United States Patent [19]

Kiess

[11] **3,713,822**

[45] **Jan. 30, 1973**

[54] **PYROELECTRIC PHOTOCONDUCTIVE ELEMENTS AND METHOD OF CHARGING SAME**

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[73] Assignee: **RCA Corporation**

[22] Filed: **Aug. 31, 1970**

[21] Appl. No.: **68,067**

[52] **U.S. Cl.** ....**96/1.5**, 96/1 R, 96/1 C, 96/1.8, 317/262 A, 317/262 AE

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

[58] **Field of Search** 96/1, 1.5, 1.8; 23/147, 148

[56] **References Cited**

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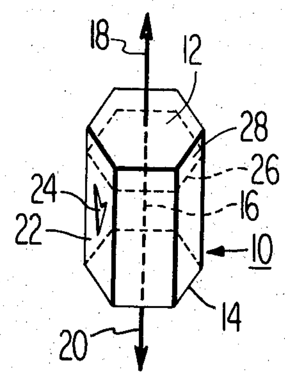
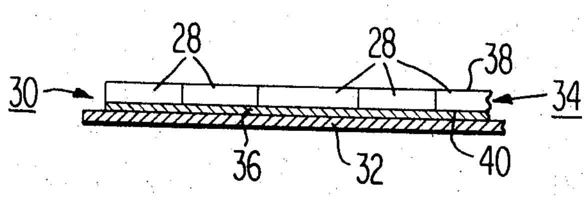
[57] **ABSTRACT**

The recording element comprises an electrically conductive substrate and a layer of a photoconductive, pyroelectric compound on the substrate. The layer comprises one or more wafers of the pyroelectric compound, each wafer being similarly oriented on the substrate so that its polar *c*-axis is transverse to the opposite large surfaces of the layer. The novel electrophotographic recording element is charged by merely changing the temperature of the layer a few degrees.

11 Claims, 6 Drawing Figures





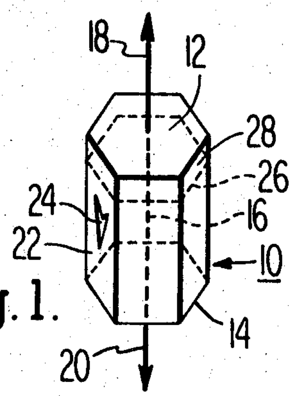


Fig. 1.

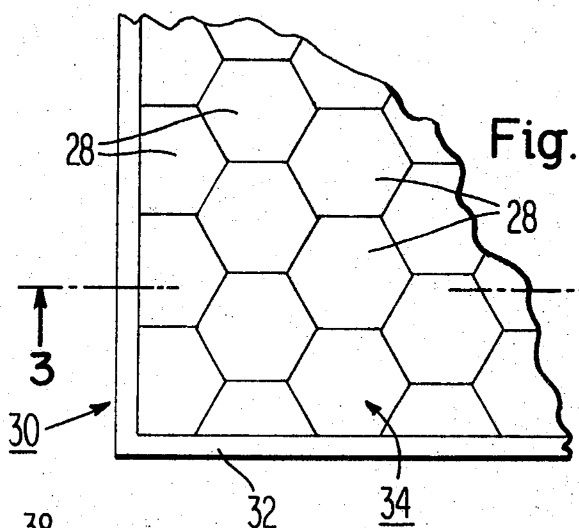


Fig. 2.

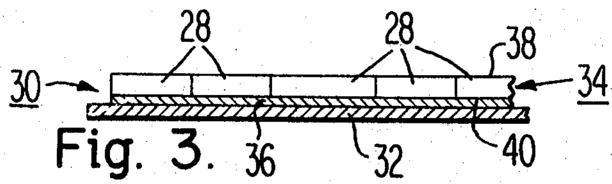


Fig. 3.

