Jan. 22, 1963 R. J. BLAZEK 3,074,816

LIGHT-TRANSMITTING, ELECTRICALLY CONDUCTING ELEMENT

Filed Oct. 28, 1960

FIG. 1.

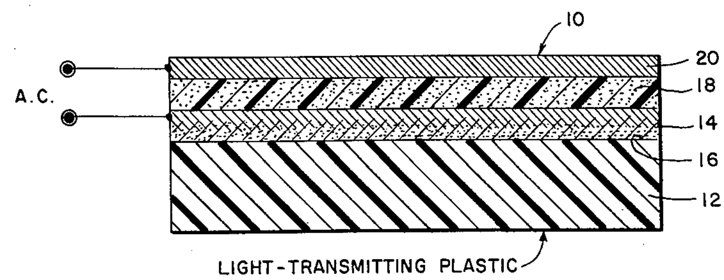


FIG. 2.

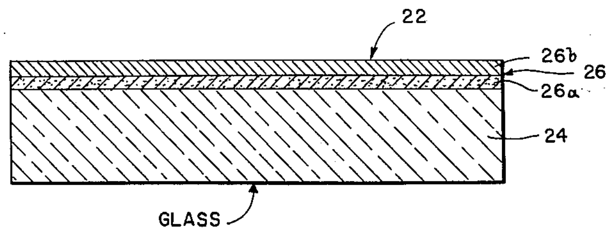


FIG. 3.

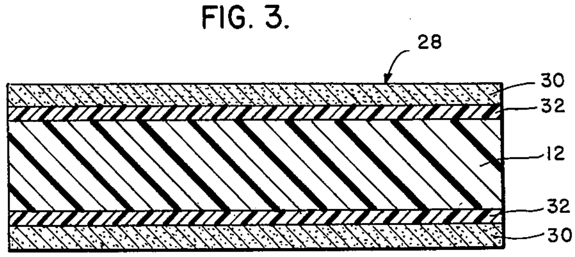
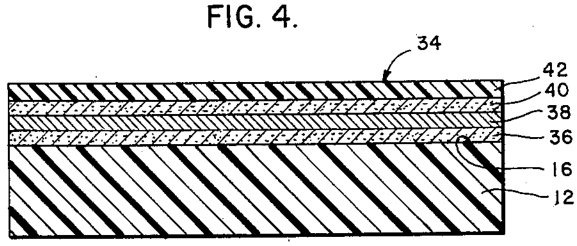


FIG. 4.



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LIGHT-TRANSMITTING, ELECTRICALLY CONDUCTING ELEMENT

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10 Claims. (Cl. 117—211)

This invention relates to light-transmitting, electrically conducting elements and, more particularly, to such elements which have both a high degree of transparency and a relatively high electrical conductivity.

Electroluminescent devices are well known and usually comprise spaced electrodes having phosphor and dielectric material included therebetween. When the phosphor is placed within the influence of an alternating electric field, it serves to convert the electric field into visible radiations. In order to pass the radiations which are generated, at least one of the spaced electrodes which bounds the phosphor-dielectric should be light transmitting. Electroluminescent devices are usually fabricated on an inorganic foundation or substrate and a light-transmitting, tin oxide electrode layer is normally formed directly on the inorganic substrate.

In the case the electroluminescent device is to be made flexible in nature, or is required to be very resistant to shocks and impacts, it is desirable to fabricate the supporting foundation or substrate of light-transmitting plastic material. The usual tin oxide electrode layers cannot be placed on such plastic material, since the temperatures of formation which are required to deposit such tin oxide electrodes would decompose the plastic. Because of this, it has been necessary to develop alternative light-transmitting electrode structures.

