United States Patent

Maissel et al.

[15] **3,650,737**

[45] **Mar. 21, 1972**

[54] IMAGING METHOD USING PHOTOCONDUCTIVE ELEMENT HAVING A PROTECTIVE COATING

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[22] Filed: **Mar. 25, 1968**

[21] Appl. No.: **715,657**

[52] **U.S. Cl.** .....**96/1 PC,** 96/1.5, 117/215, 117/218, 204/192

[51] **Int. Cl.** **G03g 13/22,** G03g 5/02

[58] **Field of Search** 96/1.5, 1.6, 1.7, 1.8; 117/215, 218; 204/92

[56] **References Cited**

UNITED STATES PATENTS

2,993,806	7/1961	Fisher et al.	204/192 X
3,251,686	5/1966	Gundlach	96/1.5
3,287,243	11/1966	Ligenza	204/192
3,149,761	12/1968	Pennebaker	204/192 X
2,860,048	11/1958	Deubner	96/1.5
2,879,360	3/1959	Floyd	252/501 X
2,886,434	5/1959	Owens	96/1.5
3,317,315	5/1967	Nicoll et al.	96/1.5 X
3,397,086	8/1968	Bartfai	96/1.5 X
3,397,982	8/1968	Lane	96/1.5
3,484,237	12/1969	Shattuck et al.	96/1.5

OTHER PUBLICATIONS

Davidse, Theory & Practice of RF Sputtering, Vacuum, Vol. 17, No. 3, pp. 139–145 (1966).

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[57] **ABSTRACT**

A transparent, protective coating overlies a photoconductive layer and is integral therewith. The coating, which has a resistivity at least equal to the dark resistivity of the photoconductive material, has a thickness in the range of 50A–4000A. The coating is deposited on the photoconductive layer by sputtering through utilization of a high frequency alternating voltage whereby the properties of the coating may be controlled. When applying the high frequency alternating voltage, the power is kept low to produce a relatively high compressive stress of the coating. Controlling the power results in controlling the compressive stress of the coating. The temperature of the photoconductive layer may be maintained at a sufficiently low temperature so that the photoconductive layer retains its photoconductive properties.