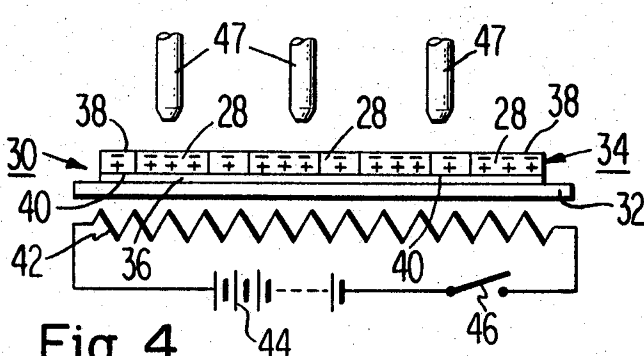


Fig. 4.

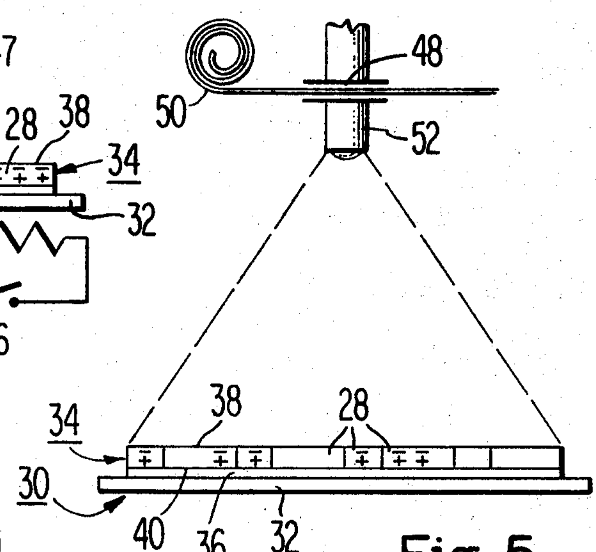


Fig. 5.

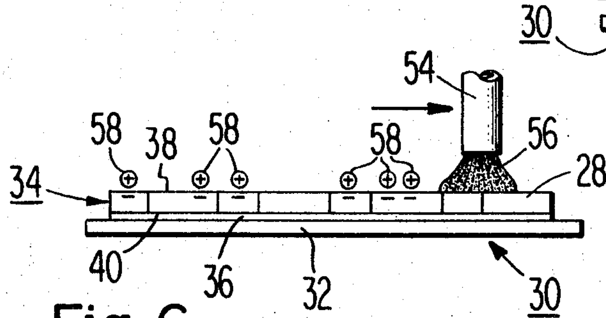


Fig. 6.

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PYROELECTRIC PHOTOCONDUCTIVE ELEMENTS AND METHOD OF CHARGING SAME

BACKGROUND OF THE INVENTION

This invention relates generally to an electrophotographic recording element and a method of charging same. More particularly, the invention relates to a novel electrophotographic plate of a pyroelectric compound and a novel method of charging the electrophotographic plate by changing its temperature. The novel electrophotographic plate and method of charging it are particularly useful in an electrophotographic process wherein an image developed on the plate is to be transferred from the plate to a transfer sheet.

It has been proposed to charge an electrophotographic recording element, comprising a photoconductive layer, by subjecting the photoconductive layer to a corona discharge from a corona discharge device. While this prior-art method is the most conventional one for charging an electrophotographic recording element, it requires a relatively expensive, high-voltage power supply, capable of generating at least 5,000 volts, and a corona discharge device that must be carefully shielded and insulated to protect an operator or maintenance personnel from electric shock. Also, unless the high-voltage equipment is suitably shielded, it can cause annoying radio and television interference.

The novel electrophotographic recording element and method of charging it make it possible to carry out an electrophotographic process without a high voltage power supply, thereby eliminating the inherent disadvantage thereof.

