SPECIFICATION

High Speed Electrophotographic Medium and Method

This invention relates to electrophotography and more particularly to an electrophotographic medium and to apparatus incorporating and a method of using said medium.

Silver halide film achieves its great speed in the case of the high speed variety by the process of development. The chemical reactions occurring in the development baths enable the achievement of ASA ratings which are of the order of hundred. Known electrophotographic media are much slower in speed than silver halide film because the latent image, when formed electrostatically, cannot be improved by further processing. This latent image is not a chemical image but is a latent charge image, being electrostatic; hence its character is established by the electrical properties of the medium and the phenomenon which produced the image, i.e. light etc.

Although a true comparison of speed between silver halide film and an electrophotographic film cannot actually be made on the basis of A.S.A or Din. rating, due to the definition of A.S.A rating, some general or roughly quantitative measure can be discussed. As stated, A.S.A ratings of silver film can extend from tens or twenties to as high as several hundred and even as high as 1000 for special film. Even low A.S.A. film can be processed in such a manner as to change its initial A.S.A. rating upward by a multiple of ten or twenty. It can be said generally that the higher the speed of silver halide film, the coarser the grain. This comment should be kept in mind in view of description of the electrophotographic medium which will be given below, since, resolution of an image on silver halide film depends upon the size of the grains of silver produced in the emulsion during development.

The known methods of electrophotography depend upon (a) charging a photoconductor surface, (b) selectively discharging the surface by means of a light or other radiant energy pattern and (c) toning to develop the latent charge image. Where the electrophotographic film used is of the type disclosed in U.S. Patent No. 4,025,339, the latent image may be read out by an electronic beam instead of toning. The speed and sensitivity of a given electro-photographic medium is related to the ability of the photoconductor to accept and to retain a charge, and its ability to discharge selectively in response to light, for example. These characteristics are inherent in the constitution of the photoconductor and its method of manufacture.

Once the latent charge image has been established on the photoconductor the duration of the image will depend upon the dark decay characteristics of the photoconductor, that is, its ability to resist self-discharge.

It has been known that a dielectric coating on a photoconductive medium will provide greater contrast than the same photoconductive medium without such coating and will enable longer retention of the latent image produced during exposure. So far as known, there has been no commercially successful medium which does not require the charging of the medium before its exposure. The inconvenience of the added step of charging and the expense of the accompanying requirement for apparatus to effect the charging when compared with a process that requires no charging obviously are great disadvantages.

The image can be transferred from the photoconductive layer to an insulating layer but the voltage which has been available for generating the latent image has been only the charge applied before imaging and retained on the medium.

One known method of imaging does not require prior charging but which has other disadvantages. Electrostatic images are produced on the surface of a dielectric film member while the dielectric member is in contact with a xerographic member. The assembly of layers compises a photoconductive layer on a conductive substrate such as metal or NESA glass which is transparent. The dielectric film member, with a conductive backing such as a transparent metallic coating, is placed in contact with the surface of the photoconductive layer. A high voltage of order of several thousand volts is applied between the conductive base of the photoconductive layer and the electrode. Simultaneously an optical image is projected onto the assembly, either through the back or front—whichever is transparent. After a brief exposure to light and the electric potential, the light is turned off and the dielectric member is separated from the photoconductor surface, the applied electric potential being maintained while this occurs. Thus it is recognized that there is an advantage to this process because the dark decay characteristic of the photoconductor need not be as great as required where it must be charged initially, exposed and then be required to retain the charge. No technique of this type is known to have been embodied in a commercial device. The important disadvantages to such technique and structure include:

A. The use of high voltage. Keeping a voltage of several thousand volts applied to members which are to be used is dangerous and leads to the need for expensive equipment and insulation materials.

B. The separation of the dielectric layer. Even at low voltages, stripping off a sheet member such as dielectric film is certain to produce breakdown of the gap and thereby deteriorate the latent image on the photoconductor and/or dielectric member.

C. The presence of the air gap. The bringing together of the dielectric member and the photoconductor cannot help but produce an air gap. The charges from the photoconductor therefore must cross the air gap in order to settle onto the dielectric member. It is impossible for the

air gap to be absolutely uniform as a result of which the transfer is uneven. There will be loss in the transfer because the air gap in addition to unevenness.

In any system which attempts to utilize an electrode and a dielectric layer, the electrode and layer must be intimately connected and the dielectric layer must be intimately connected with the photoconductive surface. Any spacing or gap produces discontinuities and unevenness. Furthermore, stripping the dielectric layer off the photoconductive layer after imaging produces sparking or corona discharge and destroys the latent image or at least, deteriorates the same. If the dielectric layer is bonded to the photoconductive surface, one must remove the electrode which means that the electrode must be removable, hence will give rise to a gap between electrode and dielectric during imaging. Among the disadvantages encountered are nonuniformity in charge distribution and the likelihood of breakdown as well.