2 Claims, 7 Drawing Figures

3 Sheets-Sheet 1

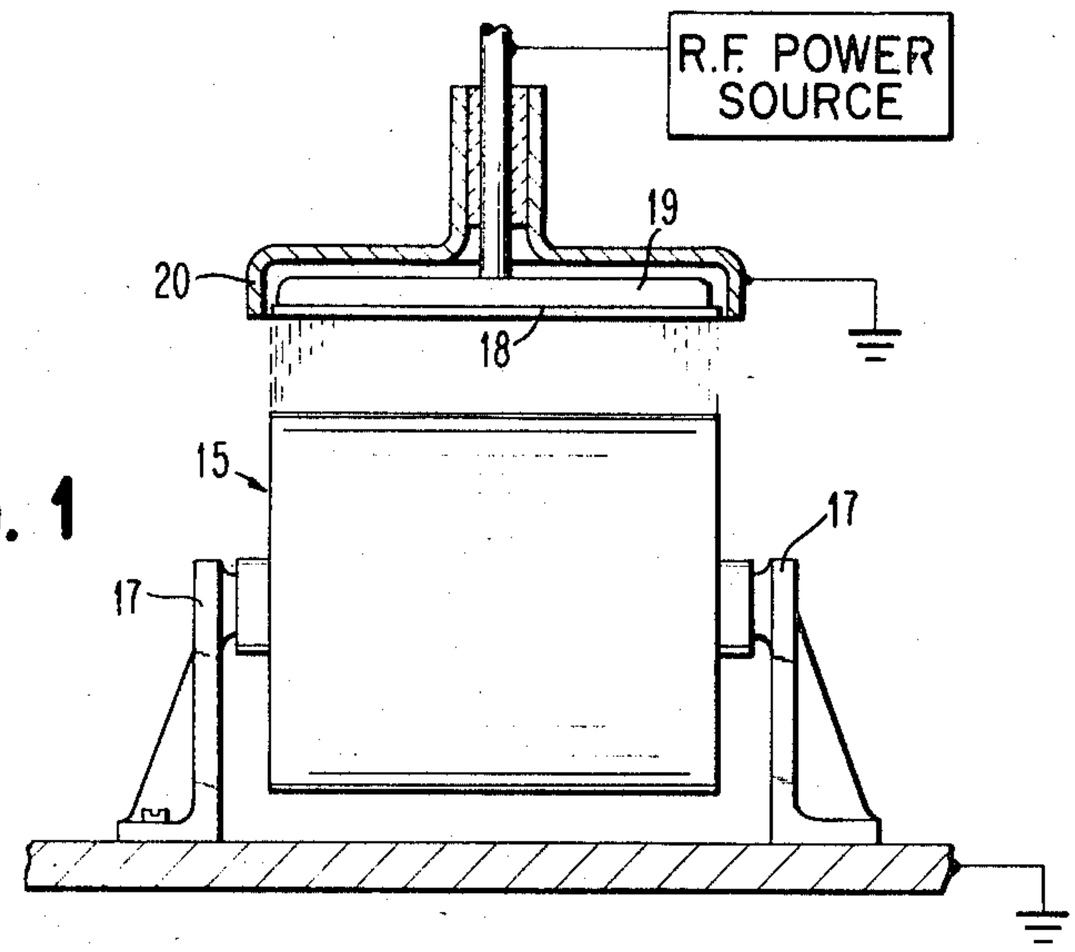


FIG. 1

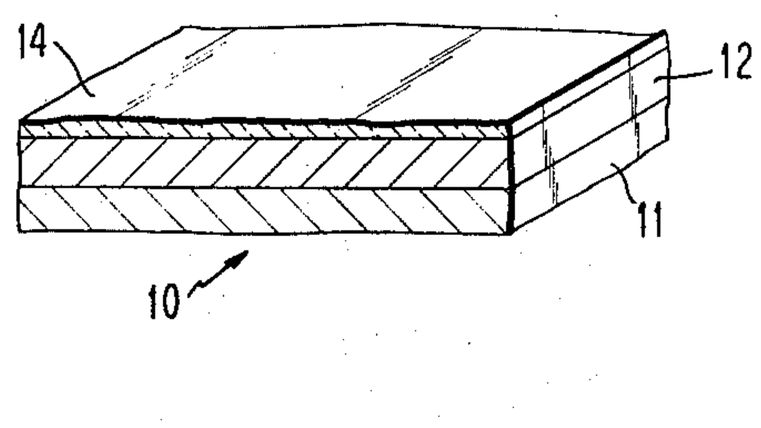


FIG. 2

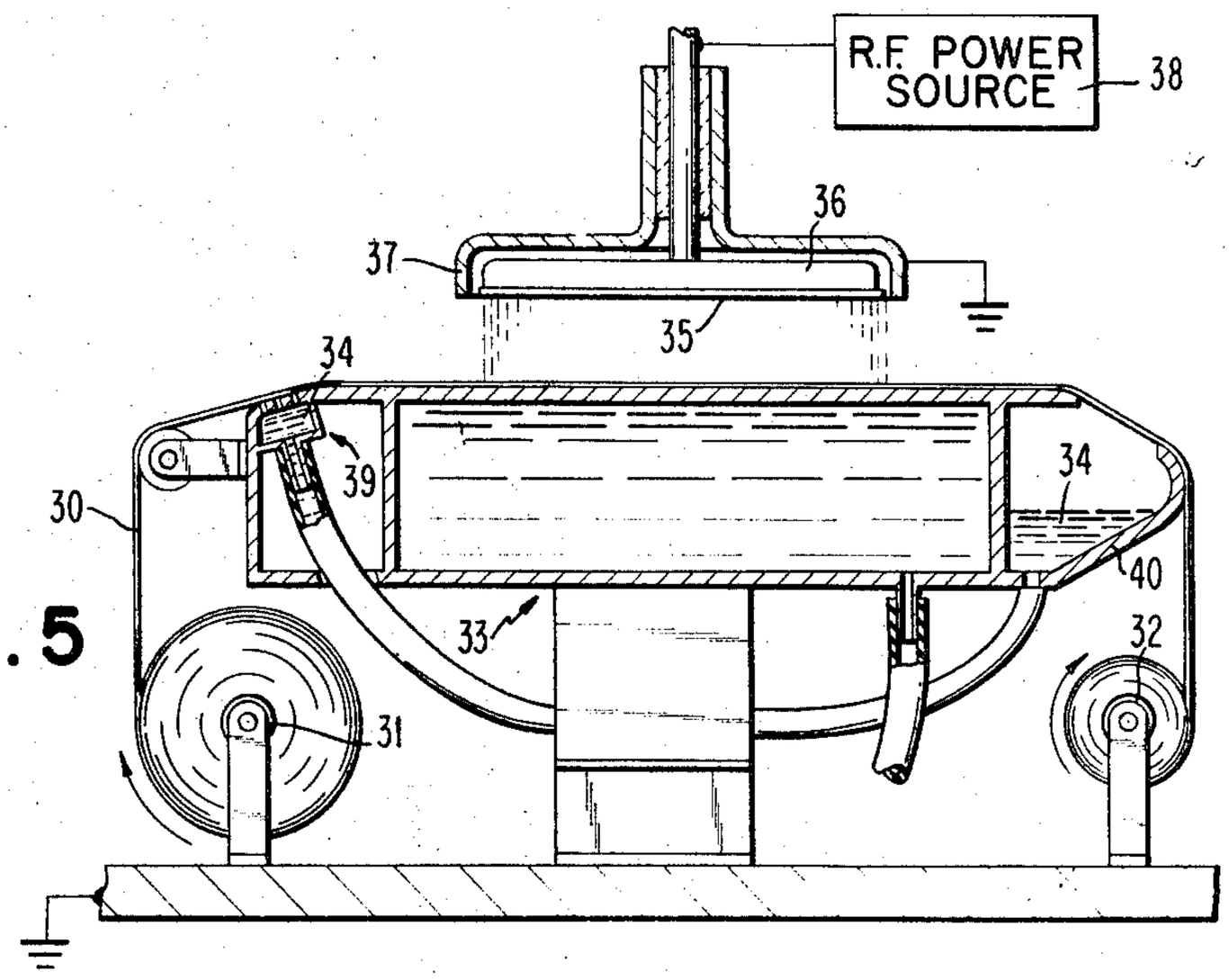