SUMMARY OF THE INVENTION

The novel electrophotographic recording element comprises a layer of a photoconductive pyroelectric material on a relatively electrically conductive substrate and in electrical contact therewith. The pyroelectric material of the layer is oriented so as to produce electrostatic charges on the opposite surfaces of the layer when the temperature of the layer is changed.

The novel method of charging the novel recording element comprises changing the temperature of the layer to produce an electrostatic charge between the opposite surfaces of the layer.

The novel recording element and method employ the principles of pyroelectricity and obviate the need for relatively expensive high-voltage power supplies, corona discharge devices, and the necessary safety precautions required therefore. The novel method is also relatively free from conditions that cause interference with radio and television reception.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a perspective view of a hexagonal, single-crystal structure of a photoconductive, pyroelectric material, zinc oxide, exhibiting its polar *c*-axis;

FIG. 2 is a fragmentary plan view of one embodiment of a novel electrophotographic recording element in the form of a plate, employing elemental bodies of the single-crystal material illustrated in FIG. 1;

FIG. 3 is a fragmentary cross-sectional view of the electrophotographic plate shown in FIG. 2, taken along the line 3—3, and viewed in the direction indicated by the arrows;

FIG. 4 is a side elevational view of the novel recording element and means, illustrated symbolically, for charging it in accordance with the novel method; and,

FIGS. 5 and 6 are side elevational views of the novel electrophotographic plate in different steps of forming an electrophotographic image thereon.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now to FIG. 1 of the drawing, there is shown a single-crystal, photoconductive, pyroelectric material, such as a compound **10**, of the type used to make the novel electrophotographic recording element. The compound **10** may be a single-crystal, hexagonal structure of zinc oxide, for example, having opposite polar (0001) surfaces **12** and **14** that are different from each other with respect to the direction of a *c*-axis **16**, the surface **14** being designated as the Zn surface and the surface **12** being designated as the O surface. While the novel recording element will be described with respect to the pyroelectric compound **10** of zinc oxide, it is within the contemplation of the present invention to use other pyroelectric compounds, such as CdS, SbSI, or CdSe, for example.

If the temperature of the pyroelectric compound **10** is changed a voltage is produced between the opposite surfaces **12** and **14** that are transverse to the *c*-axis **16**. For example, if the temperature of the compound **10** is raised about 5°C, the surface **12** acquires a negative electrostatic charge with respect to the surface **14**, the surface **14** acquiring a positive electrostatic charge. The polarities of the electrostatic charges on the surfaces **12** and **14** depend upon whether the *c*-axis **16** is pointing upwardly, in the direction of the arrow **18**, or downwardly in the direction **20** with respect to the surfaces **12** and **14**, looking at FIG. **1**. The amplitude of the voltage produced by the change in temperature is proportional to the thickness of the compound **10** between the opposite surfaces **12** and **14**.

One method of determining the polarities of the electrostatic charges produced on the faces **12** and **14** of the pyroelectric compound **10** is to etch one of the prism (1010) faces **22** with 40 percent hydrofluoric acid. A plurality of etch pits **24** (only one shown in FIG. **1**) are produced which can indicate the direction of the polar *c*-axis. Each etch pit **24** has an arrowhead-type shape that points in the positive direction of the *c*-axis. Hence, the etch pit **24**, in FIG. **1**, indicates that the polar axis **16** is positive in the direction of the arrow **20** and negative in the direction of the arrow **18**.