Some experiments have been conducted by others attempting to increase the sensitivity of electrophotographic media using an assembly consisting of a photoconductive member having prepared CdSe layers and CdSe single crystals, mounted on a grounding member and mounting an insulating film thereon with a volatile conducting fluid serving as the electrode on top of the insulating film. The photoconductive layer was charged and then the insulating film was brought against the photoconductive surface to induce an image of the latent image from the photoconductor onto the insulating film. The volatile conducting fluid was connected to the grounding member to effect the transfer of charge to the insulating film without external application of voltage. When the volatile liquid evaporated, the film was stripped off the photoconductive layer. Then the insulating film was toned to develop the image. Images were believed to be stored for several months before there was substantial loss in total surface charge. Using such process, claims of achieving A.S.A ratings of the order of 100 were made with some samples going as high as 300 A.S.A.

Now, it would be desirable to obviate the need for pre-charging; to eliminate the requirement to separate any layer from another to provide for development of the latent image; to eliminate the problems of connecting the electrode in place and disconnecting it; and to eliminate all gaps either between the electrode and dielectric layer or between the dielectric layer and the photoconductive surface.

The speed and sensitivities of prior electrophotographic media, including the experimental ones described, are so low that the ability of the media to be exposed in nanoseconds if need be or to be discharged fully in similar times cannot be achieved and would not be expected. With respect to the ability of the electro-photographic medium to respond fully to radiant energy in nanoseconds, this is essential to a high speed film. Known photoconductive materials have extremely slow transit times, either because of the thickness of the required layers or because of the nature of the material. Highly intense light is required to achieve a large volume of carriers, even when assisted by external power sources. Speeds of the general order of 500 to 1000 A.S.A. cannot be achieved. Further, one could not expect to be able to read electrostatic images from such materials with electron beams because the time for discharge of the surface charge is too great.

It would be preferred that the transit time of the carriers in passing through the photoconductive layer of the electrophotographic medium would be less than the carrier lifetime thereby sustaining the electric field during carrier travel. Further, the entire bulk of the photoconductive layer should be depleted during use to ensure uniform transit of carriers without any variations because of zones of opposite energy states. For example, if the carriers are electrons, there should be no holes which form as a zone to make transit difficult.

If the electrophotographic layer can respond with extremely high speed and the sensitivity produced because of the external power supply produce a large volume of carrriers, the medium can respond to the most minute amount of light to produce large numbers of carriers in a short time. Ideally the exposure time should be the time that it takes for the bulk of carriers to move through the thickness of the photoconductive member. Time of the order of microseconds would be of considerable advantage.

Accordingly, the invention provides an electrophotographic medium adapted to be imaged by a particular type of radiant energy to achieve at least a latent charge image of a pattern of said radiant energy, said medium comprising a modulating structure consisting of a substrate that is transparent to said radiant energy, an ohmic layer of a thin film material deposited onto a surface of said substrate in a thickness to be transparent to said radiant energy, and a thin film photoconductive layer of a wholly inorganic, crystalline, uniformly ordered and oriented crystallite, dense material having a thickness of a degree to enable the transmission of said radiant energy with less than about 30% absorption, said crystalline layer being bonded to the surface of said ohmic layer opposite the substrate; a storage structure consisting of a layer of dielectric material that is highly insulating electrically, intimately and permanently bonded to the surface of the photoconductive layer opposite the ohmic layer, an electrode overlying the dielectric layer on the surface opposite the photoconductive layer and an interfacing, intimately connecting conductive film between the electrode and the dielectric layer, said film being of a nature to enable ready separation of the electrode from the dielectric layer; means for extending a connection from each of said ohmic layer and electrode to a relatively low voltage d.c. source; and said

electrophotographic medium adapted to have said pattern projected against the bottom of the substrate, through the substrate and ohmic layer and into said photoconductive layer whereby selectively to release charge carriers for modulated movement through said photoconductive layer to effect the synthesization of said projected pattern onto the surface of the photoconductive layer opposite the ohmic layer and thence by induction through and onto the surface of said dielectric layer.

Further, the invention provides in combination with said aforementioned electrophotographic medium, the electrophotographic medium in which the photoconductive layer is sputter-deposited cadmium sulfide of high purity but for dopant, if any, having a thickness which is between about 1000 and 8000 Angstroms; the ohmic layer is an oxide of principally indium sputter-deposited and having a thickness between about 100 and 500 Angstroms; the substrate is polyester having a thickness that is a fraction of a millimeter; and the dielectric layer is an inorganic material of a thickness greater than about 500 Angstroms but substantially less than a micron.