FIG. 5

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FIG. 3

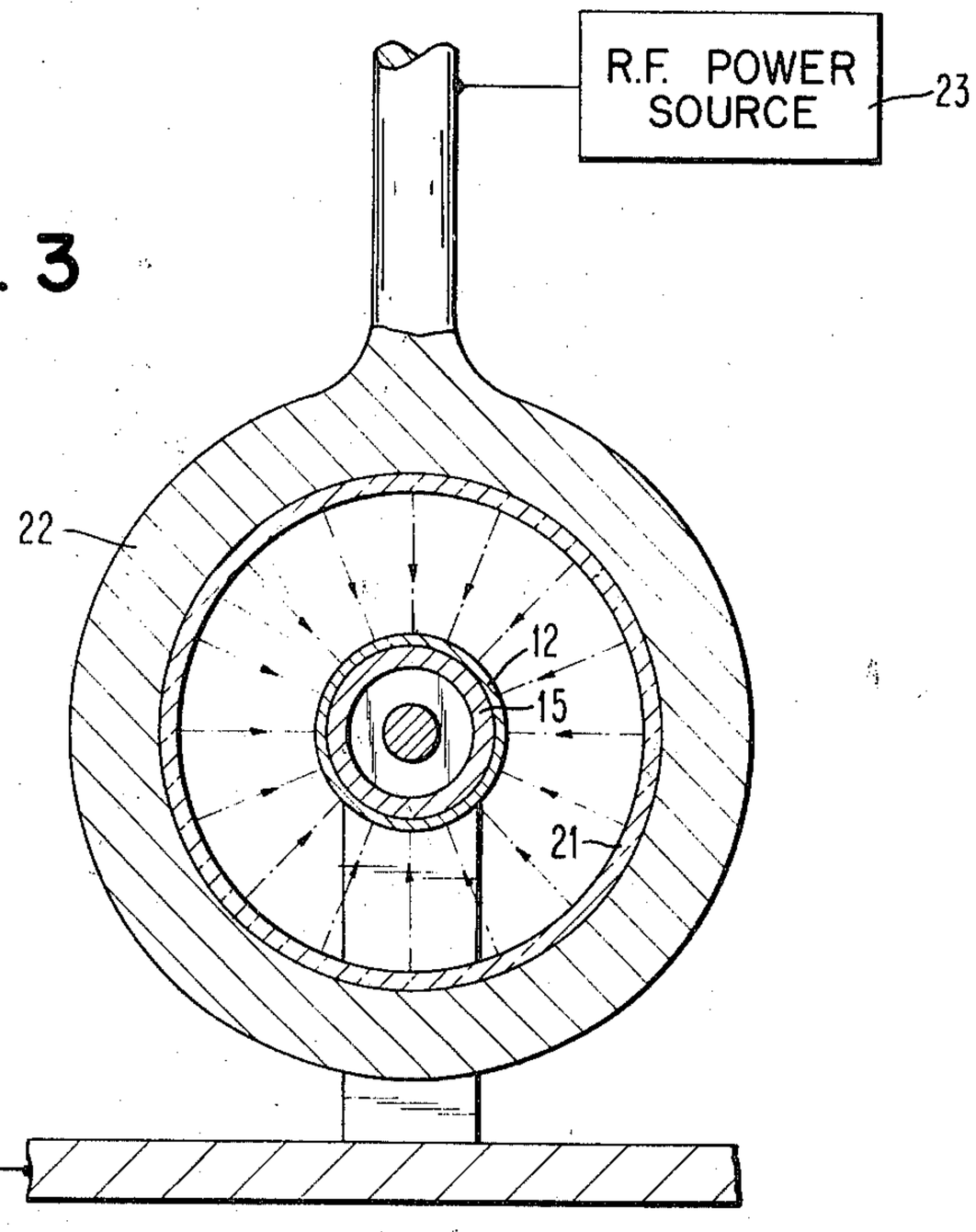
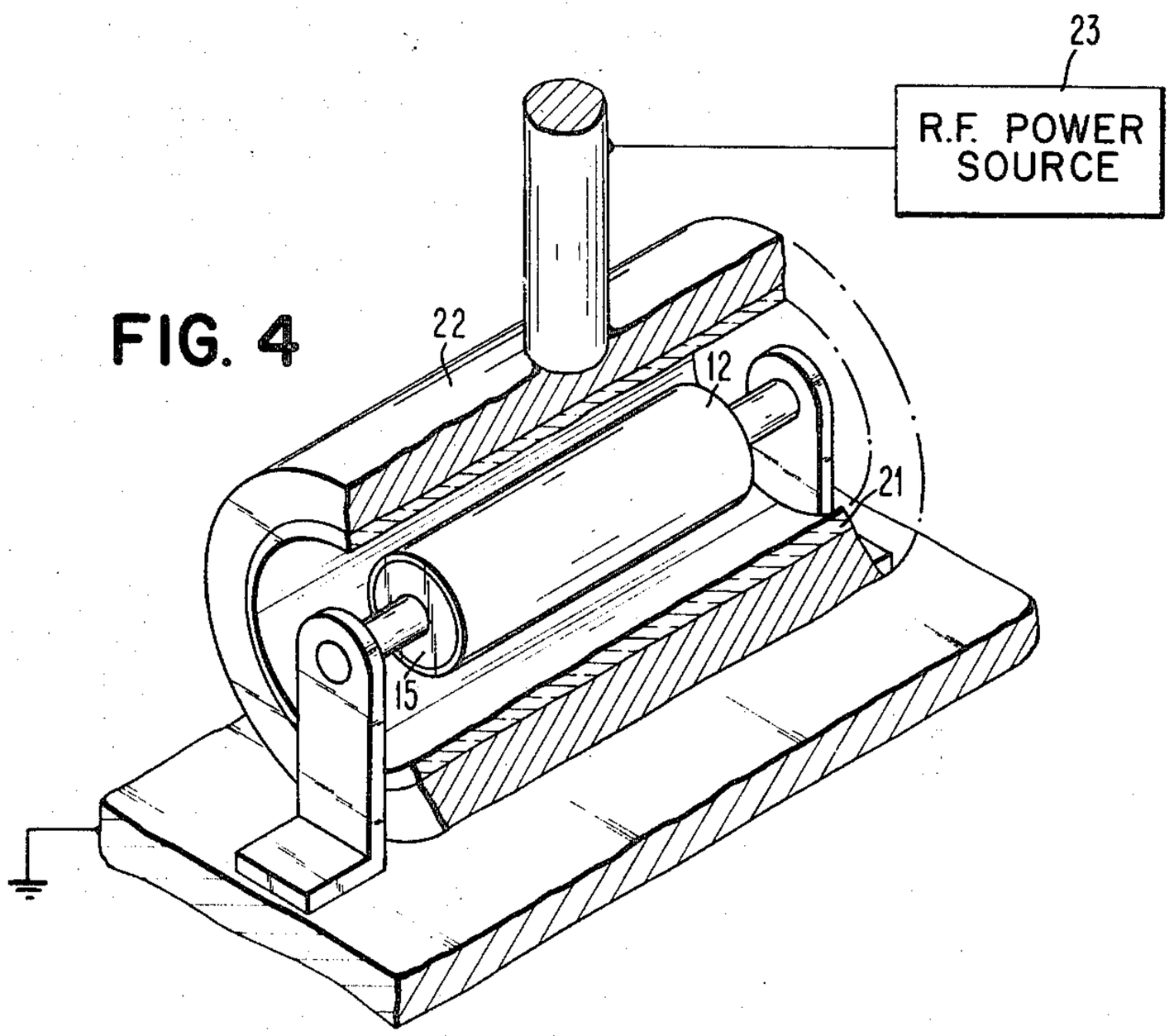


