United States Patent

Yamashita

[15] **3,652,270**

[45] **Mar. 28, 1972**

[54] RECORDING DEVICES

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[73] Assignee: **Matsushita Electric Industrial Co., Ltd.**, Osaka, Japan

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[21] Appl. No.: **793,222**

Related U.S. Application Data

[63] Continuation of Ser. No. 350,830, Mar. 10, 1964, abandoned.

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May 2, 1963	Japan	38/23220
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Oct. 25, 1963	Japan	38/57735
Oct. 28, 1963	Japan	38/58709

[52] **U.S. Cl.** **96/1.5**, 96/1.8, 252/501, 117/201, 117/17.5, 117/218, 346/1

[51] **Int. Cl.** **G03g 5/04**

[58] **Field of Search** 96/1, 1.4, 1.5–1.8; 252/501; 117/201, 215, 218

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Primary Examiner—Charles E. Van Horn

Attorney—Stevens, Davis, Miller & Mosher

[57] **ABSTRACT**

A recording device comprising in series a first electrode, a layer containing a dispersed mixture of at least a semiconductor and an electrical insulator having one side contacting said electrode, a solid layer of an electrical insulator contacting the other side of the first mentioned layer, and a second electrode disposed on the other side of the solid insulator layer in electrical contact therewith. The second electrode may be either in direct abutting contact with the solid insulator layer or may act thereon through either a fluorescent phosphor layer or a photoconductive layer. When a voltage is applied between the electrodes, a charge of the same polarity as that of the first electrode is stored in both the layer of the mixture of semiconductor and insulator and in the solid insulator layer.

1 Claims, 20 Drawing Figures

Fig. 1

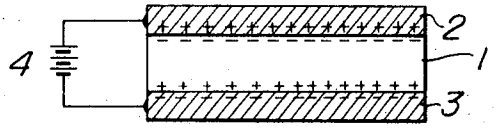


Fig. 2

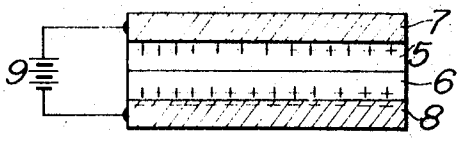


Fig. 3

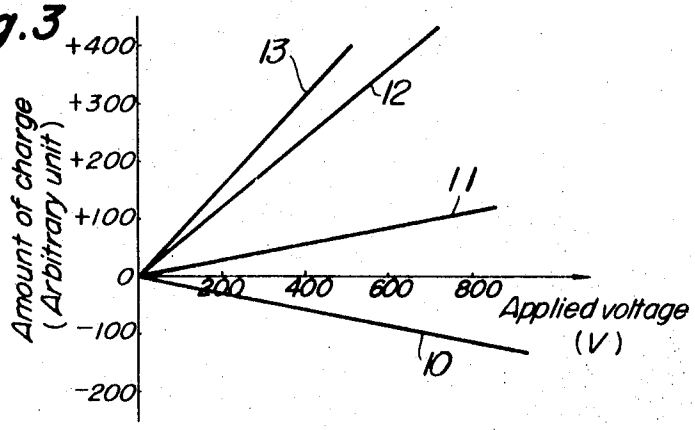
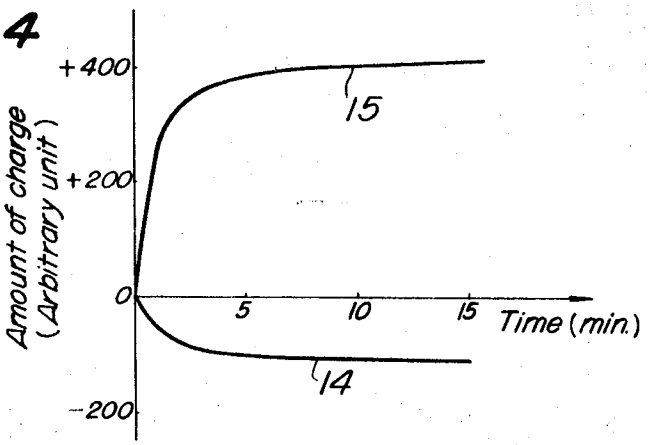


Fig. 4



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Fig. 5

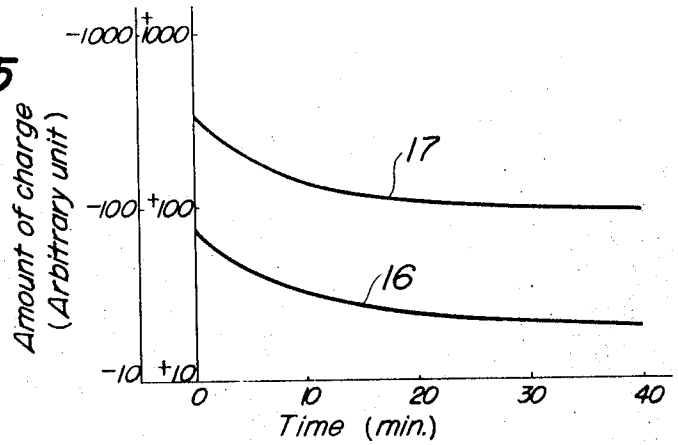


Fig. 6

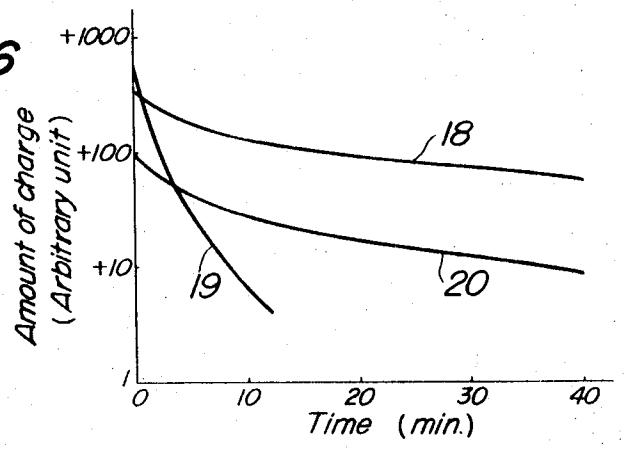
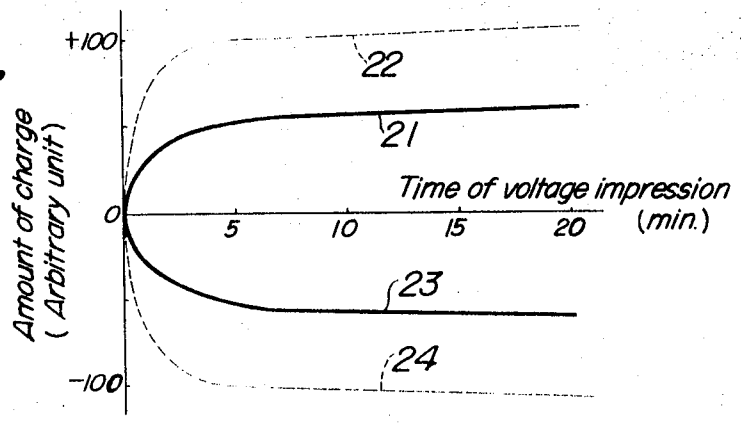