Light-transmitting electrode structures which have been used with plastic substrates include a fiberglass mesh which has been previously coated with tin oxide. Metal mesh electrodes have also been used, wherein the generated light passes from the device through the interstices of the mesh. In still another construction, gold has been vacuum-deposited or sputtered onto the plastic foundation as a continuous layer which is sufficiently thin to enable some of the generated light to be transmitted therethrough. Troubles have been encountered with such gold electrodes, however, in that if a sufficient amount of gold is deposited to achieve a desired value of conductivity, the light-transmitting characteristics of the coating suffer. It has been disclosed in U.S. Patent No. 2,852,415, dated September 16, 1958, to improve a vacuum-deposited, light-transmitting, metallic coating by incorporating therein selected amounts of selected dielectric materials. Of these additive dielectric materials, a small addition of ferric oxide to a gold coating has been found to be the best. Even with such ferric-oxide-modified gold conducting coatings, however, the light transmission has not been as good as desired.

It is the general object of this invention to avoid and overcome the foregoing and other difficulties of and objections to prior-art practices by the provision of a light-transmitting, electrically conducting element which has both a high degree of transparency and a relatively high electrical conductivity.

It is another object to provide compositions for light-transmitting, electrically conducting elements having improved performance characteristics.

It is a further object to provide light-transmitting, electrically conducting elements which incorporate plastic substrates and which have improved performance characteristics.

The aforesaid objects of the invention, and other objects which will become apparent as the description proceeds, are achieved by providing on a light-transmitting substrate, an improved light-transmitting, electrically conducting coating or film which consists essentially of gold and either tungsten oxide or a mixture of tungsten oxide and iron oxide. There are provided permissible and optimum proportions of tungsten oxide to gold, as well as permissible and optimum proportions of tungsten and iron oxide to gold, if iron oxide is to be included in the coating film.

For a better understanding of the invention, reference should be had to the accompanying drawings wherein:

FIG. 1 is a sectional elevational view of an electroluminescent device which utilizes the improved light-transmitting, electrically conducting element of this invention;

FIG. 2 is a sectional elevational view of an alternative embodiment of the light-transmitting, electrically conducting element per se, wherein the electrode film is formed as distinct film layers;

FIG. 3 is a sectional elevational view of another alternative embodiment for the element per se, wherein the electrode films are somewhat modified and are coated onto both sides of a plastic foundation by means of intermediate, bonding polymer layers;

FIG. 4 is still another alternative embodiment for the element per se, wherein the electrode film is formed as a plurality of film layers.

The improved light-transmitting, electrically conducting element of this invention has utility with any device wherein such an element is required, an example being plastic, polarized goggles which are required to be electrically heated, in order to dispel fogging. The invention has particular utility with respect to electroluminescent devices, however, and hence it has been so illustrated and will be so described.

With specific reference to the form of the invention illustrated in the drawings, the numeral **10** in FIG. 1 indicates generally an electroluminescent cell which comprises a light-transmitting, plastic foundation or substrate **12** with a light-transmitting and electrically conducting first electrode layer or film **14** carried on a smooth surface **16** of substrate **12**. A phosphor-dielectric layer **18** is carried over the film **14** and a second electrode **20** is carried over the phosphor-dielectric layer **18**. An alternating electric potential is adapted to be applied across the electrodes **14** and **20**, in order to energize the device to light emission. The general construction of the electroluminescent device **10** is conventional. As an example, the phosphor-dielectric layer **18** has a thickness of 2 mils and is formed of finely divided, copper-activated, zinc sulfide electroluminescent phosphor embedded in an equal part by weight of a light-transmitting dielectric plastic, such as polyvinyl chloride. The electrode **20** is formed of vacuum-metallized aluminum.

The light transmitting element of this invention is represented by the plastic substrate **12** and the electrode film **14**. The substrate **12** can be formed of any suitable light-transmitting plastic material such as polymonochlorotrifluoroethylene and the flexibility of the electroluminescent cell **10** is primarily determined by the flexibility of this substrate **12**. As an example, the substrate has a thickness of 10 mils. Any suitable light-transmitting plastic can be used as the substrate, additional examples being acrylates, vinyls, polyethylene, polypropylene or polystyrene.