FIG. 4



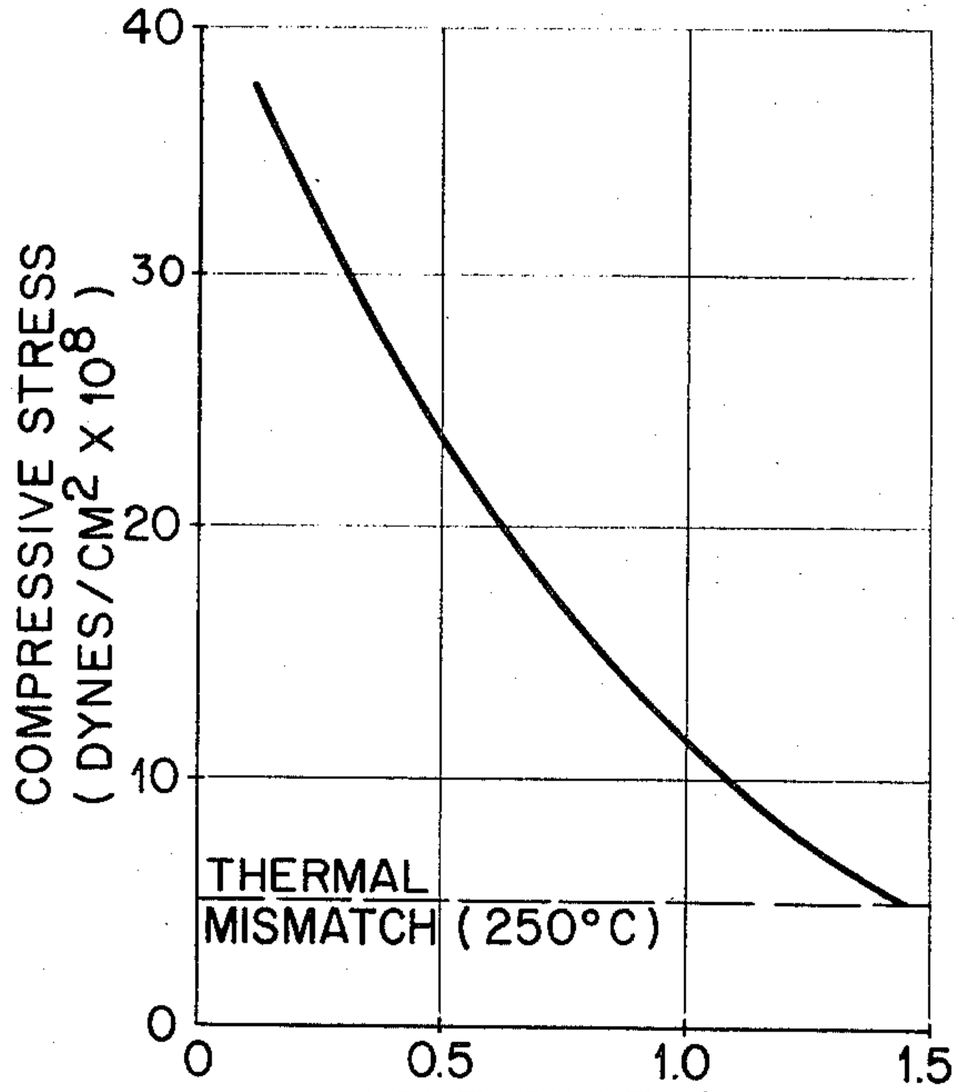

COMPRESSIVE STRESS (DYNES/CM^2 X 10^8)
40
30
20
10
0
THERMAL MISMATCH (250°C)
0
0.5
1.0
1.5
INPUT POWER(KW)

FIG. 6

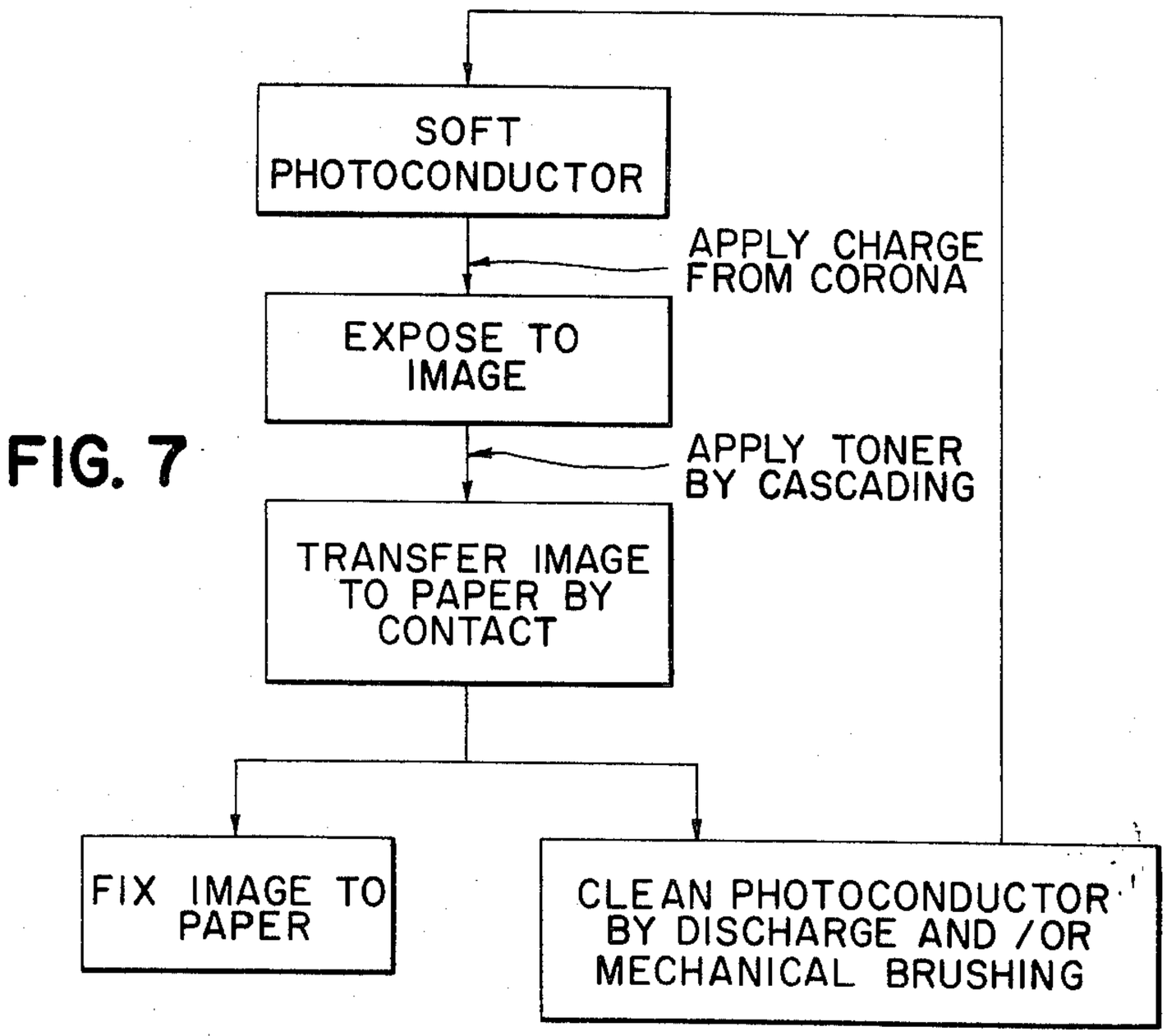

SOFT PHOTOCONDUCTOR
APPLY CHARGE FROM CORONA
EXPOSE TO IMAGE
APPLY TONER BY CASCADING
TRANSFER IMAGE TO PAPER BY CONTACT
FIX IMAGE TO PAPER
CLEAN PHOTOCONDUCTOR BY DISCHARGE AND /OR MECHANICAL BRUSHING

FIG. 7

IMAGING METHOD USING PHOTOCONDUCTIVE ELEMENT HAVING A PROTECTIVE COATING

DESCRIPTION OF THE PRIOR ART

In electrophotographic applications, the photoconductive material must have the property of a very high resistivity in the dark. Suitable examples of such a photoconductive material include selenium, anthracene and other polynuclear aromatic hydrocarbons, compositions of fluorenones and carbazoles, phthallocyanines, II–VI compounds in a binder of glass or thermoplastic, sintered crystalline II–VI compounds, and small molecules of photoconductive materials in binders. In general, all organic photoconductive materials may be utilized in electrophotographic applications if they have the property of a very high resistivity in the dark.

However, all of the foregoing photoconductive materials have the disadvantage of being relatively soft. Accordingly, when subjected to abrasion, these materials tend to wear rather rapidly so as to have a relatively short life. Thus, when subjected to the charging, developing, and cleaning operations of an electrostatic photographic operation, for example, these materials wear poorly.