The pyroelectric compound **10** of zinc oxide may be grown by any suitable method known in the art or it may be purchased from commercial vendors, as from Litton, Inc., Airtron Division, Morris Plains, New Jersey; or from the Dielectric Materials and System Division of The 3M Company, St. Paul, Minnesota. The zinc oxide crystal compound **10** may be purchased either in the uncut crystal form or in the form of wafers **28** cut from the crystal, for example, along the dashed line **26** parallel to the faces **12** and **14**. Uncut crystals are commercially available in diameters of 1mm through 5 mm and in varying lengths of 2 mm to 10 mm, depending on their diameter. Square wafers of zinc oxide compound **10** having a side of 10 mm and a thickness of at least about 5 mm are also available commercially. The zinc oxide compound **10** is preferably doped with a suitable dopant, such as copper (concentration of about 10^{19}–$10^{20}cm^{-3}$) or lithium (concentration of about $5.10^{18}cm^{-3}$) to compensate the zinc oxide with P-type carriers so as to provide it with a suitable resistivity. When doped, the dark resistivity of wafers **28** of the compound **10** is at least 10^9ohm cm, and usually much higher. The doped single-crystal, zinc oxide compound **10** possesses an illuminated resistivity of approximately 10^5 ohm cm.

Referring now to FIGS. **2** and **3**, there is shown a novel recording element in the form of an electrophotographic plate **30** suitable for use in an electrophotographic process for reproducing images. The plate **30** comprises an electrically conductive substrate **32**, such as a sheet of aluminum, copper, or stainless steel, and a photoconductive layer **34** of one or more wafers **28** of the pyroelectric compound **10**. As shown in FIGS. **2** and **3**, the photoconductive layer **34** is a composite of a plurality of the pyroelectric elemental bodies, such as wafers **28**. The wafers **28** are adhered to the substrate **32** by any suitable electrically conductive paste **36** or solder. While the wafers **28** of zinc oxide, illustrated in FIGS. **2** and **3**, are shown as being hexagonal, they may be in other shapes, such as rectangular or square. The layer **34**, however, should have its opposite (large) major surfaces **38** and **40** substantially continuous; that is, the wafers **28** should abut each other as closely as possible so as to provide substantially continuous, smooth, opposite major surfaces **38** and **40**. The lower surfaces of the wafers **28** that are in electrical contact with the substrate **32** may be coated with a very thin coating of indium so as to make a good electrical contact with the substrate **32** through the conductive paste **36**. To provide a layer **24** of a composite of wafers **28**, each wafer **28** should preferably have a thickness of at least about 0.5 mm, one major surface area of at least 2.5 mm^2, and a resistivity of at least 10^9ohm-cm in the dark.

All of the wafers **28** of the electrophotographic plate **30** are oriented so that their *c*-axes are transverse to, and preferably perpendicular to, the opposite major surfaces **38** and **40** of the lay **34**. Since the photoconductor of zinc oxide in most electrophotographic processes is charged negatively, the zinc oxide wafers **28** of the compound **10** are disposed in the layer **34** so that their *c*-axes point outwardly, as in the direction **18** of FIG. **1**, from the upper major surface **38** of the layer **34**. Thus, a negative electrostatic charge is produced upon the upper major surface **38** of the layer **34** when the temperature of the layer **34** is raised, as will be explained hereinafter. Conversely, the upper major surface **38** of the photoconductive layer **34** will exhibit a positive electrostatic charge if the temperature of the layer **34** is suddenly lowered from its ambient.

The upper surface **38** of the photoconductive layer **34** is preferably coated with a monolayer of one or more sensitizing dyes, such as fluorescence, cyanine dyes, rose bengal, or erythrosin, for example, to make the photoconductive layer responsive to visible light. In the absence of such dye sensitization, the photoconductive layer **34** of zinc oxide wafers **28** can be exposed by ultraviolet light to which it is particularly sensitive.