The electrode film **14** is shown in FIG. 1 in its preferred form. This film consists essentially of gold and either tungsten oxide or a mixture of tungsten oxide and iron oxide. The surface of this film **14**, which is adjacent the smooth surface **16** of the substrate **12**, is rich in tungsten oxide or a mixture of tungsten oxide and iron oxide. The uppermost or other surface of the film 14 is rich in gold.

The tungsten oxide and total metallic oxide portion of the film 14 constitute from 1% to 20% by weight of the gold portion of the film and if iron oxide is included in the film, it should constitute less than 10% by weight of the gold portion of the film. In the preferred composition, ferric oxide and tungsten oxide are mixed and each constitutes about 4% by weight of the gold portion of the film 14. If only tungsten oxide is to be used as the additive dielectric material, the preferred addition is about 8% by weight of the gold in the film. If less than 1% by weight of additive dielectric material is used in the film, the improved performance characteristics for the film are not realized. If more than 20% by weight of additive dielectric material is used, the formed film has an appreciable gray body color which cuts down on transmitted light. Tungsten trioxide is the preferred additive tungsten oxide. The dioxide can be used, however, as can mixtures of the trioxide and the dioxide. In addition, oxides of iron other than ferric oxide can be used. The term tungsten oxide and iron oxide as used herein are intended to be generic to any single oxide or mixture of such oxides.

In forming the electrode film 14 on the smooth surface 16 of the foundation 12, gold and tungsten oxide are placed into an electrically heated boat. Preferably, iron oxide is also included in the boat. The boat is placed into a conventional vacuum-deposition apparatus and the smooth surface 16 of the substrate 12 is placed proximate the electrically heated boat. When the apparatus is evacuated and the boat is heated, the iron and tungsten oxides will tend to deposit first. The initial vacuum deposition of the gold will be somewhat limited. After substantially all of the iron and tungsten oxides have been volatilized from the boat, the remainder of the gold will be volatilized. There will be consideralbe mixing of the deposited materials at their interface, however, so that the ultimate film will be graded with respect to its composition, with the first-deposited surface being rich in the oxides and the last-deposited surface being rich in gold. The vacuum-depostiion apparatus and boats are conventional and are not shown.

As a specific example for forming the electrode film 14, 0.003 gram of tungsten oxide and 0.003 gram of iron oxide, both in finely divided form, are placed into a tungsten deposition boat with 0.080 gram of gold. The boat has dimensions of 5.4 cm. by 1.0 cm. and a depth of 0.15 cm. and is adapted to be electrically heated. The smooth surface 16 of the substrate 12 is placed 30 cm. from this boat and the system is evacuated to a pressure of 0.05 micron mercury. The area of the surface 16 of substrate 12 is 320 sq. cm. and it is centrally disposed directly over the boat. The boat is rapidly heated to a temperature of 1200° C., at which point the iron and tungsten oxides will volatilize, along with a limited amount of the gold. Heating is continued at this indictaed temperature and mantained until the gold is substantially volatilized. The thickness of the deposited film will vary, depending upon the desired conductivity and light-transmission characteristics. As a general rule, however, the thickness of the gold, if it were to be deposited by itself, would be in the order of from 50 to 200 Angstroms and the thickness of the iron and tungsten oxides, if deposited by themselves, would be in the order of from 10 to 50 Angstroms. With films deposited in accordance with the foregoing specific example, the resistivity will be approximately 15 to 20 ohms per square and the light transmission of the films per se will be greater than 70%.

If it is desired to increase the resistivity of the electrode film, less material is deposited and, of course, the transmission characteristics will be improved. Such films have use in polarized goggles, as indicated hereinbefore.