Accordingly, if a protective coating is applied to such a photoconductive material, the life of the photoconductive material may be extended substantially. However, the properties of this protective coating must not interfere with the photoelectric effects of the photoconductor. For example, the coating should not leak the charge in the dark nor should it impede the flow of the charge in the light. Additionally, the coating must be transparent and have a dark resistivity at least equal to the dark resistivity of the photoconductive material. Thus, since the photoconductive materials have a resistivity in the dark of 10^{10} to 10^{12} ohm cm., the dark resistivity of the protective coating must at least be equal to this dark resistivity of the photoconductive material.

The coating also must have a substantially uniform thickness, otherwise, the coating may not be continuous and provide the desired protection.

It has previously been suggested to apply a protective coating to soft photoconductive materials. However, the previously suggested method and product has required a thickness substantially greater than presently contemplated. This thickness has been required because the coating has been applied by brushing, painting, or spraying. All of these methods would result in a coating of substantial thickness because of the size of some of the particles of the coating and the inherent coating process itself.

However, the previously suggested method of brushing, painting, or spraying will not produce an even coating across the entire surface of the photoconductive material. This may result in the coating not being continuous because of the uneven thickness so that portions of the photoconductive material may not be protected. Therefore, the previously suggested method of applying the coating by painting, brushing, or spraying has not produced a satisfactory protective coating.

It also has been previously suggested to apply a protective coating by vacuum evaporation. However, vacuum evaporation results in the photoconductive material, which is the substrate, being heated to a relatively high temperature. As a result, the photoconductive material may lose some of its photoconductive properties if vacuum evaporation is utilized. Vacuum evaporation has the additional problem of possible decomposition of the photoconductive coating. The properties of the coating also are difficult to control when utilizing vacuum evaporation.

It should be understood that it is necessary to control the properties of the coating. Otherwise, the coating will not have the desired dark resistivity, transparency, and wear resistance that is needed.

It has been previously suggested to form coatings on materials by pyrolytic decomposition. However, pyrolytic decomposition requires an even higher temperature of the substrate, which includes the photoconductive material, than is needed for vacuum evaporation. Accordingly, these high temperatures prevent the utilization of pyrolytic decomposition for applying a protective coating to the photoconductive material.

SUMMARY OF THE INVENTION

The present invention satisfactorily overcomes the foregoing problems by utilizing RF sputtering to deposit a coating on the photoconductive material. In RF sputtering, the chemical composition of the material, which is sputtered from the target onto the substrate, is controlled so that the composition does not change when the material is deposited on the substrate, which is the photoconductive material, from the target. Accordingly, control of the properties of the coating is readily obtained from utilizing RF sputtering.

Furthermore, the coating is applied uniformly over the entire surface of the photoconductive material so that the coating is continuous. Thus, when utilizing the sputtering method of the present invention, the coating may be applied without the photoconductive material losing any of its properties and still obtaining a uniform coating.

In sputtering, particles are kicked off the target at a high speed because of the voltage so that the particles are driven into the substrate of photoconductive material. Thus, this produces a tight, composite coating on the substrate of photoconductive material. There is no flaking off of particles from the coating as would be possible from coatings formed by other deposition methods such as vacuum evaporation, for example.

Therefore, the coating, which is deposited by the sputtering method of the present invention, has a relatively long life without any potential flaking off or other damage to the coating whereby it would lose its protective capability. The tight, composite coating, due to its being driven into the substrate, also insures adhesion to the substrate so that there is no possibility of the coating ceasing to adhere to the photoconductive material.

Additionally, the RF sputtering permits a very thin coating to be applied since it produces a relatively uniform thickness. Thus, the RF sputtering can produce a coating with a minimum thickness of 50.

A prior suggested method of applying a protective coating to the photoconductive material has suggested that the minimum thickness of the coating is 0.01 mil. This is due not only to the difficulty of applying a thinner coating by brushing, painting, or spraying but also because coatings of dielectric materials have very poor tensile stresses. Accordingly, any tensile force on the coating may tend to rupture it.

By making the thickness of the coating a minimum of 0.01 mil, this tends to reduce the possibility of the coating rupturing due to its relatively low tensile stress. However, even when the coating has a thickness of 0.01 mil, it may easily rupture when subjected to a tensile force because of its relatively low tensile stress. Therefore, the thickness of the coating has normally been greater than 0.01 mil to reduce the possibilities of the coating rupturing or fracturing since this would result in a shortened life of the photoconductive material because it is no longer protected.

The present invention satisfactorily overcomes the foregoing problem by providing a method in which a relatively high compressive stress is produced in the coating through control of the sputtering process. Since the compressive stress of the coating must be overcome before its inherent low tensile stress will cause rupture thereof, the relatively high compressive stress of the coating results in it not being ruptured or fractured as easily as presently available protective coatings.

Accordingly, the method of the present invention permits the coating for the photoconductive material to be relatively thin and still not rupture easily due to a tensile force. For example, the coating may have a thickness in the range of 50A. to 4,000A. This lower limit is a much thinner coating than has previously been available without resulting in the possibility of fracture or rupture of the coating due to tensile stress acting thereon.

The method of the present invention produces a relatively high compressive stress of the coating without causing the temperature of the photoconductive material, upon which the coating is to be deposited, to be relatively high. Thus, the photoconductive material will not lose its photoconductive properties. The temperature of the photoconductive material may be as low as 25° C.

When using RF sputtering, the compressive stress of the sputtered material will increase as the power is decreased. Thus, by maintaining a relatively low power during RF sputtering of the coating onto the photoconductive material, the method of the present invention produces a coating having a relatively high compressive stress. Accordingly, this relatively high compressive stress permits the coating to be much thinner than has previously been available without any increased danger of the coating fracturing or rupturing due to tension created in the coating by a force acting thereon. This force could be created by rubbing of the coating, for example, in an electrostatic photographic application by abrasive particles in the toner.

The compressive stress of the coating could be increased through selecting the material of the coating so that it has a smaller coefficient of expansion than the photoconductive material. For example, if the photoconductive material were a layer on a cylindrical drum and the coating were deposited around the drum, the coating could be subjected to compressive stress if the coefficient of expansion of the cylindrical drum were higher than the coefficient of expansion of the coating and the temperature reduces. However, this would require the cylindrical drum to have a relatively high temperature to produce a relatively high compressive stress of the coating. This temperature would be sufficiently high to result in the photoconductive material losing some of its photoconductive properties so that this method could not be utilized to increase the compressive stress of a photoconductive material.

The thin coating, which is deposited on the photoconductive material by the method of the present invention, has a very low resistance in the direction of the travel of the charge to and from the photoconductive material. As a result, the coating does not impede the travel of the charge. For example, if the coating has a resistivity of 10^{10} ohm cm. and a thickness of 1,000A, for example, it will have only a resistance of 10^5 ohm for each square centimeter of the coating. If the coating has a thickness of 0.01 mil, which is slightly greater than 2,500A, it is readily observed that the resistance will be 2½ times the resistance of a coating of 1,000A. formed by the method of the present invention. Therefore, the very thin coating of the present invention results in a protective coating that permits a more effective transfer of the charge to and from the photoconductive material than has been previously available.

