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COATING SURFACES
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FIG. 1

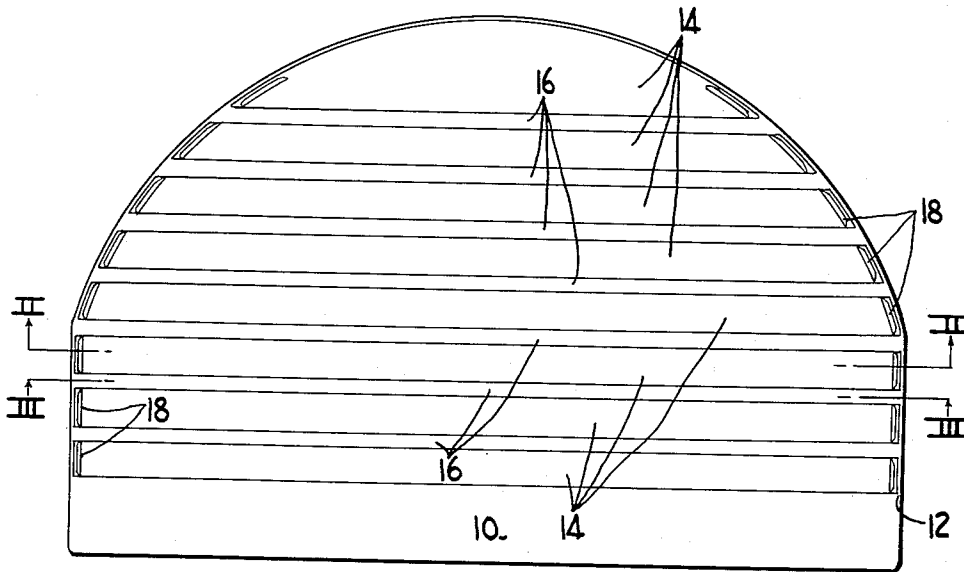


FIG. 2

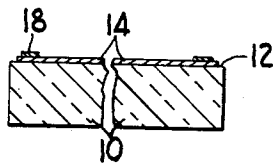


FIG. 4

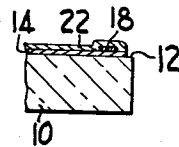


FIG. 3

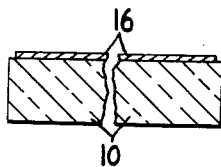
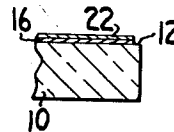


FIG. 5



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2,971,867

COATING SURFACES

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This application relates to improvements in coating surfaces, and especially relates to articles provided with transparent electroconductive coatings in the form of spaced stripes. Such articles are useful for many purposes such as where the spaced stripes are used as horizontal and/or vertical deflection plates to provide electron beam deflection control for flat cathode ray tubes such as the type described in the article entitled "Wall-Mounted TV Picture Tubes Take Giant Step," beginning at page 7 of the February 1955 issue of "Electronics," published by McGraw-Hill, and for transparent panels mounted in front of vehicle glazing closures in which televised pictures, radar screen images or other data are superimposed on the surface of the transparent panel without substantially impairing the transparency through the panel, such as the instrument described in the second paragraph of the article entitled "Cockpit Simplicity-Coming," beginning at page 13 of the February 1955 issue of "Western Aviation," published by the Occidental Publishing Company, 4328 Sunset Boulevard, Los Angeles 29, California.

Initially, it was proposed to produce such articles by applying stripes of a transparent, colorless electroconductive coating material such as the metal oxides of tin, indium, cadmium or mixtures containing same or evaporated or sputtered metals onto a partially masked base and subsequently removing the mask. However, articles containing electroconductive striped coatings separated by uncoated regions are objectionable from the standpoint of optics because lines delineating the conductive stripes from the uncoated stripes annoy observers looking through such an article.

According to the present invention, this annoyance is overcome by providing glass sheets with continuous coatings comprising stripes of colorless, transparent, electroconductive material separated by stripes of a non-electroconductive or highly resistant transparent, colorless material of substantially the same appearance by transmission and reflection as that of the electroconductive stripes. The non-conductive stripes were chosen from materials capable of withstanding voltages in excess of 10,000 volts for a 1/4 inch width.