In FIG. 2 is shown an alternative embodiment 22 for the light-transmitting element 10, as shown in FIG. 1. This alternative embodiment 22 utilizes a glass substrate 24. The electrode film 26 which is carried on the substrate 24 is quite similar to the film 14, as shown in FIG. 1, except that the gold and metallic oxide or oxides are deposited as discrete films. In forming the film 26, the iron and tungsten oxides are placed into one deposition boat and the gold is placed into a separate deposition boat. The boat containing the tungsten oxide or iron and tungsten oxides is heated first, in order to deposit these oxides completely before any gold is vacuum deposited. Thereafter the gold-containing boat is heated to vacuum deposit the gold onto the previously deposited oxide or oxides. This will form a relatively sharp line of delineation between the oxide film portion 26*a* and the gold film portion 26*b*.

In FIG. 3 is shown another alterntaive embodiment 28 wherein the substrate 12 is plastic as in the embodiment 10, shown in FIG. 1. Separate films 30 are deposited on oppositely disposed faces of the substrate 12. The electrode films 30 are also modified in that the gold and additive oxides are generlaly uniformly mixed. In depositing such films, the tungsten oxide or mixture of tungsten oxide and iron oxide are placed into one vacuum-deposition boat and the gold is placed into another vacuum-deposition boat. These boats are simultaneously heated in such manner that the metallic oxides and gold will volatilize simultaneously, thereby forming a generally uniform deposited mixture of gold and metallic oxide. The proportions of oxide to gold in each of the films 30 are as described in the previous embodiments. The embodiment 28 is also modified somewhat in that additional light-transmitting, polymer layers 32 are provided between the smooth, oppositely disposed surfaces of the substrate 12 and the adhering films 30. Such additional polymer layers are described in copending application S.N. 65,690, filed concurrently herewith, titled "Electroluminescent Device, Conducting Element and Method," by Robert J. Blazek, and owned by the present assignee.

In FIG. 4 is shown yet another alternative embodiment for a light-transmitting, electrically conducting element 34, wherein the metallic oxide or oxides, as specified hereinbefore, are first deposited to form a layer 36 which is adjacent the smooth surface 16 of the substrate 12. Thereafter, a gold film 38 is deposited onto the first-deposited metallic oxide film 36 and an additional metallic oxide film 40, similar to those specified hereinbefore, is deposited onto the gold film 38. To prevent abrasion, an additional thin layer 42 of light-transmitting plastic, such as polyvinyl chloride, is provided over the oxide film 40. In depositing the films 36, 38 and 40, two vacuum-deposition boats are used and the temperatures of these boats are controlled so as to deposit the multiple films. The tungsten oxide in the first film 36 constitutes at least 1% by weight of the gold which forms the second deposited film 38. The tungsten oxide in the third-deposited metallic oxide film 40 also constitutes at least 1% by weight of the gold which is deposited to form the film 38. The combined deposited oxide films 36 and 40 constitute from 2% to 20% by weight of the gold film 38, with the total iron oxide in these films 36 and 40 constituting less than 10% by weight of the gold film 38. One advantage of such a construction is that the outermost film of metallic oxide slightly improves the light transmission characteristics of the composite film.

The best previously known, light-transmitting, electrically conducting coatings which could be deposited on plastic have been those formed of gold, as modified with a small addition of iron oxide. When the tungsten oxide is used to replace the iron oxide in the film, the transmission is improved by approximately 3 to 4%, with the conductivity maintained the same. Alternatively, if the same transmission is to be achieved, the resistivity of the tungsten-oxide-modified gold film, as expressed in ohms per square, is approximately half that of the iron-oxide-modified gold films. As representative values, if the transmissions of both the tungsten-oxide-modified gold film and the iron-oxide-modified gold film are to be maintained at about 67%, the resistivity of the tungsten-oxide-modified film will be 11 ohms per square and the resistivity of the iron-oxide-modified film will be approximately 23 ohms per square.