Fig. 7



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Fig. 8

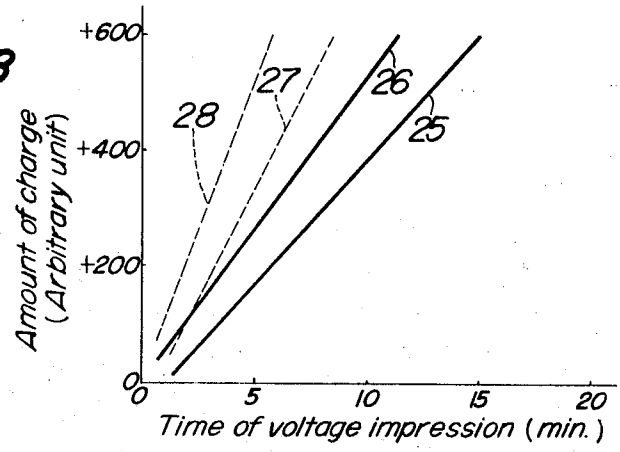


Fig. 9

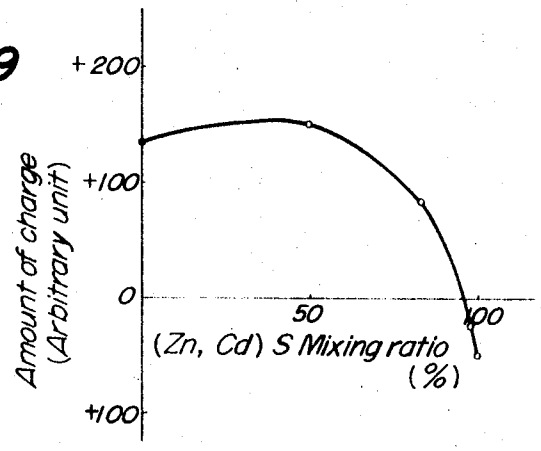
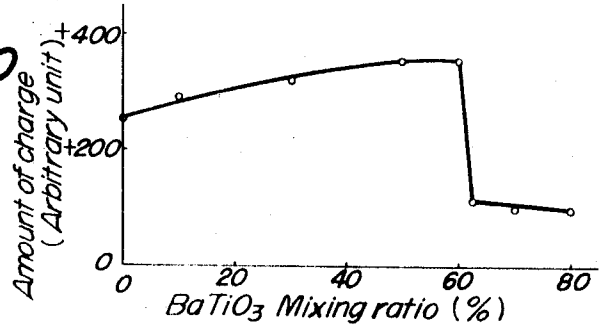


Fig. 10



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Fig. 11

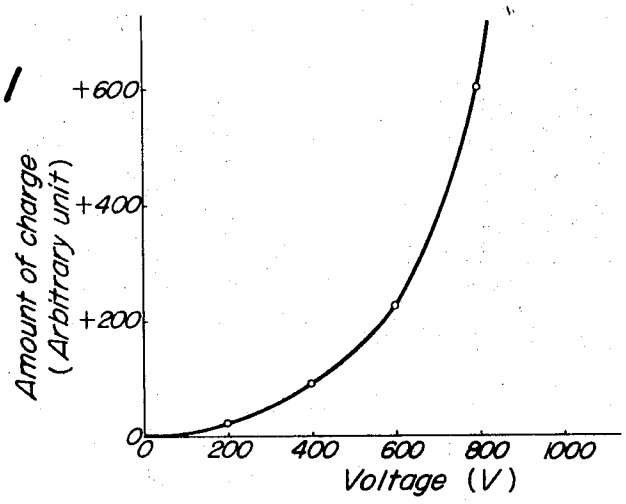


Fig. 12

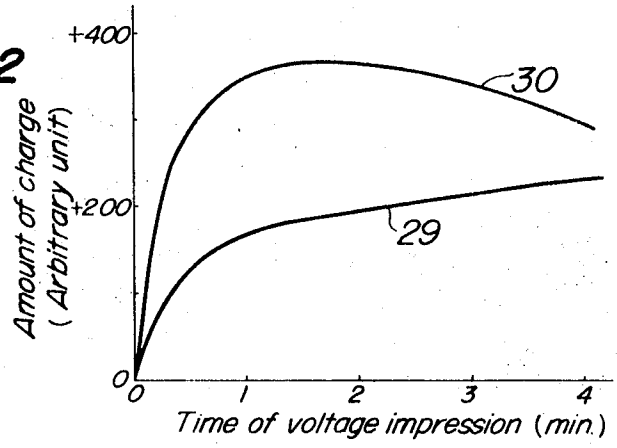
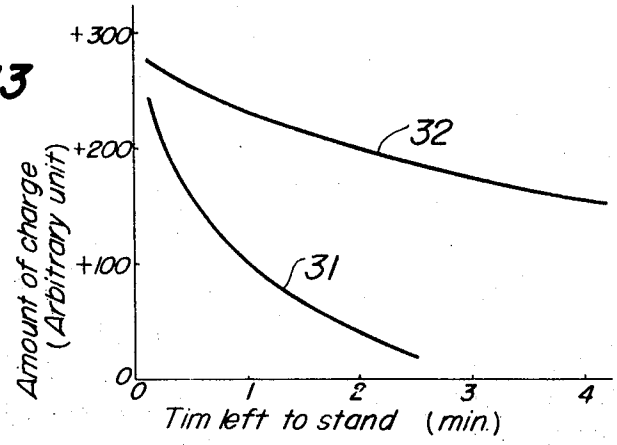


Fig. 13



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Fig. 14

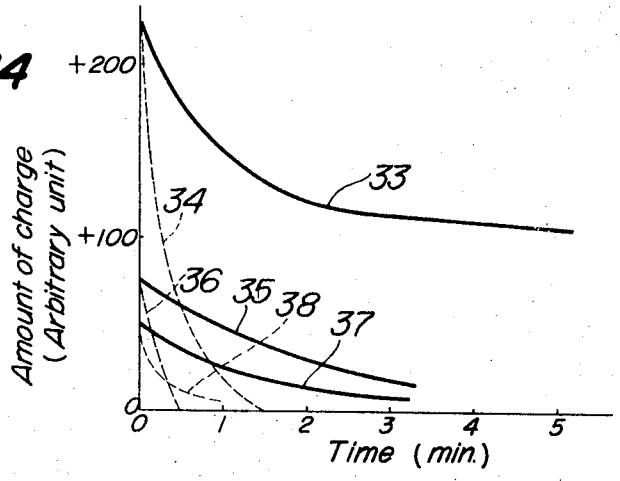


Fig. 15

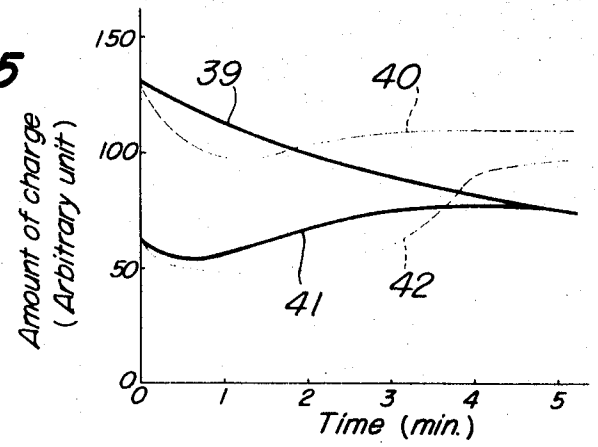
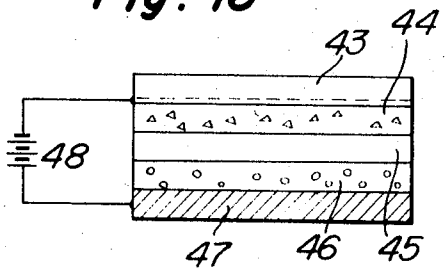
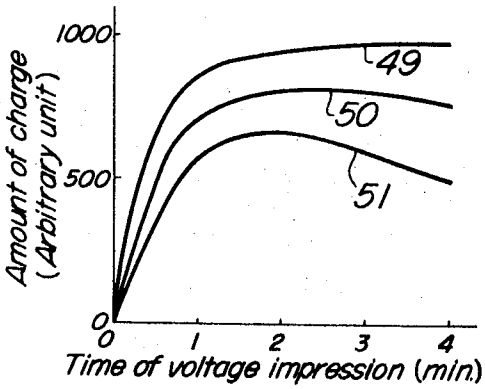


Fig. 17

Fig. 16





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Fig. 18

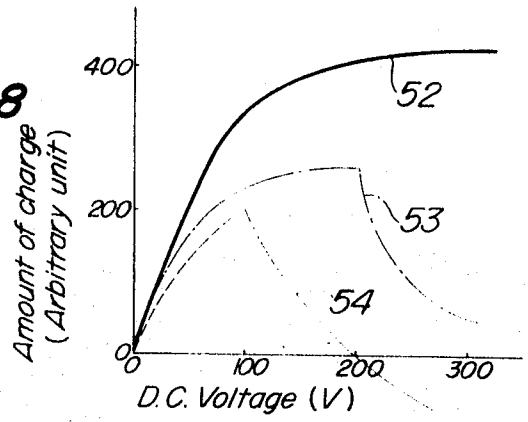


Fig. 19

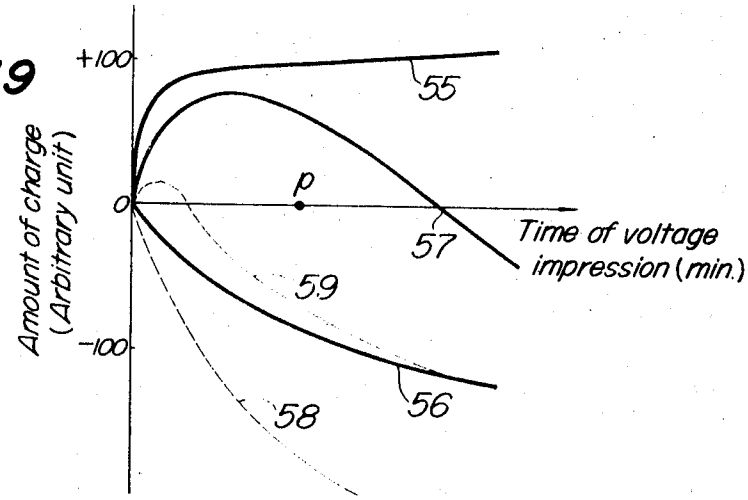
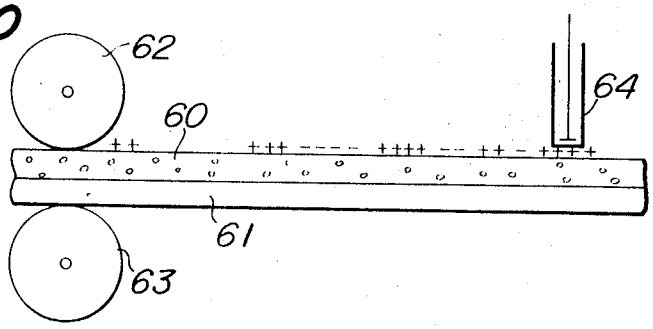


Fig. 20



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RECORDING DEVICES

This application is a continuation of Ser. No. 350,830, filed Mar. 10, 1964, and now abandoned.

The present invention relates to electrical devices and more particularly to a novel recording device of highly sensitive nature.

Sensitive paper for use in electrophotography has heretofore been offered as one type of recording device comprising a mixture of a semiconductor and an electrical insulator. The sensitive paper is sold by the commercial name of Electrofax, in which a mixture layer of zinc oxide and a synthetic resin is coated on a sheet of paper. In the sensitive paper, however, an electrode formed of a plurality of fine tungsten wires is spaced from the sensitive layer in order to charge the sensitive layer by the utilization of a corona discharge phenomenon. According to this method, a high discharge voltage of the order of 5,000 to 6,000 volts is generally required and this is apparently undesirable in view of expensive power supply equipment and dangers involved in the operation.

The invention provides a recording device with a structure which is entirely different from those of conventional devices, and the device of the invention acts in a manner that has not been known in the prior art. More precisely, the invention relates to a recording device which comprises a stack of a mixture of at least a semiconductor and an electrical insulator, a carrier transformer, such as a conductor or a semiconductor, an electrical insulator, and an electrode. A most remarkable feature of the invention resides in that an electric charge of the same polarity with that of the carrier transformer in contact with the mixture of the semiconductor and the insulator is stored in the mixture.

The primary object of the invention is to provide a highly sensitive recording device which comprises a mixture of at least a semiconductor and an electrical insulator, a carrier transformer brought into contact with the mixture, another electrical insulator brought into contact with the mixture on the opposite side of the carrier transformer, and an electrode disposed on the another electrical insulator on the opposite side of the mixture, to store in the mixture of the semiconductor and the insulator a great amount of electric charge of the same polarity as that of the carrier transformer in contact with the mixture.

Another object of the invention is to provide a recording device of said character in which the electrode is directly brought into contact with the another insulator.

Still another object of the invention is to provide a recording device of said character in which the electrode is indirectly brought into contact with the another insulator through another layer placed therebetween.

Yet another object of the invention is to provide a recording device of said character in which the semiconductor included in the mixture takes the form of a P-type semiconductor, to store in the mixture a greater amount of electric charge of the same polarity as that of the carrier transformer in contact with the mixture.

Further another object of the invention is to provide a recording device of said character in which a fluorescent phosphor is added to the mixture, to store in the mixture an electric charge of the same polarity as that of the carrier transformer in contact with the mixture and to vary the amount of electric charge by application of light thereto.

A further object of the invention is to provide a recording device of said character in which a ferroelectric substance is added to the mixture to store in the mixture a further greater amount of electric charge of the same polarity as that of the carrier transformer in contact with the mixture.

A still further object of the invention is to provide a recording device of said character in which a fluorescent phosphor and a ferroelectric substance are added to the mixture, to store in the mixture an electric charge of the same polarity as that of the carrier transformer in contact with the mixture and to vary the amount of electric charge by application of light thereto.

A yet further object of the invention is to provide a recording device of said character in which the mixture of the semiconductor and the insulator further includes a metal generating a photo-electromotive force in combination with the semiconductor in the mixture, to store in the mixture an electric charge of the same polarity as that of the carrier transformer in contact with the mixture and to vary the amount of electric charge by application of light thereto.

Another object of the invention is to provide a recording device of said character in which the another electrical insulator takes the form of such material as polystyrene or polyethylene having little residual electric charge due to absorption current, to store in the mixture an electric charge of the same polarity as that of the carrier transformer in contact with the mixture and to prevent the amount of electric charge from decreasing by an alternating electric field applied across the mixture.

Still another object of the invention is to provide a recording device of said character in which a fluorescent layer including a fluorescent phosphor therein is superposed on the another insulator in contact with the mixture, and the transparent conductive glass plate is superposed on the fluorescent layer, to store in the mixture an electric charge of the same polarity as that of the carrier transformer in contact with the mixture and to vary the amount of electric charge by application of light thereto.

Yet another object of the invention is to provide a recording device of said character in which a photoconductive layer including therein a photoconductor is superposed on the another insulator in contact with the mixture and the transparent electrode is superposed on the photoconductive layer, to store in the mixture an electric charge of the same polarity as that of the carrier transformer in contact with the mixture and to vary the amount of electric charge by application of light thereto.

There are other objects and particularities of the invention which will become obvious from the following description with reference to the accompanying drawings, in which:

FIG. **1** is a schematic sectional view of a conventional recording device;

FIG. **2** is a schematic sectional view of a novel recording device of the invention;

FIG. **3** is a graphic illustration of a relation between an amount of electric charge and applied DC voltage in the inventive and prior recording devices;

FIG. **4** is a graphic illustration of a relation between a time of voltage application and an amount of electric charge in the inventive and prior devices;

FIG. **5** is a graphic illustration of a natural decay characteristic of stored electric charges in the inventive and prior devices;

FIGS. **6–13** are graphic illustrations of various characteristics of the inventive device with the mixture of different compositions;

FIGS. **14–15** are graphic illustrations of the effect of insulators on the natural decay characteristic of stored charges in the device of the invention;

FIG. **16** is a schematic sectional view of another embodiment of the invention;

FIGS. **17** and **18** are graphic illustrations of various characteristics of the device shown in FIG. **16**;

FIG. **19** is a graphic illustration of the characteristic of the inventive device as applied to electrophotography; and

FIG. **20** is a schematic layout of the inventive device as applied to audio and video recording.

The invention will now be described with reference to the drawings. When DC voltage is applied across a common electrical insulator placed between electrodes, electric charges produced on the respective faces of the insulator have opposite polarities to those of the electrodes with which it is in contact. Or more precisely, when DC voltage derived from a DC source **4** is applied across electrodes **2** and **3** having an electrical insulator **1** interposed therebetween as shown in

FIG. 1, a layer of negative charges is formed at the boundary of the insulator 1 at which it contacts the anode 2, while a layer of positive charges is formed at the boundary of the insulator 1 at which it contacts the cathode 3. In order to produce a great amount of electric charge in the insulator 1, there is a method which utilizes the persistent internal polarization effect of a fluorescent phosphor. According to this method, a mixture of an organic insulating material and a fluorescent phosphor is used in lieu of the insulator 1 and DC voltage is applied to the mixture to cause polarization therein. The amount of polarization can be increased by illumination thereon and preserved for a long time in a dark space. Even in this case, layers of electric charges of opposite polarities to those of the electrodes are formed at the boundaries of the insulator with the electrodes as in the former case.

The device of the present invention is entirely different from such conventional devices. According to the invention, an electric charge of the same polarity with that of a carrier transformer, such as a conductor or a semiconductor, is stored in a mixture of a semiconductor and an electrical insulator in contact with the carrier transformer. In FIG. 2, the device of the invention is schematically shown and comprises a mixture 5 of an electrical insulator and a semiconductor and an electrical insulator 6 placed between electrodes 7 and 8 which are connected to a DC source 9. When, as shown in FIG. 2, DC voltage is applied across the electrodes 7 and 8, an unipolar electric charge is stored in the mixture 5 and the insulator 6. Such effect was discovered by the inventor and designated as a unipolar charge storage effect by the inventor. The inventor considers that such effect is caused by the injection of electric charges from the electrode 7 into the mixture 5. The inventor believes this to be the case because the electric charge stored in the mixture will have an opposite or negative polarity if an electrical insulator is placed between the electrode 7 and the mixture 5.

Hereinafter, the recording device with such feature of the invention will be explained in further detail. In the present invention, any of well-known semiconductors such as Ge, Si, Se, CU_2O, ZnO, PbO, NiO, CdS, ZnSe and anthracene may be used, and any of electrical insulators such as glass, porcelain, silicone resin, polyvinyl chloride, polyvinyl acetate, epoxy resin, polyvinyl butyral and wax may be used. There may be many methods for manufacturing a material having the unipolar charge storage effect by the use of these semiconductors and insulators. One of the methods includes mixing the semiconductor with the insulating material of organic nature such as the resin or wax, while another method includes mixing the semiconductor with the insulating material of inorganic nature such as glass, porcelain, or sulfur.

1. Basic characteristics

Description will hereinunder be made with regard to basic characteristics of the recording device of the invention. The effect of the invention will not vary by employing either a conductor or a semiconductor as a carrier transformer. A mixture including 70 percent of Cu_2O, a P-type semiconductor, and 30 percent of silicone resin is prepared and coated on a sheet of paper. The paper carrying the mixture thereon is placed between two electrodes in order to obtain a structure as shown in FIG. 2. For the sake of comparison, a mixture including 70 percent of (Zn, Cd)S, being a fluorescent phosphor showing a persistent internal polarization effect, and 30 percent of silicone resin is prepared and placed between two electrodes in order to obtain a conventional structure as shown in FIG. 1.

1–1. Voltage characteristic

FIG. 3 shows a relation between an amount of electric charge and applied voltage when DC voltage is applied for 4 minutes to the inventive and prior devices. In FIG. 3, the positive value shows an amount of positive charge and the negative value an amount of negative charge. Curves 10 and 11 represent the characteristic of the prior device wherein the curve 10 therein shows a variation in the amount of charge at the surface of the mixture layer at which it is in contact with the anode, while the curve 11 shows a variation in the amount of charge at the surface of the mixture layer at which it is in contact with the cathode. From the curves 10 and 11, it will be seen that the negative charges are induced on the surface of the mixture layer which is in contact with the anode and the positive charges are induced on the surface in contact with the cathode. Curves 12 and 13 show the case of the invention, in which the curve 12 shows a variation in the amount of charge at the surface of the mixture layer which is in contact with the anode and the curve 13 shows a variation in the amount of charge at the surface of the insulator layer which is in contact with the cathode. From the curves 12 and 13, it will be seen that the electric charge of the same polarity with that of the electrode with which the mixture layer is in contact is stored in the mixture layer. This is the unipolar charge storage effect which has not been found heretofore. The amount of stored charges increase rectilinearly with relation to the applied voltage, and the effect of the invention appears already in a low voltage range. Therefore, it will be known that such effect is not produced by some secondary cause such as local discharge but by the phenomenon of charge injection which has not been found in any of prior devices.

1–2. Voltage application time characteristic

FIG. 4 shows a relation between a time of voltage application and an amount of electric charge when DC voltage of 600 volts is applied on the samples. A curve 14 therein shows a case of the prior device and it will be seen that negative charges are obtained on the side of the anode. In a curve 15 showing the case of the present invention, positive charges are obtained on the side of the anode. In both cases, the stored charges abruptly increase simultaneously with the application of voltage and saturation takes place after about 4 minutes. These curves can be approximately expressed as a formula $P = P\infty\,[1 - \exp(-\lambda t)]$, where $P\infty$ is an amount of charge after application of voltage for a long period, and λ is a constant which is compared with a reciprocal of a dielectric relaxation time.

1–3. Natural decay characteristics

FIG. 5 shows a variation in the amount of stored charge with relation to time when the inventive and prior devices are left to stand, or a natural decay characteristic. Curves 16 and 17 show variations in the amounts of negative and positive charges when measurement is taken on the side of the anodes of the prior and inventive devices, respectively. It will be seen from the curves that the amount of stored charge decreases greatly in an initial period of time and the decay becomes gradually less thereafter. These curves can be approximated by a formula $P = P_0 \exp(-t/\tau)$, where P_0 is a constant and τ is a time constant.

From the foregoing description with regard to the basic characteristics of the device of the invention, it will be understood that, by the feature of the invention, it is possible to store in a mixture of a semiconductor and an insulator an electric charge of the same polarity with that of an electrode with which the mixture is in contact and to obtain a greater amount of charge than by the prior device. Therefore, the recording device of the invention is advantageous in that loss of electric charge is less when the electrode is spaced from the mixture due to the fact that both have the same polarity and in that a good sensitivity can be obtained owing to a great amount of electric charge stored therein.

2. Effect of different compositions of mixture

Description will now be made with regard to the effect of various semiconductors used in the mixture and addition of fluorescent phosphors, ferroelectric substances and metals thereto.

2–1. Effect of P-type semiconductor

Cu_2O which is a P-type semiconductor is mixed with an organic electrical insulator in the form of silicone resin. The mixture is coated on a Mylar film, being an electrical insulator, to obtain a structure as shown in FIG. 2. After application of DC voltage of 600 volts for 1 minute, measurement is taken of the amount of charge at the surface of the mixture at the side of the anode to obtain the natural decay characteristic,

and a curve **18** in FIG. **6** is obtained. In this case, positive charges are also stored in the mixture of the anode side thereof. In case Se, one of similar P-type semiconductor, is used, a curve **19** in FIG. **6** is obtained under the same condition. It will be apparent from the curve **19** that, though a great amount of electric charge is stored in the initial period of time, its decay is quite rapid.

2–2. Effect of N-type semiconductor

ZnO is used as a N-type semiconductor and silicone resin is used as an electrical insulator. In this case, an electric charge of single polarity is also stored by the application of voltage as in the case of foregoing paragraph 2–1, but an amount of charge is less than about one half of the case of Cu_2O. The stored electric charges can be preserved for a long time in a dark space, but, in the case of ZnO, decrement of the charges is more rapid than in the case of Cu_2O, as shown by a curve **20** in FIG. **6**. The N-type semiconductor has a remarkably smaller amount of stored charge than in the P-type semiconductors and similar results have been obtained on other N-type semiconductors. Especially when CdS, another N-type semiconductor, is used, almost no charge can be stored.

2–3. Effect of joint use of semiconductor and fluorescent phosphor

A P-type semiconductor in the form of Cu_2O, an organic insulator in the form of silicone resin and a fluorescent phosphor in the form of (Zn, Cd)S are mixed together with a solvent comprising toluene, coated on a sheet of paper of insulating material, and sufficiently dried. A brass plate and a plate of transparent conductive glass having thereon a tin oxide film are used as electrodes. The glass electrode is used for the purpose of observing an effect of illumination on the mixture.

A sample without Cu_2O therein, that is, a sample in which powder of (Zn, Cd)S is solely dispersed in the silicone resin is prepared and DC voltage of 600 volts is applied thereon in a dark space or with illumination thereon. Then, a layer of negative charge is formed on the anode side and a layer of positive charges is formed on the cathode side. FIG. **7** shows a relation between an amount of charge thereby formed and a time of voltage application. Curves **21**, **22**, **23** and **24** in FIG. **7** show a case wherein voltage is applied in a dark space and measurement is taken on the cathode side, a case wherein voltage is applied simultaneously with illumination with light of 50 luxes and measurement is taken on the cathode side, a case wherein voltage is applied in a dark space and measurement is taken on the anode side, and a case wherein voltage is applied simultaneously with illumination with light of 50 luxes and measurement is taken on the anode side, respectively. From the curves, it will be seen that layers of electric charges having the polarities opposite to those of the electrodes are formed in the silicone resin wherein the fluorescent phosphor is dispersed.

Then, the semiconductor, Cu_2O, is mixed with the fluorescent phosphor, (Zn, Cd)S, at a ratio of 1 to 10 and the mixture is dispersed in the silicone resin to obtain a sample. By applying DC voltage of 600 volts thereto in the above manner, an unipolar electric charge is stored in the sample. FIG. **8** shows a relation between an amount of charge and a time of voltage application in this case. Solid lines **25** and **26** therein show a case wherein voltage is applied in a dark space and measurement is taken on the anode side, and a case wherein voltage is applied in a dark space and measurement is taken on the cathode side, respectively. Dotted lines **27** and **28** show cases wherein voltage is applied while illuminating with light of 50 luxes and measurement is taken on the anode and cathode sides, respectively. It will thus be seen that, by the addition of the semiconductor for example Cu_2O, the mixture stores therein an electric charge of the same polarity with that of the electrode with which it contacts and the amount of charge so stored is extremely great. Further, the amount of charge increases in proportion to the time of voltage application. The electric charge of single polarity thus formed can be storaged for an extended period of time, especially even in a light space. The charge may be extinguished by the application of an infrared light or by heating.

Then, a sample including 30 percent of an insulator or silicone resin and 70 percent of a mixture of a semiconductor for example Cu_2O and a fluorescent phosphor or (Zn, Cd)S is prepared, and the mixing ratio of (Zn, Cd)S in the mixture is varied to obtain a relation between an amount of charge and the mixing ratio of (Zn, Cd)S, which is shown in FIG. **9**. The amount of charge is measured on the anode side. It will be seen that positive charges are obtained by the mixture of the semiconductor, Cu_2O, of about 2 percent and the unipolar charges can thereby be stored. In the case of the mixture of Cu_2O and the silicone resin, there is virtually no increase in electric charges by illumination, but addition of (Zn, Cd)S is effective to increase the amount of charge by application of light thereto.

2–4. Effect of joint use of semiconductor and ferroelectric substance

A P-type semiconductor in the form of NiO is mixed at various ratios with a ferroelectric substance in the form of $BaTiO_3$ and silicone resin is used as an insulator. The mixture of these elements is coated on a Mylar film to obtain a structure as shown in FIG. **2** and voltage is applied thereto. As a result thereof, an electric charge of the same polarity with that of the electrode **7** is storaged in the mixture **5**. FIG. **10** shows a variation in the amount of stored charge when the mixing ratio of $BaTiO_3$ to NiO is varied. It will be seen that the amount of charge increases at the $BaTiO_3$ content of less than 60 percent, but abruptly decreases when the $BaTiO_3$ content exceeds 60 percent. This tendency is quite similar for any other ferroelectric substances.

2–5. Effect of joint use of semiconductor, fluorescent phosphor and ferroelectric substance

A semiconductor in the form of NiO, a fluorescent phospher in the form of (Zn, Cd)S and a ferroelectric substance in the form of $BaTiO_3$ are mixed at a ratio of 80:10:10 and dispersed in silicone resin to prepare a sample. FIG. **11** shows a relation between an amount of charge and applied voltage when voltage is applied on the sample in a dark space. Measurement is likewise taken on the anode side, and it will be seen that the charge of the same polarity with that of the electrode with which the mixture contacts in storaged in the mixture. It will thus be known that, by the addition of the fluorescent phosphor and the ferroelectric substance, the amount of charge increases in a logarithmic manner and great increase is effected especially in a high-voltage region.

2–6. Effect of joint use of semiconductor and metal

The effect of the invention can equally be obtained by a mixture of a semiconductor and a metal. Especially by employing a metal which may develop a photovoltaic effect through contact with a semiconductor, it is possible to vary an amount of charge stored in the mixture by varying the amount of light applied thereto. Cu_2O is now selected as the semiconductor showing the photovoltaic effect. Cu_2O, Cu and silicone resin are mixed at a ratio of 65 percent, 5 percent and 30 percent. In this case, both of Cu_2O and Cu are mixed in a powdered state. The mixture is coated on a Mylar film to provide a sample. The powder of Cu_2O and Cu may preferably have a similar grain size and may be as fine as possible, in the order of 2 to 3 microns. This sample is incorporated in a structure as shown in FIG. **2** and voltage is applied thereon in a dark or a light space. A plate of transparent conductive glass is selected as the electrode **7** in order to see an effect of illumination. FIG. **12** shows a relation between an amount of charge (in an arbitrary unit) stored in the mixture layer and a time of application of voltage of 600 volts with the transparent electrode **7** operating positive. Curves **29** and **30** therein show the characteristic in the dark space and the characteristic when illuminated with light of 100 luxes simultaneously with the application of voltage, respectively. From FIG. **12**, it will be apparent that the amount of stored charge was increased by the illumination, and in both cases, a positive charge is stored and has the same polarity with that of the electrode with which the mixture layer is in contact. This is considered that the amount of charge is increased due to the photovoltaic effect produced

by the combination of Cu_2O and Cu when subjected to light. It is further considered that this increased charge is not evolved from the interior of the mixture layer by the photovoltaic effect, but by additional charges drawn out of the electrode by an electric field produced by the photovoltaic effect.

FIG. 13 shows a decrement of the stored charges when left to stand in a dark and a light space. A curve 31 therein shows a variation in the amount of charge stored in the mixture when voltage of 600 volts is applied on the sample for 1 minute in a dark space with the transparent electrode operating positive and then the sample is left to stand in the dark space. A curve 32 shows a variation in the amount of charge stored in the mixture layer when voltage of 600 volts is likewise applied on the sample for 1 minute in a dark space with the transparent electrode operating positive and then the sample is left to stand while being illuminated with light of 100 luxes. From the curves, it will be seen that the charge decreases less in the light space than in the dark space. It is considered that this is because an electric field is formed by the photovoltaic effect between Cu_2O and Cu by the application of light and any extinction of the charge is thereby prevented. These phenomena are also observed, for example, in the combination of Se and Cd, and Si of P-type and N-type, in addition to the above-described combination of Cu_2O and Cu.

3. Effect of residual electric charge in insulator

In the recording device of the invention, the insulator 6 as shown in FIG. 2 is absolutely necessary. This insulator has a remarkable influence on the unipolar charge stored effect, and a great amount of storaged charge can be obtained by virtue of the presence of the insulator. Next description will be directed to the effect of such insulator.

A P-type semiconductor such as Cu_2O is mixed with silicone resin as in the former cases, and the mixture is coated on various insulators to provide samples having a structure as shown in FIG. 2. DC voltage and AC voltage are applied across the samples in superposed relation. In FIGS. 14 and 15, solid lines show a natural decay characteristic, or a variation in an amount of stored charge when the charge is first storaged in the samples by the application of DC voltage of 200 volts and AC voltage of 100 volts and subsequently the samples are left to stand at no load, while dotted lines therein show a relation between an amount of stored charge and a time of AC voltage application when AC voltage of 100 volts is solely applied. Curves 33 and 34, 35 and 36, and 37 and 38 in FIG. 14 represent the cases of a Mylar film, paper and a cyanoethylcellulose, respectively, while curves 39 and 40, and 41 and 42 in FIG. 15 represent the cases of polystyrene and polyethylene, respectively. Prominent results thereby obtained are that, although the charge decreases by the application of AC voltage in the Mylar film, paper and cyanoethylcellulose in which exists a residual electric charge due to absorption current, the charge would not decrease by the application of AC voltage in the polystyrene and polyethylene in which there exists almost no residual electric charge due to absorption current as shown in FIG. 15.

4. Effect of superposition of another layer on insulator layer

In the foregoing, the description has been made with regard to the recording device having the structure as shown in FIG. 2, but hereinunder, description will be made with regard to a structure wherein a fluorescent layer or a layer including therein a fluorescent phosphor, or a photoconductor layer or a layer including therein a photoconductor is superposed on the insulator 6 of FIG. 2.

4–1. Superposition of fluorescent layer including therein fluorescent phosphor

By superposing a fluorescent layer or a layer including therein a fluorescent phosphor on the insulator layer, an amount of electric charge can be varied by application of light thereto. FIG. 16 shows a structure of such device, which comprises a plate 43 of transparent conductive glass, a layer 44 including a fluorescent phosphor having an internal polarization effect, a layer 45 of an insulator, a layer 46 of a mixture of a semiconductor and an insulator, and a metal electrode 47. When, in this device, DC voltage is applied across the transparent conductive electrode 43 and the metal electrode 47, a layer of charges having the same polarity with that of the electrode 47 is formed at the face of the mixture layer 46 which contacts the metal electrode 47. When light is applied from the side of the transparent conductive electrode 43, the amount of charge in the fluorescent layer 44 varies and the amount of charge in the mixture layer 46 is thereby varied.

Now, suppose that the device of FIG. 16 comprises the fluorescent layer 44 of a mixture of (Zn, Cd)S and silicone resin, the insulator layer 45 of a Mylar film, and the mixture layer 46 of Cu_2O and silicone resin. FIG. 17 shows a relation between an amount of charge at the surface of the mixture layer 46 on the side of the metal electrode 47 and a time of voltage application when DC voltage of 500 volts is applied to the device while applying light of various illuminations. Curves 49, 50 and 51 therein show a case of voltage application in a dark space, and cases of illumination with light of 20 and 40 luxes simultaneously with voltage application, respectively. It will be seen that any of the charges has the same polarity with that of the metal electrode 47 and the amount of charge varies depending upon the illumination of light.

4–2. Superposition of photoconductive layer including therein photoconductor

In lieu of the fluorescent layer, a photoconductor layer or a layer including therein a photoconductor may be superposed on the insulator layer to vary the amount of charge by application of light. A photoconductor layer is substituted for the fluorescent layer in the structure of FIG. 16. The photoconductive layer comprises powder of cadmium sulfide dispersed in silicone resin and is coated in a thickness of about 60 microns on a plate of transparent conductive glass. Then a film of polyethylene terephthalate of 12 microns thick is bonded on the photoconductor layer, and a mixture layer comprising Cu_2O power dispersed in silicone resin is coated thereon in a thickness of 60 microns. A brass plate is used as an opposite electrode to obtain a structure as shown in FIG. 16. DC and AC voltages are applied in superposed relation across the transparent conductive glass electrode and the metal electrode. The AC voltage has a value of 100 volts at 60 cycles and the DC voltage is varied over various values with the metal electrode operating positive. A curve 52 in FIG. 18 shows a relation between the DC voltage applied in a dark space and an amount of charge in the mixture layer. From the curve 52, it will be seen that, in a dark space, the amount of charge of the same polarity with that of the metal electrode increases with relation to an increase in the DC voltage. Curves 53 and 54 show a variation of an amount of charge when the voltage is applied in the same manner under exposure with light of 20 and 100 luxes, respectively. In each case, the amount of charge increases at first with the increase in the DC voltage, but suddenly decreases at a certain voltage. The device with such structure is suitable for recording a signal in the form of light.

5. Application

In the foregoing description, detailed explanation has been given with regard to the unipolar charge storage effect forming the basic principle of the invention and this principle can readily be applied to provide various useful devices.

5–1. Electrophotography

Electrophotography has heretofore been carried out according to the following method. In the prior method, a high voltage of 5,000 to 6,000 volts is applied to generate a corona discharge to thereby charge ZnO sensitive paper or Se sensitive plate uniformly all over its entire surface. By projecting an image on the charged ZnO sensitive paper or Se sensitive plate, charges on portions hit by the light solely disappear due to photoconductivity of ZnO or Se. Therefore, charged portions and non-charged portions are formed on the ZnO sensitive paper or Se sensitive plate and a latent image is produced by the distribution of the charges. Development can be effected by applying thereto colored powder having charges opposite in polarity to the charges on the sensitive paper or plate.

There has also been proposed an electrophotography, that is, P.I.P. applied electrophotography which utilizes the persistent internal polarization effect of a fluorescent phosphor. According to such method, voltage of about 500 to 1,000 volts is applied on sensitive paper having thereon a fluorescent phosphor to charge the sensitive paper by the persistent internal polarization effect of the fluorescent phosphor. By projecting an image thereon, the charges on portions hit by the light solely disappear and a latent image of electric charges is formed on the sensitive paper. A photograph is obtained by developing the image in a manner similar to the former method. In any of both methods, the latent image on the surface of the sensitive paper is defined by charged portions and non-charged portions. Such manner of charge distribution is defective in that boundaries between the charged portions and the non-charged portions are not so clearly defined. Due to such drawback, in the P.I.P. applied electrophotography, an electric field opposite to the one used in the charging operation is simultaneously applied during the image projection to form the latent images on the surface of the sensitive paper by the charges of opposite polarities to each other to thereby improve the sharpness of the image. This method, however, involves a troublesome operation of changing over the electric field.

According to the invention, however, latent images with charges of opposite polarities to each other can be formed on the surface of sensitive paper by the utilization of the unipolar charge storage effect without any troublesome procedure of changing over the electric field. In the invention, a material adapted for the purpose comprises a mixture of a semiconductor and a fluorescent phosphor dispersed in an insulator and is incorporated in a structure as shown in FIG. 2. Fluorescent phosphors showing the persistent internal polarization effect are preferred, which are (Zn, Cd)S, ZnS, CdS and the like.

FIG. 19 shows a relation between an amount of charge and a time of voltage application in various samples. Measurement of the amount of charge is taken at the anode side. A curve 55 in FIG. 19 represents a case of a sample including a mixture of a semiconductor and an insulator. It will be seen that charges of the same polarity with that of the electrode with which the mixture contacts are formed in the mixture by the unipolar charge storage effect of the invention. The amount of charge is almost free from the influence of light. A curve 56 represents a case of a sample including a mixture of a fluorescent phosphor and an insulator, corresponding to the case of the prior P.I.P. applied electrophotography, and shows an amount of electric charge in a dark space. A curve 57 shows a variation in an amount of charge in a dark space in a sample including a fluorescent phosphor and a semiconductor dispersed in an insulator. It will be seen that the polarity of charge is reversed after a certain time. This is because the curve 57 is actually a resultant curve of the curves 55 and 56. A curve 58 shows a variation in the amount of charge when light is projected on the mixture of the fluorescent phosphor and the insulator simultaneously with the application of voltage, and it will be seen that the amount of charge increases with the application of light.

When light is projected on the mixture of the fluorescent phosphor, semiconductor and insulator, an increase in the amount of charge takes place solely in the fluorescent phosphor component, and a curve thereby obtained takes the form of a combination of the curves 55 and 58, or a resultant curve 59 in which it will be seen that the polarity of charge is reversed in a short time. When, therefore, the mixture of the fluorescent phosphor, semiconductor and insulator is used as a material for electrophotography, and an image is projected thereon under application of voltage, portions which are not hit by the light are charged in a manner as shown by the curve 57. Then, when the application of voltage and image projection are ceased at a time corresponding to point P, latent images of positive and negative charges are formed on the surface of the sample on the anode side thereof. A positive and a negative image can be obtained by applying colored powder which is charged negative and positive, respectively. According to the invention, an image of high sharpness can easily be obtained by virtue of the latent images by the positive and negative charges, unlike the prior electrophotography which relies on a corona discharge. Further, the wellknown P.I.P. applied electrophotography requires a troublesome operation of reversing the electric field, but according to the invention, the application of voltage and image projection are simultaneously made so that latent images of positive and negative charges can be obtained at a time. The invention is further advantageous in that a working voltage less than 800 volts suffices.

5–2. Audio and video recording device.

A prior video recording method comprises applying an electrical signal corresponding to pictures to a tape having thereon a ferromagnetic material to thereby record the signal in the form of a magnetic signal. According to the invention, however, video recording can be effected in a simple and inexpensive manner by the utilization of the unipolar charge storage effect. A tape 61 carrying thereon a mixture 60 having the unipolar charge storage effect is made to pass between electrodes 62 and 63 as shown in FIG. 20. The mixture 60 is composed of a semiconductor and an insulator, and the tape 61 is made of an insulating material such as a plastic, while the electrodes 62 and 63 are of brass of cylindrical shape. When voltage is applied across the electrodes 62 and 63, positive or negative charges are formed in the mixture 60 depending on the positive or negative polarity of the electrode 62. The amount of charge so formed corresponds to the magnitude of the applied voltage. By applying the voltage signal in the form of a video signal, charges corresponding to the video signal are formed on the tape. The charged tape can be preserved for an extremely long time in a dark space and for a fairly long time in a light space too. The charges will however disappear by application of an intense infrared light.

The charges thus formed on the tape are then detected by a detector 64, taken out in the form of an alternating current corresponding to potentials on the tape, and reproduced as pictures. An advantageous feature in this case is that the detector 64 need not abut the tape, which is therefore free from being injured. Further, the charges still remain on the tape even after they have been taken out as the electrical signal by the detector 64 and remain effective for repeated use. The charges carried on the tape can be erased by the application of an intense infrared light thereto and the tape is ready for subsequent video recording. According to the invention, it is possible to attain close recording of even minute portions compared with the prior method in which a magnetic material of considerable great size is used, and to obtain markedly high resolving power and fidelity which are of vital importance for a video recording device.

In accordance with the same principle, sound can likewise be recorded on the tape. By applying a voltage corresponding to a sound current to the tape, charges corresponding to the sound can be formed on the tape. The tape is then fed past the detector, which takes out the charges in the form of an electrical signal for reproduction of the sound. Other features can be derived as in the case of the video recording.

6. Summary

The particularities of the invention described in the above are summarized as follows:

1. The invention relates to a recording device which comprises a mixture of at least a semiconductor and an electrical insulator, a carrier transformer brought into contact with the mixture, another electrical insulator brought into contact with the mixture on the opposite side of the carrier transformer, and an electrode either directly or indirectly brought into contact with the another electrical insulator on the opposite side of the mixture.

2. The device according to the invention has a prominent effect that an electric charge is storaged in the mixture of the semiconductor and insulator, which charge has the same polarity with that of the carrier transformer with which the mixture is in contact.

3. An amount of charge stored in the mixture varies depending upon applied voltage and a time of voltage application, and can be preserved even in a light space.

4. When the semiconductor contained in the mixture is of P-type in which holes act as majority carriers, a remarkably greater amount of charge can be obtained than with a N-type semiconductor.

5. By the addition of a fluorescent body to the mixture, the amount of charge stored therein can be varied by application of light thereto.

6. By the addition of a ferroelectric substance to the mixture, the amount of charge stored in the mixture can be increased.

7. By the addition of both of the fluorescent phosphor and the ferroelectric substance to the mixture, the increased amount of charge stored therein can be varied by application of light thereto.

8. By the addition of a metal, which shows a photovoltaic effect in combination with the semiconductor included in the mixture, to the mixture, the amount of charge stored therein can be increased by application of light thereto.

9. By bringing the mixture into contact with an insulator such as polystyrene or polyethylene having little residual charge due to absorption current, the amount of stored charge can be abruptly varied by application of light and AC voltage to the mixture.

10. By interposing a fluorescent layer between the insulator and the electrode of transparent nature, the amount of charge stored in the mixture can be varied by application of light thereto.

11. By interposing a photoconductor layer between the insulator and the transparent electrode, the amount of charge stored in the mixture can be varied by application of light thereto.

12. By adding a fluorescent phosphor to the mixture of the semiconductor and the insulator, latent images of positive and negative charges can simultaneously be formed and thus it is possible to obtain a sensitive layer suitable for electrophotography having a remarkably high resolving power and sensitivity.

13. The device of the invention, when applied to audio and video recording, can provide a high degree of resolving power and fidelity.

From the foregoing detailed description, it will be understood that the present invention is based on a principle that a mixture of at least a semiconductor and an insulator is brought into contact with a carrier transformer, and electric charges are injected into the mixture from the carrier transformer in contact with the mixture, the charges being prevented from further movement by another insulator brought into contact with the mixture and thus storaged in the mixture. This principle has not been known at all in the prior art, and therefore the device of the invention based on this principle is quite novel.

What is claimed is:

1. A recording device comprising a cohesive layer of a mixture of semiconductor particles dispersed in an electrical insulator, a first electrode contacting one side of said layer, a solid electrical insulator having one side contacting the opposite side of said layer, a transparent second electrode disposed adjacent the opposite side of said solid electrical insulator, and a photoconductive layer interposed between and in physical contact with both said solid electrical insulator and said transparent electrode, said cohesive and photoconductive layers being coextensive with each other, the amount of said semiconductor particles dispersed in said cohesive layer being effective upon application of a voltage between said electrodes to result in a charge of the same polarity as said first electrode being stored in said cohesive layer.

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