Referring now to FIG. **4**, means are shown to electrostatically charge the novel electrophotographic plate **30** by changing its temperature, in darkness, in accordance with the novel method. To this end, a heater **42**, such as a hot plate, is disposed adjacent to the electrophotographic plate **30**. The heater is connected in series with a suitable voltage source **44** and a switch **46**. Thus, to charge the electrophotographic plate **30**, the switch **46** is closed to energize the heater **42**. The voltage developed pyroelectrically across the photoconductive layer **34** of the electrophotographic plate **30**, in darkness, is proportional to the thickness of the layer **34**; that is, the thickness of the wafers **28**, and to the change in the temperature of the layer **34**. A thickness of the photoconductive layer **34** of about 0.7 mm will provide a voltage thereacross of about 250 volts when the temperature of the layer **34** is raised about 5°C. If the *c*-axes of the wafers **28** are pointing outwardly from the upper surface **38** of the photoconductive layer **34**, the upper surface **38** of the photoconductive layer **34**, the upper surface **38** is charged negatively and the lower surface **40** is charged positively, as indicated symbolically in FIG. **4**. If the *c*-axes of the wafers **28** were pointing downwardly from the upper surface **38**, the charges on the surfaces **38** and **40** of the photoconductive layer **34** would be reversed.

A change in temperature of the photoconductive layer **34** of between about 5°C and 30°C from the ambient has been found suitable to charging the novel electrophotographic plate **30** for processing in an electrophotographic process. A change in temperature of less then 5°C may not develop a sufficient charge on a very thin layer **34**, while a change in temperature of more than 30°C may render the layer **34** too conductive to retain the charge for a desired period.

Although a preferred method of charging the novel electrophotographic late **30** is by raising its temperature from the ambient, it is within the contemplation of the novel method to charge the electrophotographic plate **30** by cooling it between about 5°C and 30°C from the ambient. This may be accomplished by blowing refrigerated air onto the surface **38** of the layer **34**, from any suitable source, through a plurality of jets **47** disposed above the photoconductive layer **34**, as shown in FIG. **4**. Any other means of cooling, such as by Peltier elements, for example, may also be used.

The charged electrophotographic plate **30** can now be exposed to a light image to be reproduced, whereby to discharge the electrophotographic plate **30** selectively and to provide an electrostatic latent image on the photoconductive layer **34**. This operation in the electrophotographic process is illustrated in FIG. **5**. A transparency **48** of the image to be reproduced, as a frame of a motion picture film **50**, for example, is projected through a light projector **52** to the upper surface **38** of a charged (previously heated) photoconductive layer **34**. The exposure step should be carried out as soon as possible after the charging step to prevent a loss of the charge with a change in temperature. Those portions of the photoconductive layer **34** that are struck by light are discharged proportionately in accordance with the intensity of light impinging thereon, leaving the electrostatic latent image thereon. The exposure time is dependent upon the dimensions of the electrophotographic plate **30** and the intensity of the exposure, and can be in the neighborhood of about 1 second.

The latent electrostatic image on the electrophotographic recording element **30** may now be developed by any suitable developing means known in the electrophotographic art. For example, the surface **38** may be brushed with a magnetic brush comprising a magnet **54** and a triboelectric mixture **56** of iron and toner particles, as taught in U.S. Pat. No. 2,874,063, issued on February **17, 1959**, to H. G. Greig for Electrostatic Printing. The toner particles **58** are positive in the triboelectric mixture **56** and are attracted to the negative charges of the latent electrostatic image, thereby developing the latent image, as shown in FIG. **6**. The developed image may be fixed, as by heating, on the surface **38** of the photoconductive layer **34**, or, if desired, the unfixed image may be transferred to a transfer sheet by any suitable means and methods well known in the art for transferring an unfixed image from an electrophotographic plate to a transfer sheet.

Although the improved electrophotographic plate has been shown and described as comprising single-crystal, photoconductive, pyroelectric wafers of zinc oxide which is white, the photoconductive layer of the plate may comprise other pyroelectric, photoconductive compounds. While some of the pyroelectric compounds, such as CdS, SbSI, or CdSe, are not white, they are quite suitable for producing unfixed images on the novel electrophotographic plate for transfer purposes to transfer surfaces. The novel method of charging the novel electrophotographic plate eliminates the need of the high voltage power supply of the prior art and the attendant disadvantages inherent herein. The dimensions of the embodiments of the electrophotographic plate and conditions of the method of charging it described herein are merely illustrative and are not intended to be considered in a limiting sense.