Another problem with photoconductive materials is the accumulation of a film of ink on the surface of the photoconductive material. This film of ink results from the toner cascading on the surface of the photoconductive material. Thus, to obtain good images, it is necessary to periodically clean the photoconductive material by removing the film of ink therefrom. For a machine with substantial use, this cleaning operation must be performed weekly. Additionally, removal of the film of ink must be by utilizing a solvent. Thus, not only must the operation be performed at relatively short intervals of time but it also requires a chemical solvent that must be carefully handled by a skilled person.

The present invention satisfactorily overcomes the foregoing problem since the film of the ink may be readily removed from the coating on which it collects by a soft dry cloth rather than requiring a solvent to be employed. As a result, the cleaning operation may be performed in a shorter period of time and could be performed by an unskilled person. This feature of the coating of the present invention to permit removal of the film of ink therefrom by a soft dry cloth is due to the smoothness of the coating.

An object of this invention is to provide a relatively thin protective coating for a photoconductive material.

Another object of this invention is to provide a method of depositing a protective coating on a photoconductive material.

The foregoing and other objects, features, and advantages of the invention will be more apparent from the following more particular description of the preferred embodiments of the invention as illustrated in the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a schematic vertical view of a portion of a sputtering apparatus for coating a photoconductive material on a cylindrical drum.

FIG. **2** is a fragmentary perspective view, partly in section, of a photoconductive element having a coating applied thereto by the method of the present invention.

FIG. **3** is a sectional view of a portion of another form of a sputtering apparatus for coating a photoconductive material on a cylindrical drum.

FIG. **4** is a perspective view, partly in section, of the structure of FIG. **3**.

FIG. **5** is a sectional view of a portion of a sputtering apparatus for depositing a coating on a strip of photoconductive material.

FIG. **6** is a curve showing the relationship between compressive stress of a sputtered coating and RF input power when using an RF sputtering apparatus.

FIG. **7** is a block diagram of an electrostatic photographic process.

GENERAL DESCRIPTION

Referring to the drawings and particularly FIG. **2**, there is shown a photoconductive element or member **10** including a support **11** of an electrically conductive material having a layer **12** of photoconductive material. The photoconductive material of the layer **12** may be any suitable material such as selenium, organic materials, small molecules of a photoconductive material in a binder, II–VI compounds in a glass binder such as described in U.S. Pat. No. 3,248,261 to Narken et al., II–VI compounds in a thermoplastic binder such as described in U.S. Pat. No. 2,663,636 to Middleton, and II–VI sintered crystalline compounds such as cadmium selenide, cadmium sulfide, cadmium telluride, cadmium sulfoselenide and those described in U.S. Pat. No. 3,238,062 to Sunners et al., for example.

The organic photoconductive materials may be any of a plurality of different types of materials. For example, the organic photoconductive materials could be an anthracene or other polynuclear aromatic hydrocarbons or a composition of fluorenone and carbazole such as described in the copending patent application of M. D. Shattuck et al., Ser. No. 556,982, filed June 13, 1966, now U.S. Pat. No. 3,484,237 and assigned to the same assignee as the assignee of the present application. The organic photoconductive materials also could be those described in U.S. Pat. Nos. 3,294,763 and 3,341,472 to Hewett et al. Likewise, U.S. Pat. Nos. 3,037,861 and 3,169,060 to Hoegl and U.S. Pat. Nos. 3,162,532 and 3,232,755 to Hoegl et al. disclose various polymeric organic photoconductive materials. The organic photoconductive material also could be phthallocyanine.

The small molecules of photoconductive material in a binder may be those described in the copending patent application of N. J. Clecak, Ser. No. 668,696, filed Sept. 18, 1967, now U.S. Pat. No. 3,501,293, the copending patent application of N. J. Clecak, Ser. No. 668,703, filed Sept. 18, 1967, now U.S. Pat. No. 3,489,558, and the copending patent application of B. F. Dowden et al., Ser. No. 690,775, filed Dec. 15, 1967. All of the three foregoing applications are assigned to the same assignee as the assignee of the present application.

The aforesaid Clecak applications disclose a photoconductive material of bis-thiazole in a binder while the aforesaid Dowden et al. application discloses a photoconductive material of thiobarbituric acid in a binder. The binder is the limiting

ingredient when using the combination of small molecules of photoconductive material in a binder insofar as the temperature at which damage to the compound will occur. That is, the binder melts or degrades before the photoconductive materials lose their photoconductive properties.

The binders may be a natural material, a synthetic, or a copolymer, for example. The binders may include balsam; phenol resins modified with rosin; conmarone resins; indene resins; cellulose esters such as cellulose ether, for example; polyvinyl chloride; vinylidene chloride; polyvinyl acetate; acrylic polymers; polyvinyl alcohol; polystyrene; polyvinyl formaldehyde; condensation polymers such as polyethylene terephthalate, polyester terephthalate, polycarbonate, and polyisobutydiene, for example; alkyd resins; maelic acid resins; phenol formaldehyde resins; polyamides; and polyurethanes.

A coating **14**, which is transparent and formed of a suitable dielectric material, overlies the layer **12** of photoconductive material and is integral therewith. The coating **14** may be formed of any suitable dielectric material such as silicon dioxide, titanium dioxide, aluminum oxide, glass (especially borosilicates), silicon carbide, and silicon nitride. Any other oxide, nitride, carbide or boride of a metal or alloy capable of deposition in the sputtering chamber and will provide insulation also may be employed. All coatings in this thickness range contemplated are transparent. The material of the coating **14** must have a dark resistivity at least equal to the dark resistivity of the layer **12** of photoconductive material.

The coating **14** must have a relatively high compressive stress. The material of the coating **14** also must be wear resistant and transparent. Any material which meets the foregoing property requirements will be satisfactory.

An apparatus for coating a photoconductive material is shown in FIG. **1**. The photoconductive element **10** is in the shape of a cylindrical drum **15**, which is supported for rotation about its longitudinal axis. The drum **15** may be rotated at a desired rate of rotation by any suitable motive means such as a motor, for example. The drum **15** functions as the anode in an RF sputtering apparatus and is grounded through one of its supports **17**. It should be understood that the layer **12** of photoconductive material is on the exterior surface of the drum **15**.

A target **18**, which contains the material to be deposited on the layer **12** of photoconductive material, is disposed in spaced substantially parallel relation to the layer **12**. The target **18** is supported by an electrode **19** in the manner more particularly shown and described in U.S. Pat. No. 3,669,991 to Pieter D. Davidse et al. The target **18** and the electrode **19** have a grounded shield **20** disposed in close relation thereto in the manner more particularly shown in the aforesaid Davidse et al. patent and more particularly described therein.