The present invention will be better understood with reference to the accompanying drawings wherein like reference characters are applied throughout to refer to identical structural elements.

In the drawings forming part of the present disclosure, Figure 1 is a plan view of an article coated in accordance to the teaching of the present invention suitable for use as a face plate for a flat cathode ray tube;

Figure 2 is a fragmentary cross sectional view taken along the lines II—II of Figure 1;

Figure 3 is another fragmentary cross-sectional view taken along the lines III—III of Figure 1; and

Figures 4 and 5 are fragmentary cross-sectional views similar to those of Figures 2 and 3, respectively, of another embodiment of the present invention.

A particular embodiment suitable for use in a flat cathode ray tube comprises a glass base 10 terminating in a

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peripheral margin 12. The margin 12 serves to attach the base through a marginal spacer to another glass body, such as a flat sheet containing a transparent electroconductive coating and an electroluminescent coating activated by electron impingement. If the electroluminescent coating is transparent, viewing is possible through a data imparting panel.

The surface of glass base 10 is partially coated with stripes 14 of a colorless, transparent, electroconductive material such as tin oxide and, additional stripes 16 of a non-conductive, colorless, transparent material such as antimony oxide or titanium oxide having substantially the same appearance by transmission and reflection as that of stripes 14, extending between the stripes 14 in abutting relation to adjacent conductive stripes.

The transparent electroconductive stripes have a surface resistivity on the order of 30 to 1000 ohms per square, whereas the non-conductive separator stripes 16 have a surface resistivity on the order of 100 to 1000 megohms per unit square and over. The term "surface resistivity" is a measurement of the resistivity of a square unit area of film covering a portion of the glass sheet surface.

At the opposite extremities of the conductive stripes 14, bus bars 18 are located in electrical contact therewith. These bus bars are preferably of ceramic silver material and of dimensions 1/8 inch wide by .001 inch thick, although thicknesses up to .005 inch are also desirable. The bus bars are tapered at their extremities to a width of 1/16 inch.

The coated regions terminate 5/8 inch short of the outer edge of the peripheral margin 12 to provide space 1/8 inch wide for a frit fillet utilized in attaching the margin 12 to another body of glass or metal 1/2 inch thick.

In order for the lines of demarcation between the electroconductive and the non-conductive stripes to be invisible to the human eye, it is necessary that the conductive stripes have the same optical transmission and reflection properties as the non-conductive stripes. These properties depend upon the relative thickness, the absorption coefficient and the index of refraction of the materials used to provide the transparent coating stripes. Tin oxide coatings have an index of 2.0. Antimony oxide has an index slightly in excess of that of tin oxide, ranging between 2.087 and 2.35. The index of refraction of titanium oxide coatings ranges from 2.493 to 2.903. With films consisting essentially of stripes of tin oxide separated by stripes of antimony oxide, the stripes can have substantially the same actual thickness without causing annoyance due to observability of the lines of demarcation between stripes.

Where reflection at the coated surface presents a problem, the surface reflection can be minimized by superimposing a continuous film 22 of a colorless transparent coating material having an index of refraction less than those of the materials comprising the stripes on the coating of alternating stripes. Materials having relatively low refractive indices such as silica and magnesium fluoride are especially suitable for such overcoating. Articles with such overcoating are shown in Figures 4 and 5.

Example I

The following technique has been employed effectively in producing articles such as shown in Figures 1 through 3. The glass was first cleaned and then immersed in a mixture of carbon tetrachloride, acetone and silicon tetrachloride, such as one containing 94.2 percent by volume CCl₄, 4.9 percent by volume CO(CH₃)₂ and 0.9 percent by volume SiCl₄. After immersion, the glass was withdrawn immediately and allowed to dry. A powdery residue which formed on the glass was wiped off with a dry cloth. This operation was repeated where necessary to prepare the glass for further processing.

A silk or metal stencil screen having a desired pattern was aligned with the glass sheet so that the areas not to be coated with electroconductive transparent coating were aligned with the interstices of the screen. A masking paste was applied through the stencil screen.

A suitable masking paste so used contains 50 percent by weight of finely divided (2.5 micron average diameter, for example) titanium dioxide in an oil vehicle such as a pine oil mix, for example, one sold commercially as Vitro 56-G. The two ingredients were mixed thoroughly until a smooth masking paste resulted. This paste was then applied through the openings in the stencil screen.

The partially masked glass sheet was then heated between 400° F. and the temperatures at which the glass base becomes molten. A preferable temperature was obtained by heating a glass sample 8 inches by 10 inches by 1/4 inch in a furnace maintained at approximately 1200° F. for four minutes. The heated sample was sprayed with 10 cubic centimeters of a tin oxide film forming composition in a time of from 3 to 5 seconds. The spray composition consisted essentially of anhydrous SnCl_4 dissolved in methanol and distilled water and containing phenyl hydrazine hydrochloride and a small amount of HF. The film resulting on the unmasked areas was colorless and had a surface resistivity of about 1000 ohms per square.

The spray composition was prepared as follows:

400 grams of dioctyl sodium sulfosuccinate were dissolved in 2 liters of methanol and 2 liters of distilled water were added. 230 cc. of the resulting solution was mixed with 1765 cc. of distilled water, 565 cc. of methanol and 160 grams of phenylhydrazine hydrochloride. After mixing, 2200 cc. of anhydrous SnCl_4 was added. Four grams of 48% HF were added to 100 cc. of the solution resulting after the addition of SnCl_4 . The resulting solution was diluted by dissolving it in methyl alcohol in the ratio of one part solution to eleven parts by volume of methyl alcohol. The diluted solution was used for spraying.

After the glass cooled, it was subjected to a water rinse to wash off the masking paste. Then bus bars were applied to the ends of the conducting stripes by applying a ceramic silver through a silk screen stencil. Care should be taken to insure that the thickness of the bus bars does not exceed .005 inch and preferably that the bus bar thickness is on the order of .001 inch. After screening, the bus bars were dried at 250° F. to 300° F. for one hour. The coated stripes of the glass sheet were then masked with a stencil screen having a pattern the reverse of the screen previously used. Thus, the coated stripes and bus bars were covered with masking paste and the uncoated stripes exposed for a second filming.

The partially coated glass sheet was then dried as before. The sample was then heated to about 1200° F., which fired the bus bars, removed from the furnace and immediately sprayed with 10 cc. of a solution of SbCl_5 in methanol. This solution preferably contains 5 percent by volume of the antimony pentachloride. The glass sheet was sprayed for from 3 to 5 seconds. The resulting film was clear and colorless and had a surface resistivity in excess of 1000 megohms.

After the filmed glass sheet was permitted to cool, the masking paste was washed off by a water rinse. The resulting articles were clear and colorless and did not have observable boundary lines between the high conductive and low conductive areas.

It is understood that various techniques may be employed for applying the stripes of coating material, such as coating the entire sheet with a metal oxide and removing stripes of coating. For example, with tin oxide films, local applications of pulverized zinc and HCl may be employed to remove portions of the film.

Various transparent, electroconductive, colorless metal

oxide films can be utilized in lieu of tin oxide, such as indium oxide, cadmium oxide and mixtures of various metal oxides. Furthermore, thin coatings of metals such as gold and other well known metals which are susceptible of producing thin electroconductive films on glass by vacuum evaporation, cathode sputtering, etc., may also be employed.

Non-conductive or high resistance stripes of coating may be composed of antimony oxide, titanium dioxide, "poisoned" tin oxide such as mixtures of tin oxide and zinc oxide, mixtures of tin oxide with boric oxide, mixtures of tin oxide and cobalt oxide, as well as zinc oxide and silicon dioxide.

Metals which are known to produce iridized metal oxide films by heating the glass to a temperature in the neighborhood of sufficiently below its softening point to avoid distortion and contacting it for a few seconds with a metal compound in fluid form, that is, an atomized solution or the vapor of the compound of metals such as zinc, cadmium, aluminum, indium, thallium, silicon, titanium, germanium, zirconium, tin, lead, thorium, columbium, antimony and tantalum, all of which produce substantially colorless oxide films.

For the production of the thin metal oxide films which can be used for one of the striped components depending upon the conductivity of the film formed, any compound of one of the above recited metals which is or can be in fluid form, that is, the vapor or atomized solution of the compound, can be used. Both inorganic and organic compounds are suitable for the most part. Examples of some salts of inorganic acids include the chlorides, which are generally most suitable, the iodides, bromides, fluorides, sulfates, nitrates, and the like. Organic salts and compounds of the recited metals are generally not as easily available but such as are available can be used provided they are dissolved or diluted if not with water, then with a solvent such as an alcohol, toluene, benzene, or other miscible liquid. Such compounds may include open chain compounds such as acetates, lactates, oleates, oxalates, salicylates, stearates, tartrates, and the like, and aromatic compounds such as the benzoates, phenolates, phenolsulfonates, and so forth. Some organic compounds of tin, which are particularly suitable are dibutyl tin diacetate, dibutyl tin dilaureate, dibutyl tin oxide, dibutyl diphenyl tin, dilauryl tin dichloride, dibutyl tin dichloride, diphenyl tin dichloride, dibutyl tin ethylate, tetraphenyl tin, tetrabutyl tin, dibutyl tin diethylate, and so forth.

To produce such thin metal oxide films, preferably a solution of the metal compound is atomized and sprayed as a fine mist against the heated glass. Substantially the same result is obtained by evaporating the metal compounds, if volatile without the composition, and contacting the surface of the hot glass with the resultant fumes. Upon coming into contact with the hot glass, the metal salt or compound is converted to the corresponding metal oxide which adheres with great avidity and in a very thin uniform layer to the surface of the glass.

Suitable adherent metal oxide films or coatings may also be produced by evaporating the metal oxide adjacent the cool glass surface in a vacuum and condensing the vapor on the glass or by evaporating the metal in a like manner and thereafter heating the metal coated glass in air or in air enriched with oxygen to convert to its oxide.

A masking technique especially useful for stripe-coating sheets shaped by pressing to include a flange at their margin for use as a marginal spacer as an integral structural component may involve the use of masking tape rather than stencils, especially when the sheets are sharply bent.

Of all the possibilities recited, the optimum results are obtained when all the stripes are produced by the

masking technique of Example I and the conductive stripes 14 are composed of tin oxide and the non-conductive or highly resistant stripes 16 are of antimony oxide or tin oxide poisoned by the inclusion of other metal oxides in combination therewith in sufficient quantity to increase the resistivity appreciably.

The description of a particular embodiment of the present invention has been for purposes of illustration rather than limitation. Reference to the latter may be obtained from studying the accompanying claims.

What is claimed is:

1. In a transparent electroconductive article comprising a transparent base of non-conductive material, spaced stripes of transparent, substantially colorless electroconductive material fixed to the base and stripes of transparent, substantially colorless substantially non-electroconductive material fixed to the base and extending between adjacent stripes of transparent electroconductive material, the improvement comprising stripes of substantially non-conductive material of sufficient width and thickness to provide a continuous coating of uniform light transmission wherein interfaces between the electroconductive and non-conductive stripes are not noticeable to the naked eye.
2. The article according to claim 1, wherein the base is glass.
3. The article according to claim 1, wherein the transparent electroconductive material comprises a metal oxide taken from the class consisting of tin oxide, indium oxide and cadmium oxide.
4. The article according to claim 1, wherein the transparent substantially non-electroconductive material comprises a metal oxide taken from the class consisting of antimony oxide, titanium dioxide, silicon dioxide, zinc oxide and mixtures of metal oxides taken from the class consisting of tin oxide plus zinc oxide, tin oxide plus boric oxide, tin oxide plus cobalt oxide and tin oxide plus titanium dioxide.
5. The article according to claim 1, including a continuous coating, having an index of refraction less than those of either of the transparent materials comprising the stripes superimposed on the stripes, in permanently bonded relation thereto.
6. In a transparent electroconductive article comprising a transparent glass base, spaced stripes of transparent, substantially colorless electroconductive metal oxide fixed to the base, and stripes of transparent, substantially colorless substantially non-electroconductive metal oxide fixed to the base and extending between adjacent stripes of electroconductive metal oxide the improvement comprising stripes of substantially non-conductive metal oxide of sufficient width and thickness to provide a continuous coating of uniform light transmission wherein interfaces between the electroconductive and non-conductive stripes are not noticeable to the naked eye.
7. A transparent electroconductive article as in claim 6, including a continuous coating, having an index of refraction less than those of either of the transparent materials comprising the stripes, superimposed on the stripes in permanently bonded relation thereto.
8. In a transparent electroconductive article comprising a transparent glass base and a substantially continuous, transparent, substantially colorless coating on the base, said coating comprising alternating stripes of a transparent substantially colorless highly electroconductive material and stripes of a transparent substantially colorless less electroconductive material, the improvement wherein the relative thickness of the strips in such that the interfaces between stripes are not noticeable to the naked eye.
9. A transparent electroconductive article as in claim 8, including a continuous coating, having an index of refraction less than those of either of the transparent materials comprising the stripes, superimposed on the stripes in permanently bonded relation thereto.

10. In a transparent electroconductive article comprising a glass base, a substantially continuous transparent coating in the form of elongated transparent, substantially colorless stripes arranged in side by side relation to each other, adjacent stripes being composed of different transparent materials having significantly different electroconductive properties, the improvement wherein the thickness of adjacent stripes is such that they have substantially identical appearance by transmission and reflection, whereby interfaces between adjacent dissimilar stripes are invisible to the naked eye.

11. A transparent electroconductive article as in claim 10, including a continuous coating, having an index of refraction less than those of either of the transparent materials comprising the stripes, superimposed on the stripes in permanently bonded relation thereto.

12. In a transparent electroconductive article comprising a glass base, a substantially continuous transparent, substantially colorless coating in the form of alternate transparent, substantially colorless stripes of tin oxide and a transparent material having significantly less electroconductivity than that of tin oxide, the improvement wherein the thickness of adjacent stripes is such that they have substantially identical appearance by transmission and reflection, whereby interfaces between adjacent dissimilar stripes are invisible to the naked eye.

13. A transparent electroconductive article as in claim 12, including a continuous coating, having an index of refraction less than those of either of the transparent materials comprising the stripes, superimposed on the stripes in permanently bonded relation thereto.

14. An article according to claim 12, wherein the transparent material having different electroconductivity from that of tin oxide contains antimony oxide.

15. An article according to claim 12, wherein the transparent material having different electroconductivity from that of tin oxide contains titanium oxide.

16. An article according to claim 12, wherein the transparent material having different electroconductivity from that of tin oxide contains a mixture of tin oxide and another metal oxide.

17. A method of providing on a surface of a transparent base a continuous coating of stripes of alternating materials of significantly different conductivity but of substantially identical appearance by transmission and reflection comprising coating a first transparent material in the form of spaced stripes to a surface to be coated, masking the coated stripes only, applying a second transparent material having significantly different electroconductivity from that of the first material to the partially coated transparent base in an amount sufficient to match the appearance of the stripes of the first transparent material by transmission and reflection and removing the masking material.

18. The method according to claim 17, wherein the stripes of the first transparent material are applied by first masking the portions of the sheet to be coated with the second transparent material, then producing a coating on the partially masked base and removing the masking.

19. The method according to claim 17, wherein the masking material used comprises a mixture of finely divided titanium dioxide in an oil vehicle.

20. In a transparent electroconductive article comprising a transparent base and a substantially continuous transparent, substantially colorless coating on the base, said coating comprising alternating stripes of a highly electroconductive material and stripes of a less electroconductive material, the improvement wherein the relative thickness of the stripes is such that the interfaces between stripes are not noticeable to the naked eye.

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