I claim:

1. An electrophotographic recording element comprising;

a substrate of electrically conductive material, and

a layer of photoconductive, pyroelectric material comprising a composite of similar crystalline elemental bodies, said layer being in electrical contact with said substrate, and said elemental bodies of said material being similarly oriented with respect to their crystal axes to produce electrostatic charges of the same polarity on an exposed surface of said recording element when the temperature of said layer is changed.

2. An electrophotographic recording element as described in claim **1**, wherein

said material is a compound selected from the group consisting of single-crystal ZnO, CdS, CdSe, and SbSI, and

said layer comprises one or more elemental bodies of said compound.

3. An electrophotographic recording element as described in claim **3**, wherein

each of said elemental bodies has a *c*-axis, and said *c*-axes extend in the same direction and are substantially perpendicular to said surface of said layer.

4. An electrophotographic recording element as described in claim **1**, wherein

said material is single-crystal ZnO,

said layer comprises a plurality of wafers of said single-crystal ZnO, and

each of said wafers has a *c*-axis extending outwardly from said exposed surface and said layer.

5. An electrophotographic recording element as described in claim **1**, wherein

said material is single-crystal zinc oxide,

said layer comprises one or more bodies of said single-crystal zinc oxide, and

each of said bodies has a *c*-axis pointing toward said substrate.

6. An electrophotographic recording element as described in claim **4**, wherein

each of said wafers has a thickness of at least 0.5 mm, a large surface with an area of at least 2.5 mm^2, and a resistivity of at least 10^9ohm-cm in the dark.

7. In an electrophotographic method of the type wherein a photoconductive layer of a recording element is sequentially electrostatically charged, selectively discharged with a light image to provide an electrostatic latent image, and said latent image is developed with an electroscopic toner to provide a visible image on said layer, the improvement of charging said recording element comprising the steps of:

providing said photoconductive layer in the form of one or more similar crystalline elemental bodies of a photoconductive, pyroelectric material on an electrically conductive substrate, each of said elemental bodies being similarly oriented with respect to their crystal axes to produce electrostatic charges of opposite polarity on the opposite large surfaces, respectively, of said layer when the temperature of said layer is changed, and

changing the temperature of said layer to produce said electrostatic charges, whereby to charge said layer.

8. In an electrophotographic method of the type described in claim **7**, wherein

the step of changing the temperature of said layer to produce said electrostatic charges comprises raising the temperature of said layer between 5°C and 30°C.

9. In an electrophotographic method of the type described in claim **7**, wherein

the step of changing the temperature of said layer to produce said electrostatic charges comprises lowering the temperature of said layer between 5°C and 30°C.

10. In an electrophotographic method of the type described in claim **7**, wherein

the step of providing said photoconductive layer comprises providing a layer of one or more wafers of single-crystal, photoconductive zinc oxide on an electrically conductive substrate, each of said wafers of zinc oxide having a *c*-axis that is pointing in the same direction and oriented substantially perpendicularly to opposite large surfaces of said layer, and

the step of changing the temperature of said layer comprises heating or cooling said layer at least about 5°C.

11. In an electrophotographic method of the type described in claim **10**, wherein

said layer has one surface in electrical contact with an electrically conductive substrate, and

said *c*-axes of said wafers of zinc oxide point outwardly from the opposite large surface of said layer.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,713,822 Dated January 30, 1973

Inventor(s) Helmut Gustav Kiess

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

Claim 3, Col. 5, line 55

"Claim 3" should be --Claim 1--

Claim 4, Col. 5, line 65

Cancel "and" and insert --of--

Column 4, line 36

Cancel "late" and insert --plate--

Column 5, line 29

Cancel "herein" and insert --therein--

Signed and Sealed this

twenty-seventh **Day of** *April 1976*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks