A** and **303A**, respectively, and an opposed second nozzle, **302B** and **303B**, respectively, for dispensing a reducing solution. Section **300** also includes a mutually opposed pair of reciprocating water pipes **304** and **305** arranged for cross-fire rinsing. As shown, spray gun sets **302** and **303** are supported for transverse reciprocating movement, for example, in the manner described for reciprocating spray guns **211** and **214** in connection with FIG. 4. However, it should be noted that the gun set in section **300** must reciprocate much faster than those in section **200** or than those employed in conventional spray techniques for depositing silver, for example. In this connection, it has been found that uniformly and controllably transparent metal-boron coatings can best be made in accordance with the present invention only when the gun sets of section **300** are reciprocated at a rate of at least about 60 to about 65 single passes per minute, and preferably from about 72 to about 76 single passes per minute, when the plates being coated are about 4 feet wide and are advanced at a rate of from about 3 to about 6 feet per minute. Thus, for a 4-foot wide plate advancing at a rate of 3½ feet per minute, i.e., 42 inches per minute, a spray gun set reciprocating at 74 single passes per minute will complete about 1.75 single passes over each inch segment of the advancing plate.

Accordingly, if the width of the applied spray in a direction of travel of the plate is from 10 to 12 inches, each inch segment of the plate will receive from about 17.5 to about 21.1 applications of solution per gun set. Of course, the required number of passes per minute will vary somewhat in accordance with changes in magnitude of the various parameters discussed herein. For example, the required number of passes would increase when the plate being coated or advanced more rapidly than approximately 3 to approximately 6 feet per minute.

Spray guns of each set **302** and **303** are connected through respective supply lines (not shown) to air under pressure at about 20 to about 60 pounds per square inch. In turn, the respective supply lines are in fluid communication with prepared metal and reducing solutions stored in separate solution tanks or containers (not shown), preferably of such size to hold a reasonable supply of fluid, such that when the prepared solutions are injected into the supply lines by any conventional means (not shown), the solutions are fed through the lines and sprayed from the guns in a fan-shaped pattern. It will be appreciated that the magnitude of air pressure required for a satisfactory spray varies considerably with the design of the guns of the various parameters of the solutions employed. In this connection, satisfactory results have been obtained with pressures as low as about 20 pounds per square inch and as high as about 55 pounds per square inch. Pressures in the range of about 25 to about 40 pounds per square inch are preferred. The rates at which the respective prepared solutions are sprayed from each gun may vary, but it is preferred that the rates of flow be maintained at about 300 to about 2000 milliliters per minute per gun.

As illustrated in FIGS. 8, 9 and 10, each of the nozzles **302A** and **302B** in the metal depositing spray gun set **302** is preferably designed to provide a substantially fan-shaped stream which opens only a few degrees in the direction transverse to the advancing plate, and which opens in the direction of travel of the plate such that the stream contacts the advancing plae in an elliptical pattern having a major diameter of from about 8 inches to about 14 inches, and preferably from about 10 inches to about 12 inches in length (FIG. 8). Spray gun set **303** functions in the same manner.

The nozzles in each metal salt-reducing solution set are arranged to have an included angle of from about 80 to about 120 degrees between the streams of composition they dispense. To accomplish this end, each of the metal salt solution dispensing guns is inclined obliquely from the vertical about 40° to about 60° toward a mutually opposed reducing solution dispensing gun, and vice versa in a vertical plane common to the dispensing guns of the set (FIG. 10). This arrangement is desirable so that the metal and reducing solutions are effectively and thoroughly mixed as they approach and strike the surface of the activated glass plate.

Referring to FIG. 11, there is shown a schematic perspective view of an apparatus illustrating the state of the art prior to the present invention. FIG. 11 shows a metal-boron composition dispensing spray gun set **302** reciprocating along the X axis and applying solution to the transparent sheet **3** as said sheet travels along its article movement path Y. Note that set **302** produces a rear wave **306** and a front wave **307** on the surface of the glass sheet **3**. The rear wave comprises a mixture of fresh solution and spent solution containing precipitated nickel, decomposed reactants, rinsing medium and gas bubbles. This mixture reaches and covers the sensitized surface of the glass sheet **3** before the sheet reaches a position where its upper surface is sprayed with fresh solution from gun set **302**. As pointed out above, when the advancing glass sheet is contacted initially with spent solution, the resultant coating does not posess uniform optical properties. Further, note that the boundary **308** of rear wave **306** does not extend across the sheet in a straight line. Rather, it extends transversely of article movement path Y in a finger-like pattern, causing non-uniform surface coverage and, therefore, streaks in the final coating. In addition, the amount of old solution per unit area of glass sheet covered and the age of the old solution is not uniform for all portions of the rear wave **306**. This non-uniformity of amount and age of coating manifests itself in inhomogeneities in the resulting film.