The structure of FIG. **1** would be mounted within a partially evacuated chamber in the manner more particularly shown and described in the aforesaid Davidse et al. patent. Thus, either only the material of the target **18** could be deposited on the layer **12** of the photoconductive material or one of the oxides or nitrides thereof. If only the material of the target **18** is deposited, then only an inert gas, such as argon, for example, is supplied to the partially evacuated chamber in the manner more particularly shown and described in the aforesaid Davidse et al. patent. However, if an oxide, nitride, sulfide, or carbide of the material of the target **18** is to be deposited on the layer **12** of the photoconductive material, then the inert gas must contain a suitable gas to produce reactive sputtering within the partially evacuated chamber and either DC or RF sputtering could be used. Any metal, semiconductor, or alloy that is capable of reaction with the gas or gases in the chamber under sputtering conditions can be utilized. Of course, the material of the target **18** could be the oxide or nitride, if desired, so that only argon would be needed and RF sputtering would be used.

When using an RF sputtering apparatus of the type more particularly shown and described in the aforesaid Davidse et al. patent, tests have been run when silicon dioxide has been sputtered from a target onto a silicon substrate. The curve of FIG. **6** resulted therefrom. This curve shows that the compressive stress of the coating increases as the power input decreases. Accordingly, by appropriately controlling the RF input power, the compressive stress of the coating can be selected.

The thermal mismatch is the compressive stress that is introduced in the coating due to the coefficient of expansion of the substrate being greater than the coating. However, the remainder of the compressive stress is due to regulation or control of the RF power.

While the curve is shown for sputtering silicon dioxide on silicon, it should be understood that a similar type of curve would be applicable to any other dielectric coating that is sputtered by an RF sputtering apparatus of the type more particularly shown and described in the aforesaid Davidse et al. patent. While the temperature of the substrate might be different and the exact value of the compressive stress for a particular power input might be different, the curve would be substantially the same. That is, as the power input decreases, the compressive stress increases irrespective of the material of the coating, the material of the substrate, and the temperature of the substrate.

As shown in FIG. **6**, the stress will then increase from about 5×10^8 dynes/cm.^{2}at 1.5 kilowatts to 22×10^8 dynes/cm.^{2} at 0.5 kilowatt. Thus, a substantial increase in the compressive stress of the material of the coating is obtained by keeping the input power to the RF sputtering apparatus relatively low.

The of the coating **14** is determined by the length of time that the material from the target **18** is sputtered onto the layer **12** of the photoconductive material on the drum **15** and its rate of deposition. Thus, the coating **14** may be very thin.

Another apparatus for coating the layer **12** of the photoconductive material on the drum **15** is shown in FIGS. **3** and **4**. In this apparatus, a hollow cylindrical target **21** is mounted in spaced relation to the drum **15**. A hollow cylindrical electrode **22** surrounds the target **21** and supports the target **21**. The electrode **22** is connected to an RF power source **23** in a manner similar to that more particularly shown and described in the aforesaid Davidse et al. patent. If necessary, it should be understood that coolant may be supplied to the electrode **22** in the manner more particularly shown and described in the aforesaid Davidse et al. patent.

As shown in FIG. **4**, the drum **15** is grounded and it functions as the anode in the same manner as described for the structure of FIG. **1**. However, since the drum **15** is surrounded by the target **21**, it is not necessary for the drum **15** to be rotated in the apparatus of FIGS. **3** and **4**. Accordingly, the coating **15** will form an even layer around the entire surface of the layer **12** of photoconductive material on the drum **15**.

It should be understood that the drum **15**, the target **21**, and the electrode **22** are mounted within a partially evacuated chamber in a manner similar to that more particularly shown and described in the aforesaid Davidse et al. patent. Thus, either the target **21** may contain the material to be deposited on the layer **12** of the photoconductive material or the chamber may have a suitable gas introduced therein to form a desired oxide or nitride with the material of the target **21** by reactive sputtering. The gas flows between the target **21** and the layer **12** of photoconductive material on the drum **15**.

The power is controlled in the same manner as described for the structure of FIG. **1** whereby the compressive stress of the coating **14** is selected. Thus, the coating **14** has the desired relatively high compressive stress.

Instead of being mounted on the drum **15**, the layer **12** of the photoconductive material could be mounted on a film or strip of plastic, for example, such as the polyester resin sold under the trademark MYLAR by duPont; the resin is polyester terephthalate. A suitable apparatus for coating the layer **12** of photoconductive material when it is on a strip **30** of MYLAR film is shown in FIG. **5**. The strip **30** has one end connected to a supply spool **31** and its other end connected to a

takeup spool **32**. The strip **30** passes over a heat sink member **33**, which may be cooled by any suitable coolant passing through a cooling chamber in heat exchange relation with the heat sink member **33**.

In order to maintain the strip **30** at a desired temperature during sputtering, it is necessary to provide a heat transfer medium **34** between the strip **30** and the heat sink member **33**. The heat transfer medium **34** may be any of the materials shown and described in U.S. Pat. No. 3,294,661 to Maissel or silicone grease, for example. The heat transfer medium **34** must wet both the bottom surface of the strip **30** and the top surface of the heat sink member **33**, Furthermore, the heat transfer medium **34** must have a negligible vapor pressure (less than 10^{-8} torr) at its operating temperature. The heat transfer mediums of the aforesaid Maissel patent and silicone grease have these properties.

The heat sink member **33** is disposed adjacent to a target **35** of the material that is to be deposited on the strip **30** when it passes therebeneath. Thus, the layer **12** of photoconductive material of the strip **30** is coated only on the portion of the strip **30** disposed at any time on the heat sink member **33** beneath the target **35**.

The target **35** is supported on an electrode **36** in the manner more particularly shown and described in the aforesaid Davidse et al. patent. The electrode **36** is connected to a suitable RF power source **38** in the manner more particularly shown and described in the aforesaid Davidse et al. patent. A grounded shield **37** is disposed adjacent the electrode **36** and the target **35** in the manner more particularly shown and described in the aforesaid Davidse et al. patent.

It should be understood that the apparatus of FIG. **5** is mounted within a partially evacuated chamber in the manner more particularly shown and described in the aforesaid Davidse et al. patent. Thus, if an oxide or a nitride is desired, for example, the target **35** could contain the material from which the oxide or nitride is to be formed while the argon, which is introduced into the chamber, would include oxygen or nitrogen to produce reactive sputtering or the material of the target **35** could be formed of the oxide or nitride.

The power of the RF power source **38** will be controlled in the previously described manner so that the power is relatively low. As a result, the compressive stress of the coating **14** on the layer **12** of photoconductive material, which is integral with the strip **30**, will have a relatively high compressive stress. Furthermore, the relatively low temperature, which is due to the low power, permits the heat sink member **33** to remove sufficient heat from the strip **30** to prevent any deterioration thereof or the loss of the photoconductive properties by the layer **12** of photoconductive material.

The heat transfer medium **34** is supplied from a dispenser **39**, which is supported on the heat sink member **33**. The dispenser **39** may be an suitable type of dispenser that may be controlled to regulate the quantity of the heat transfer medium **34**, which is supplied to the bottom surface of the strip **30**.

The heat sink member **33** also carries a protruding portion **40** at its opposite end from the dispenser **39**. The portion **40** serves to remove the heat transfer medium **34** from the bottom surface of the strip **30** after it has left the heat sink member **33** and to collect the removed heat transfer medium **34**.

Any of the foregoing apparatuses will produce the coating **14** on the layer **12** of the photoconductive material with a desired thickness. The coating **14** will have a relatively high and selected compressive stress so that its thickness may be as low as 50 A.

If the layer **12** of photoconductive material should not be smooth, it would present minute peaks and valleys. As a result, a coating having only a thickness of 50 A, for example, might not completely cover all of the peaks or could be easily penetrated by an abrasive particle engaging the coating adjacent a high peak. Accordingly, when the layer **12** of photoconductive material is to be coated, it is desirable that it have a smooth and even surface. Thus, various types of plastic fillers having a high dark resistivity may be utilized to coat the layer **12** without affecting the properties of the photoconductive material.

Suitable examples of these fillers are urethane, epoxy resin, cellulose butyrate, cellulose acetate, polyvinyl chloride, and acrylic such as the sheet sold under the trademark PLEXIGLAS by Rohm and Haas.

The coated layer **12** of photoconductive material may be utilized in any area in which there is electrophotographic application. For example, the photoconductive element **10** could be employed in an electrostatic photographic method such as that shown in FIG. **7**.

The process of FIG. **7** shows the production of an image on a piece of paper from a soft photoconductive material. The photoconductor is charged and then exposed to the image. Thereafter, a toner, which contains abrasive particles, is applied by cascading. Contact of the paper with the photoconductor transfers the image to the paper. The image is fixed to the paper when the paper is no longer in contact with the photoconductor. The photoconductor is cleaned by discharging and/or mechanical brushing after the paper has been removed from contact with the photoconductor. As shown in FIG. **7**, another cycle of operation may occur after the photoconductor has been cleaned.

The following is an example in detail of the method of the present invention used to form a coating of a transparent and wear resistant material on a layer of photoconductive material. The example is included merely to aid in the understanding of the invention, and variations may be made by one skilled in the art without departing from the spirit and scope of the invention.

A strip of MYLAR film, which was 6 inches square, was clamped in an aluminum frame. The MYLAR film was coated on its upper surface with a photoconductive material. The photoconductive material was the composition of 1 mole of 2, 4, 7-trinitro-9-fluorenone per mole of monomeric unit of poly-N-vinylcarbazole. This is the material described in the aforesaid Shattuck et al. application. If softens below 100° C. and breaks down above 160° C. Its photoconductive properties begin to deteriorate if the compound is subjected to a temperature of 150° C. for more than thirty minutes.

The back surface of the MYLAR strip was coated with silicone grease. A plate was then pressed into the silicone grease on the back of the strip to grease the plate.

The plate was next pressed onto a water cooled anode. One surface of the plate was in engagement with the anode while the other surface of the greased plate was in engagement with the back of the MYLAR strip. Accordingly, there was heat transfer from the MYLAR strip, which is the substrate, to the anode.

The foregoing structure was then placed within a chamber, which could be evacuated. A cathode was disposed 1 5/16 inches from the upper coated surface of the MYLAR strip and contained a target of silicon dioxide.

By applying a power of 100 watts, which is a power density of approximately 2.7 watts per square inch for the cathode employed, for 80 minutes, a coating having a thickness of approximately 3,000A. was deposited on the surface of the layer of the photoconductive material. This provided a transparent and wear resistant coating without affecting the properties of the photoconductive material.

The pressure within the chamber was 5 millitorr, and the temperature was 50° C. Thus, this low temperature could not damage the photoconductive material.

Tests were made with the coated photoconductive material of the foregoing example being utilized in a photoconductive process. This process included applying a charge to the photoconductor, exposing the photoconductor to the image to be developed, applying a toner to the photoconductor, and then transferring the image to the paper and cleaning the photoconductor. After 35,000 cycles of the foregoing process, there was no surface deterioration of the material.

Tests also were run on the same photoconductive material through the same photoconductive process in which the photoconductive material did not have the coating of the foregoing example thereon. These tests showed that the photoconductive material had such damage after 35,000 cycles that it was almost unusable. In fact, after 5,000 cycles of the foregoing photoconductive process, the damage to the uncoated photoconductor was sufficient for it to no longer be satisfactory. Thus, these tests disclose that the coating of the present invention adds substantial life to a soft photoconductive material.

Furthermore, the ink film, which forms on the uncoated photoconductive material, due to the toner, forms on the coating of the coated photoconductive material of the foregoing example. However, the film of ink was readily cleaned from the coating with a dry cotton material. In the photoconductive material without the coating of the foregoing example, this is not possible since a solvent must be employed to remove the film of ink. This solvent must be applied directly to the photoconductive material and may affect its life.

Because of the long wearing life of the photoconductive material with the coating of the present invention thereon, a long continuous loop, for example, of the coated photoconductive material could be employed. This would permit several images to be formed on spaced portions of the loop whereby the speed of producing the images could be increased. This is because the long wearing life of the photoconductive material with the coating of the present invention would not require replacement for a substantially long period of time. In addition, the capability of removing the film of ink by a soft clean cloth would reduce the number of service calls necessary for a photostatic machine, for example, using a photoconductive material with the coating of the present invention thereon.

An advantage of this invention is that it permits a relatively thin coating of a wear resistant material to be formed on a photoconductive material without affecting the properties of the photoconductive material. Another advantage of this invention is that it increases the life of the photoconductive material. A further advantage of this invention is that the coating will not rupture or break as easily as prior protective coatings for photoconductive materials.

While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that the foregoing and other changes in form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. An imaging method comprising:

providing an electrophotographic plate comprising a photoconductive layer overlaying a conductive layer, the photoconductive layer having a transparent, continuous, and protective coating of silicon dioxide overlaying said photoconductive layer, the transparent, continuous, and protective coating having a compressive stress greater than that produced by thermal mismatch between the coating and the layer, a dark resistivity at least equal to the dark resistivity of the photoconductive layer, and a substantially uniform thickness of about 3,000 A;

applying a uniform electrostatic charge to the plate;

exposing the plate to an image to be developed to produce a latent electrostatic image; and

developing the latent image whereby a visible image is formed.

2. The method according to claim 1 in which the photoconductive layer is selenium.

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