The preferred conducting film, which will provide best transmission and conductance characteristics, is that in which mixed tungsten and iron oxides, as specified hereinbefore, are used. The transmission of the combined oxide-modified coatings is approximately 8% greater than the iron-oxide-modified coating, when the resistivity of the films, as expressed in ohms per square, is approximately the same.

The mechanism by which the added dielectric material serves to enhance the conductivity of the conducting, vacuum-deposited gold films is not clearly understood. Apparently when the gold is deposited onto or with the dielectric oxide materials as specified, the individual gold particles display a minimum of aggregations, thereby increasing the conductivity which is obtained for any given amount of deposited gold. If a similar amount of gold, per se, were to be deposited, the conductivity would not be as good. If a sufficient amount of gold, per se, were to be deposited to achieve a conductivity of 15 to 20 ohms per square, for example, the transmission through such a deposited conducting film would be relatively poor.

The foregoing embodiments for the light-transmitting, electrically conducting articles, as shown in FIGS. 1–4 and as described hereinbefore, are subject to considerable modification. As an example, any of the present electrode film embodiments, as specified, can be placed on one or both sides of a light-transmitting substrate. This is true for both glass and plastic substrates. Such constructions have utility for forming multiple-layer electroluminescent devices. Also, any of the embodiments which utilize a plastic substrate can incorporate intermediate polymer layers, in order to improve the adherence of the conducting films to the substrate. In such case, the polymer layers essentially form a part of the light-transmitting substrate. Further, any of the embodiments can be provided with an exterior film formed of the dielectric metallic oxide, such as the film 40 as shown in FIG. 4.

As a further alternative construction, additional thin films of material can be used to grade the refractive index between the exterior film surface and the atmosphere. An example of such an additional film is magnesium fluoride which has a relatively low index of refraction. Another example is a suitable plastic film, such as light-transmitting film of polyvinyl chloride. As still another alternative, the conducting films, as specified hereinbefore, can be deposited by sputtering, although vacuum deposition is preferred because of the ease of control.

It will be recognized that the objects of the invention have been achieved by providing an improved light-transmitting, electrically conducting element which has both a high degree of transparency and good electrical conductivity. Compositions for such elements have been provided and these elements can be deposited onto plastic substrates.

While best embodiments of the invention have been illustrated and described hereinbefore, it is to be particularly understood that the invention is not limited thereto or thereby.

I claim:

1. An electrically conducting light-transmitting article comprising, a light-transmitting electrically insulating substrate having a smooth surface, an electrically conducting light-transmitting continuous film supported on the smooth surface of said substrate, said film consisting essentially of gold and one additive material of the group consisting of tungsten oxide and a mixture of tungsten oxide and iron oxide, the total additive oxide portion of said film constituting from 1% to 20% by weight of the gold portion of said film, the tungsten oxide portion of said film constituting at least 1% by weight of the gold portion of said film, and iron oxide included in said film constituting less than 10% by weight of the gold portion of said film.

2. An electrically conducting light-transmitting article comprising, a light-transmitting electrically insulating plastic substrate having a smooth surface, an electrically conducting light-transmitting continuous film supported on the smooth surface of said substrate, said film consisting essentially of gold and a mixture of tungsten oxide and iron oxide, the total additive oxide portion of said film constituting from 1% to 20% by weight of the gold portion of said film, the tungsten oxide portion of said film constituting at least 1% by weight of the gold portion of said film, and the iron oxide included in said film constituting less than 10% by weight of the gold portion of said film.

3. An electrically conducting light-transmitting article comprising, a light-transmitting electrically insulating plastic substrate having a smooth surface, an electrically conducting light-transmitting continuous film supported on the smooth surface of said substrate, said film consisting essentially of gold and tungsten oxide, and the tungsten oxide portion of said film constituting from 1% to 20% by weight of the gold portion of said film.

4. An electrically conducting light-transmitting article comprising, a light-transmitting electrically insulating plastic substrate having a smooth surface, an electrically conducting light-transmitting continuous film supported on the smooth surface of said substrate, said film consisting essentially of gold and a mixture of tungsten trioxide and ferric oxide, the total additive oxide portion of said film constituting from 1% to 20% by weight of the gold portion of said film, the tungsten trioxide portion of said film constituting at least 1% by weight of the gold portion of said film, and the ferric oxide included in said film constituting less than 10% by weight of the gold portion of said film.

5. An electrically conducting light-transmitting article comprising, a light-transmitting electrically insulating plastic substrate having a smooth surface, an electrically conducting light-transmitting continuous film supported on the smooth surface of said substrate, said film consisting essentially of a mixture of gold and one additive material of the group consisting of tungsten oxide and a mixture of tungsten oxide and iron oxide, the total additive oxide portion of said film constituting from 1% to 20% by weight of the gold portion of said film, the tungsten oxide portion of said film constituting at least 1% by weight of the gold portion of said film, and any iron oxide included in said film constituting less than 10% by weight of the gold portion of said film.

6. An electrically conducting light-transmitting article comprising, a light-transmitting electrically insulating substrate having a smooth surface, electrically conducting light-transmitting continuous films supported on the smooth surface of said substrate, said films comprising, a first film adjacent the smooth surface of said substrate and selected from one material of the group consisting of tungsten oxide and a mixture of iron oxide and tungsten oxide, a second film overlying said first film and consisting essentially of gold, said first film constituting from 1% to 20% by weight of said second film, the tungsten oxide included in said first film constituting at least 1% by weight of said second film, and any iron oxide included in said first film constituting less than 10% by weight of said second film.

7. An electrically conducting light-transmitting article as specified in claim 6, wherein a third film overlies said second film, said third film selected from one material of the group consisting of tungsten oxide and a mixture of iron oxide and tungsten oxide, said third film constituting

at least 1% by weight of said second film, said first and third films constituting from 2% to 20% by weight of said second film, the tungsten oxide included in said third film constituting at least 1% by weight of said second film, and any iron oxide included in said first and third films constituting less than 10% by weight of said second film.

8. An electrically conducting light-transmitting article comprising, a light-transmitting electrically insulating substrate having oppositely disposed smooth surfaces, electrically conducting light-transmitting continuous films supported on the oppositely disposed smooth surfaces of said substrate, said films consisting essentially of gold and one additive material of the group consisting of tungsten oxide and a mixture of tungsten oxide and iron oxide, the total additive oxide portion of each of said films constituting from 1% to 20% by weight of the gold portion of said films, the tungsten oxide portion of each of said films constituting at least 1% by weight of the gold portion of each of said films, and any iron oxide included in each of said films constituting less than 10% by weight of the gold portion of said films.

9. An electrically conducting light-transmitting article comprising, a light-transmitting electrically insulating substrate having a smooth surface, an electrically conducting light-transmitting continuous film supported on the smooth surface of said substrate, said film consisting essentially of gold and one additive material of the group consisting of tungsten oxide and a mixture of tungsten oxide and iron oxide, the surface of said film adjacent the smooth surface of said substrate being rich in material of said group and the other surface of said film being rich in gold, the additive oxide portion of said film constituting from 1% to 20% by weight of the gold portion of said film, the tungsten oxide portion of said film constituting at least 1% by weight of the gold portion of said film, and any iron oxide included in said film constituting less than 10% by weight of the gold portion of said film.

10. An electrically conducting light-transmitting article as specified in claim 9, wherein an additional film overlies said metallic oxide-gold film, said additional film selected from one material of the group consisting of tungsten oxide and a mixture of iron and tungsten oxides, the tungsten oxide in said additional film constituting at least 1% by weight of the gold in said metallic oxide-gold film, the total material of said group included in said metallic oxide-gold film and said additional film constituting from 2% to 20% by weight of the gold in said metallic oxide-gold film, and any iron oxide included in said films constituting less than 10% by weight of the gold in said metallic oxide-gold film.

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