Front wave **307** is principally composed of spent solution and rinsing medium. In the case of any front wave, spent solution is contacting the surface of a substrate after fresh solution has been applied. Since spent solution does not adhere as readily to a metal surface as it does to a glass surface, front wave **307** does not affect the uniformity of the finished coating to the extent that rear wave **306** affects it.

The terms "front" and "rear" refer to the direction of movement of glass sheets along the article movement path as defined by the direction of arrow Y. In addition, the following description uses the terms "upstream" and "downstream" to define the direction of glass sheets along the article movement path. The sheets are presumed to travel in a downstream direction.

According to the present invention, rear wave **306** has been completely eliminated and front wave **307** has been reduced in size by the use of a stationary squeegee/shield apparatus **301** immediately upstream of the first spray gun set **302**, as shown in FIG. 5. The squeegee/shield apparatus **301** extends in direction X that is transverse to the article movement path Y, and it functions to control the thickness of rinse water remaining on the surface of sheet **3** from rinse pipes **215** and **216** to form a water film of uniform thickness on the glass surface

when said sheet **3** and said spray gun set **302** are in alignment, while avoiding the formation of finger-like waves of solution upstream of said spray gun set. Unlike spray gun sets **302** and **303**, and rinse pipes **304** and **305**, the squeegee/shield apparatus is stationary and does not reciprocate along the X axis.

Referring to FIG. 12, there is shown the details of a first embodiment **301A** of a squeegee/shield made in accordance with the present invention, together with spray gun set **302**. Squeegee/shield **301A** includes a splash shield **310** and a squeegee **312** mounted beneath splash shield **310**. Squeegee **312** comprises, for example, a loop made of soft rubber approximately 0.010 inch thick. The loop forms a lip portion **314** that engages the coated upper sensitized surface of each moving sheet of glass **3** that enters a spraying station. Squeegee **312** is held in place beneath shield **310** by any suitable means, such as, for example, an angular plate **316** which is bolted to a flange **318**. The squeegee is made of an elastomeric material having a durometer hardness of from about 50 to about 90, and preferably about 70. Examples of suitable materials are: natural rubber, neoprene, silicone rubber and plasticized polyvinyl chloride. Stiff plastics such as Teflon, Mylar, Lexan and many polycarbonates tend to scratch the sensitized surface.

Shield **310** and squeegee **312** prevent the spray-fan M from gun set **302** from splashing onto the glass surface and congregating in an upstream area **320** of set **302**. Squeegee **312** prevents any of the spray M from flowing beneath shield **310** to upstream area **320**. Together, the shield **310** and the squeegee **312** eliminate the rear wave and its associated problems.

Shield **310** may be constructed of any material that is capable of adding structural integrity to the apparatus **301** and is not attacked by the spray-fan M. Stainless steel is an example of a material suitable for use with a nickel-boron spray. Actually, the squeegee could be extended upward to replace the shield and perform its splash prevention function, as long as some measure is taken to add structural integrity to the apparatus. This could be done by, for example, reinforcing the upper portion of the squeegee or varying its thickness so that it is thicker, and therefore stronger, at its upper portion.

The squeegee **312** and particularly lip portion **314** performs two additional functions. Some of the rinse water from pipes **215** and **216** remains on the glass sheet **3** in a random manner as it approaches gun set **302** along the article movement path Y. If this rinse water is allowed to sit on the glass surface beneath gun set **302**, there will be a non-uniform dilution of the spray solution and a coating with inferior optical properties will result. Lip portion **314** acts as a wiper to insure that no puddles of rinse water pass beneath gun set **302**. It allows only a thin uniform rinsing film of from about 0.03 inch to about 0.10 inch, and preferably about 0.05 inch, to sit on the glass beneath the coating station. In addition, lip **314** is positioned so that it slightly overlaps the side edge **309** of spray-fan M by about ⅛ or about ¼ of an inch at the upper glass surface to intercept a portion of spray M. Ideally, the tip of lip **314** should just touch the side edge of spray-fan M to insure that fresh spray solution contacts the glass surface first, but it is impractical to maintain this relationship with precision. If the squeegee is positioned so that lip **314** does not either touch the side edge or intercept a portion of spray-fan M, spent solution may contact the glass surface in random areas before fresh solution contacts the surface in those areas and a coating having non-uniform optical properties may result. Moving the squeegee downstream so that the tip of lip **314** is one-half inch from the side edge of the spray-fan M produces streaky coatings. As a practical matter, if the squeegee intercepts too much of the spray M, such as, for example, about 1 inch, an unnecessary amount of solution is wasted.

Referring to FIGS. 13, 14 and 15, alternate embodiments of the present invention are shown with similar numerals used to indicate similar parts. FIG. 13 shows a squeegee/shield **301B** including a squeegee **322** comprising a thin plastic reinforcement **324** enclosed within a looped elastomeric covering **326**. The covering **326** may be made, for example, of soft material, similar to the ones described in connection with squeegee **312**. The reinforcement **324** can be made, for example, of polyvinyl butyral, approximately 0.030 inch thick.

Referring to FIG. 14, there is shown a third embodiment **301C** of the squeegee/shield apparatus of the present invention. In this embodiment, the squeegee comprises a curtain **332** approximately ¾ of an inch to 1½ inches long and approximately 0.007 to approximately 0.040 inch thick, hanging freely from splash shield **310**. The curtain **332** may be made of any of the suitable materials described above in connection with squeegee **312**.

Referring to FIG. 15, there is shown a fourth embodiment **301D** of the squeegee/shield apparatus of the present invention. In this embodiment, the squeegee is in the form of a roller **340**, driven by friction at the sensitized surface. It is possible to drive roller **340**, but this is unnecessary and can lead to complications if roller **340** is not driven at the exact speed as the rollers **2** beneath the glass sheet **3**. The roller may be made of any of the above-mentioned squeegee materials, but is preferably made of closed cell foam rubber. Enclosed within the foam rubber is a metallic tube **342**. Shield **344** includes a sheet **346** and rods **348** with ribs **350** connecting the sheet to the rods. Axle **352** is rotatably connected to the base of rods **348** and roller **340** rotates about axle **352**. In the embodiments illustrated in FIGS. 13–15, the squeegee operates to perform the functions described in connection with the embodiment of FIG. 12.

It is customary to use either two or three, or sometimes even four, spray gun sets. It might occur to one skilled in the art to use a squeegee/shield apparatus prior to each spray gun set. It has been discovered, however, that the installation of any squeegee/shield apparatus after the first spray gun set is detrimental in that it damages the freshly coated metal-boron surface. Further, a subsequent spray gun set appears to be able to sweep the spent solution from the surface of substrate **3** without damaging the prior coating. This can be explained by the fact that the spent solution does not adhere as readily to the fresh coating as it does to sensitized glass. Therefore, the use of squeegee/shield apparatus after the first spray gun set is unnecessary and even undesirable.

The shields **310** and **344** have been illustrated as being oriented at an angle of about 30° with the vertical, but this angle is not critical. Actually, the shield may even lie within a vertically extending plane. By tilting the shield to an angle of from about 15° to about 50° with the vertical, the top portion of the shield is spaced from gun set **302** to make gun set **302** more accessible.

As the plate advances beyond each spray gun set **302** and **303**, the intermixed film forming composition which is uniformly distributed on the surface of the plate is permitted to rest relatively quietly. This quiescent period or period of minimum turbulence is highly desirable since it enables the film forming composition to deposit a transparent coating which is substantially free from visual defects normally attributed to turbulence or agitation of the filming composition during deposition. In addition, it is during this quiescent period that the intermixed filming compositions contemplated herein undergo a change in their capacity for depositing a film such that the rate of film deposition, which is initially relatively rapid, decreases and then effectively completely ceases while the deposited film is still transparent. While the time required for this change in filming capacity to occur will vary considerably depending upon the chemistry of the actual filming composition employed, a filming composition comprising equal amounts of the nickel acetate solution and

borohydride reducing solution, illustrated respectively in Tables I and II of U.S. patent application Ser. No. 57,451, will normally undergo a substantial decrease in its filming capacity within from about 10 seconds to a few minutes, e.g. 5 minutes. In this regard, a glass plate that is coated with a metal and boron-containing film at room temperature by a single 15-second spray application of the above-illustrated intermixing filming composition will normally have a luminous transmission of from about 30 to about 40 percent when the filming capacity of the composition has depleted and filming has effectively ceased.

Referring once again to FIGS. 1 and 5, it will be appreciated that once the film forming composition has become dead, i.e., depleted of its filming capacity, it may be removed from the plate by any convenient means without affecting the thickness, and thus the transparency of the film. It will also be appreciated that the lowest degree of transparency obtainable will depend primarily upon the amount of film that will deposit from a given film forming composition before it becomes dead, the number of gun sets in section **300**, and the distance between each gun set. The effect of these variables on the thickness, uniformity and transparency of the metal-boron films formed in accordance with this invention will be more fully appreciated in light of the example recited hereinbelow.

After undergoing the quiescent period after its exposure to the mixed composition dispensed by spray gun set **303**, the plate has a luminous transmittance of about 15 to 25 percent. If a third spray gun set is used (not illustrated), a luminous transmittance of as little as 10 percent may be obtained. Each additional gun provides a quiescent period designed to allow the partially formed metal-boron film to increase in thickness uniformly in the substantial absence of adverse effects caused by turbulence. Even more important, however, this period is designed to allow sufficient time for the film forming composition on the surface of the plate to become substantially depleted of its film-forming capacity so that the rate of deposition of the metal-boron film will have materially slowed down, and preferably effectively ceased, before the plate is rinsed under pipes **304** and **305**. In this latter connection, it will be appreciated that the necessary distance between pipes **304** and **305** and the last metal depositing gun set **303** is related to the rate at which the plate is advanced. Thus, while maintaining all of the various parameters within the bounds described herein, the distance between the final rinse pipes **304** and **305** and the last spray gun set **303** should be at least about 30 inches, and preferably at least about 35 to 40 inches to provide a final film thickness corresponding to a luminous transmittance of about 20 percent.

After undergoing a final water rinse under rinse pipes **304** and **305**, the plate **3** advances into section **400** of the coating apparatus where it is dried by means of a suitable air knife **401** (FIG. 6). The air knife **401** may comprise any conventional blow-off device, but it is preferred to employ a high volume-low pressure knife to avoid disturbing the quality of the metal-boron film. For example, it is desirable to employ a knife that operates at a pressure of about 3 to 7 ounces per square inch, while forcing from about 300 to about 400 cubic feet of air per minute against the metal-boron coated glass plate.

After passing beneath the air knife, the completed metal-boron coated plate passes into section **500** where the thickness of the deposited film is measured by a conventional measuring device **501**. Thereafter, the transparent glass plate is removed from the rollers **2** and is ready for use.

The present invention is applicable in forming transparent metal-boron films on clear plastic (e.g. polymethyl methacrylate) and glasses, especially soda-lime-silica glasses, but can be used to film a wide variety of glass, ceramic, glass-ceramic, siliceous and calcareous based compositions. For example, this invention can be used to provide metal-boron and particularly nickel-boron films on the following types of glasses: soda-lime-silica glasses; alkali-alumina-silica glasses, such as those containing lithia as a component alkali; alkali-zirconia-silica glasses; alkali-alumina-zirconia-silica glasses; borosilicate glasses, etc. Bearing this in mind, the present invention is described hereinbelow with specific reference to soda-lime-silica glass.

The soda-lime-silica glass to be treated can be a clear glass or it can be a colored glass tinted by the introduction of various conventional materials into the glass forming batch. These latter glasses are often referred to as heat absorbing glasses especially when they contain iron oxide. Representative soda-lime-silica glass bases which can be treated in accordance with this invention usually contain 65 to 75 percent by weight SiO_2, 10 to 18 percent by weight Na_2O, 5 to 15 percent by weight CaO, 1 to 5 percent by weight MgO, 0 to 1.0 percent by weight Na_2SO_4, 0 to 5 percent by weight aluminum oxide (Al_2O_3), 0 to 8 percent by weight K_2O, 0 to 8 percent by weight B_2O_3, 0 to 1 percent by weight iron oxide (Fe_2O_3), and 0 to 0.7 percent by weight of NaCl, SO_3, As_2O_5, BaO, NiO, CoO and Se and combinations thereof.

A representative range of composition for soda-lime-silica glasses is listed as follows (wherein the given amounts of metals listed are determined as their oxides, except as otherwise noted):

Component:	Percent by weight
SiO_2	68–73.5
Na_2O	12–17
CaO	7–12
MgO	2–4
$NaSO_4$	0–0.8
NaCl	0–0.3
Fe_2O_3	0.05–0.09
Al_2O_3	0–3.5
B_2O_3	0–6
K_2O	0–1.5
As_2O_5	0–0.5
BaO	0–0.7
NiO	0–0.1
CoO	0–0.1
SO_3	0–0.5
Se	0–0.1

The invention will be further understood from the specific example which follows. It should be noted, however, that the present invention is not necessarily limited to specific materials, temperatures, contact times, and pH values noted in the below example:

EXAMPLE

A 40 inch x 70 inch x ¼ inch commercial soda-lime-silica glass plate is coated with a nickel-boron film with the apparatus illustrated schematically in FIG. 1. Four blockers are used, each comprising a 3-inch thick cattle hair felt disc of 8-inch diameter. The blockers are arranged at 12-inch centers in the direction parallel to the rollers, hereafter referred to as the transverse direction, and are rotated at about 350 revolutions per minute. The blockers are oscillated about 4 inches in the transverse direction at a frequency of about 15 cycles per minute. Four 6-inch diameter rotary cup brushes are arranged at 12-inch centers in a transverse direction such that the longitudinal distance between the blockers and the rotary cup brushes is about 9 inches. The rotary cup brushes are equipped with No. 12 nylon bristles and are rotated at about 350 revolutions per minute. The brushes are also oscillated about 4 inches in the transverse direction at a frequency of 15 cycles per minute. During operation, the blockers are supplied with a mixture of cerium oxides and

tap water, while a spray of tap water is apply beneath the rotary cup brushes. The rotary cylinder brush has a 6-inch diameter, comprising No. 13 nylon bristles, and has its axis disposed 8 inches from the rotary cup brushes. The first, second and third rinse sets, as well as the tin composition dispensing gun and the palladium composition dispensing gun, i.e., all of the rinse sets and the guns in section **200**, are mounted from a single boom that reciprocates in a transverse direction at a rate of about 45 single passes per minute. Each of the rinse nozzles comprises a single UniJet-T8002 spray nozzle (manufactured by Spraying Systems Company, Dellwood, Ill.) and is operated at a pressure of about 40 pounds per square inch, at an average flow rate of about 0.2 gallon of demineralized water per minute. Each of the tin and palladium composition dispensing guns comprises a single, type C, spray gun equipped with a Paasche U2, F2–8 nozzle, manufactured by Paasche Air Brush Company, Chicago, Ill., and operated at an air pressure of about 70 pounds per square inch and a flow rate of about 500 milliliters of the solution described below per minute. The distance between the rotary cylinder brush and the first rinse pipes **201** and **202** is about 30 feet, while the distance from each gun to the next respective gun is about 5 feet.

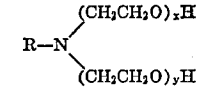
The gun sets in section **300** of the apparatus are spaced apart from those in section **200** such that the distance between rinse pipes **215** and **216** and gun set **302** is about 10 feet. In addition, gun set **302** is spaced about 3 feet from gun set **303**. The distance between the tip of the gun dispensing nickel solution and the tip of the gun dispensing reducing solution in each respective set is about 10 inches. All of the guns in section **300** employ Paasche U2, F2–8 nozzles, which are arranged so that the tip of each nozzle is about 7 inches above the surface of the glass being coated, and so that each respective gun set generates a fan-shaped stream of intermixed film forming solution that contacts the glass surface in a generally elliptical pattern having a major diameter of about 11 inches extending in a longitudinal direction. All of the rinse sets and the spray guns in section **300** are mounted from a single boom that reciprocates in the transverse direction at a rate of about 72 passes per minute which is equal to 36 round trips per minute. During operation, each of the metal deposition gun sets in section **300** is maintained at a pressure of about 40 pounds per square inch and a flow rate of about 800 milliliters of solution per minute, while the final cross-fire rinse pipes **304** and **305** are operated at a pressure of about 40 pounds per square inch at an average flow rate of about 0.2 gallon of demineralized water per minute per nozzle. The distance between rinse pipes **304** and **305** and the last metal depositing gun set **303** is about 70 inches.

The air knife **401** comprises an elongated metal housing having a 0.002-inch wide delivery slot extending along the length of its bottom wall. The knife **401** is disposed at a 45° angle relative to the advancing plate and had its centermost portion spaced about 8 feet from the final rinse pipes **304** and **305**. The air knife is operated at about 5 ounces per square inch and at a flow rate of about 350 cubic feet per minute. The ambient air temperature is about 82° F., while the temperature of the demineralized and tap water used throughout this example is about 63° F. The glass plate is advanced at a rate of about 5 feet per minute, while the slot opening of the air knife is spaced about ½ inch from the plate. On the basis of a liter of solution, each of the prepared aqueous solutions employed has the following composition:

NICKEL SOLUTION

Nickelous acetate	5.0 grams.
Boric acid	2.5 grams.
Sodium gluconate	9.0 grams.
Hydrazine sulfate	0.5 gram.
Water	Added to 1 liter.
Ammonium hydroxide	Added to pH 7.4.
Ethomeen C–20 [1]	0.06 gram.

[1] Ethomeen C–20 (trademark of Armour and Company) is a cocoamine having an average molecular weight of 645 and the following generalized formula:



wherein R is derived from a cocoamine and $x+y=$ VJ.

REDUCING SOLUTION

Sodium borohydride	0.5 gram.
Water	Added to 1 liter.
Sodium hydroxide	Added to pH 11.6.
Ethomeen C–20	0.30 gram.

TIN SOLUTION

Stannous chloride	0.02 gram.
Hydrochloric acid (12 N)	0.04 milliliter.
Water	Added to 1 liter.

PALLADIUM SOLUTION

Palladous chloride	0.02 gram.
Hydrochloric acid (12 N)	0.04 milliliter.
Water	Added to 1 liter.

The temperature of each of these solutions is about 70° F. The pH of the intermixed nickel and borohydride solutions is about 7.7. A nickel film is formed which contains about 5 to 10 percent by weight boron and the resulting coated plate has a luminous transmission of about 22 percent. The film is very adherent to the glass plate and is very uniform in appearance. It has an initial resistivity of 300 ohms per square.

Having now fully disclosed the invention, what I claim is as follows:

1. In a method of coating a surface of an article wherein the article is conveyed through a rinsing station to apply a rinsing medium to the surface and a coating station to apply a coating composition onto the rinsed surface, the improvement comprising:

removing a portion of the rinsing medium from the rinsed surface as the article is conveyed into the coating station to form a rinse medium film of uniform thickness on the surface of the article while avoiding the formation of a wave of the coating composition upstream of the coating station to provide a coating having uniform optical properties.

2. The method according to claim **1** wherein the coating composition is applied in a fan-shaped spray toward the surface of the article including the step of:

shielding succeeding portions of the surface conveyed into the coating station from a minor portion of the fan-shaped spray upstream of the coating station to eliminate finger-like flows of the coating composition upstream of the coating station wherein elimination of the finger-like flows prevents subsequent formation of streaks in the coating.

3. The method according to claim **2** wherein about ¼ of an inch of the fan-shaped spray is shielded from the succeeding portions of the surface conveyed into the coating station.

4. In a method of coating a surface of an article wherein a sensitizing composition is applied to the surface, and thereafter the article having the sensitized surface is conveyed through a rinsing station to apply a rinsing medium to the sensitized surface and a coating station to apply a coating composition onto the rinsed, sensitized surface, the improvement comprising:

removing a portion of the rinsing medium from the rinsed, sensitized surface as the article is conveyed into the coating station to form a rinse medium film of uniform thickness on the surface of the article while avoiding the formation of a wave of the coat-

ing composition upstream of the coating station to provide a coating having uniform optical properties.

5. The method according to claim 4 wherein the coating composition is applied in a fan-shaped spray toward the surface of the article and including the step of:

shielding succeeding portions of the surface conveyed into the coating station from a minor portion of the fan-shaped spray upstream of the coating station to eliminate finger-like flows of the coating composition upstream of the coating station wherein elimination of the finger-like flows prevents subsequent formation of streaks in the coating.

6. The method according to claim 5 wherein about ¼ of an inch of the fan-shaped spray is shielded from succeeding portions of the surface conveyed into the coating station.

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EDWARD G. WHITBY, Primary Examiner

U.S. Cl. X.R.

117—33.3, 64, 124 B, 130 E; 118—73

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,761,305 Dated September 25, 1973

Inventor(s) Helmut Franz

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 16, line 52, in the third line of Claim 2, after the word "article" insert the word --and--.

Signed and sealed this 25th day of December 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents

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