Additionally, the invention provides a method of producing a charge image of a pattern of radiant energy and making the same available for utilization which comprises: forming a multilayer sandwich of materials consisting of a substrate having a thin film layer of ohmic material bonded to one surface and a thin film layer of crystalline, sputter-deposited wholly inorganic, dense, highly ordered and oriented crystallite, substantially panchromatic photoconductor material bonded to said ohmic layer and a thin film layer of dielectric material bonded to the photoconductive layer, overlaying an electrode onto the layer of dielectric material and interposing a conductive film material between the electrode and dielectric layer to estabish an intimate bond therebetween, applying a low voltage source of d.c. between the ohmic layer and the electrode for a predetermined period of time, projecting the radiant energy pattern onto the photoconductive layer for the time that said connection is established whereby to release carriers from the photoconductive layer to effect the synthesization of a latent charge image of said pattern on the dielectric layer and removing the electrode and conductive film to uncover the dielectric layer.

The preferred embodiments of this invention now will be described, by way of example, with reference to the drawings accompanying this specification in which:

Figure 1 is a diagrammatic fragmentary sectional view through an electrophotographic medium illustrating the invention connected in a basic arrangement for use;

Figure 2 is a fragmentary sectional view similar to that of Figure 1 but illustrating a modified form of the invention;

Figure 3 is a highly simplified circuit diagram of the electrical equivalent of the basic electrophotographic medium of the invention;

Figure 4 is a simplified block diagram of apparatus used in connection with the invention to provide a practical system for utilizing the invention;

Figure 4A is similar to Figure 4 but shows only a portion of the block diagram for a modified form of control;

Figure 5 is a simplified block and symbolic diagram illustrating a modified form of the invention; and

Figure 6 is a fragmentary sectional view through a portion of the electrophotographic medium used in explaining the operation of the invention and a theory supporting the same.

Briefly, the concept of the invention is concerned with a modulating structure, field and current producing means, a storage structure and time control means. The modulating structure is responsive to radiant energy such as light to provide selective distribution of charge throughout the structure. The field and current producing means comprise an external current source that gives the necessary carriers for movement and establishes a driving field of constant intensity. The storage structure stores the image resulting from proper use of the invention. The time control means comprises switching means responsive to the conditions of the incident radiant energy for controlling the operation of the modulating structure to achieve optimum results. The time control means are operated by use of a radiant energy measuring device that is adjusted to take into account the properties of the modulating structure.

In the course of carrying out this concept, the sensitivity of the modulating structure when compared with its use in any previous manner has been so increased that the equivalents of A.S.A. ratings in the thousands have been achieved. In one example detailed below, it is shown how the A.S.A. rating of a practical example of the electrophotographicmedium of the invention is used to achieve an A.S.A. rating of the order of 30,000. This, of course, is completely outside of the scope of any known electrophotographic medium and even beyond the extent that sensitivity and speed which can be achieved with any known photographic medium.

When considering the ordinary electrophotographic medium, the photoconductive receptor of the medium has to be charged and this provides a surface potential which, with the resulting carriers in the medium, form the only basis for synthesizing an electrostatic image. The number of carriers is limited and the driving force decreases with time, being relatively low in any event. Even in the high gain electrophotographic medium of U.S. Patent 4,025,339, referred to above, the maximum surface potential utilized is of the order of 30 to 40 volts and potential decreases in darkness slowly, making the need for imaging as soon after charging as possible to have the benefit of the largest available electric field.

In the electrophotographic medium of the invention there is a fixed voltage connected between the ohmic layer and the electrode on top of the dielectric layer which furnishes a constant driving force, but more importantly, which furnishes an almost infinite source of carriers capable of being utilized to create the desired latent image. The driving force is substantially greater than that which can be achieved through the use of the electrophotographic film consisting only of the photoconductive layer and ohmic layer backed up by the substrate, this latter film comprising the modulating structure of the medium of the invention. Further, the storage capabilities of dielectric material are greatly improved over those of even the best of photoconductive materials so that retention of the resulting latent charge image is very substantially increased. For example, a latent image can be retained for perhaps a few minutes on some of the well-known photoreceptors before its quality starts to deteriorate. The electrophotographic medium described herein can retain images in high quality for months without deterioration.

Mention has been made of the fact that high speed silver halide films achieve their speed at the expense of grain size which is a result of the processing, among other reasons. In an imaging system and method to be detailed hereinafter, resolution of the image developed from a latent charge image is in no way related to the speed of the medium but is dependent upon the size of the particulate matter which is contained in the toner used or the diameter of the electron beam used to read the image electronically. This is because the type of photoconductive material which is preferably used to form the electrophotographic medium is a crystalline material that has individual field domains produced by crystallites that are less than a tenth of a micron in diameter thereby establishing the smallest line pair resolution of which the material is capable—namely 10,000 line pairs per millimeter.

The general effect of the phenomena occurring herein can be likened to amplification, where the carriers released by the photoconductive material are moved in a more efficient manner and in substantially greater amounts than in the case the photoconductive material were used without the dielectric layer on top and without the constant external d.c. voltage connected across the same.

In Figure 1 there is illustrated an embodiment of the invention during use thereof which comprises the modulating structure 10 and the storage structure 12.

The modulating structure is not greatly different from an electrophotographic film which is disclosed in said U.S. Patent 4,025,339. As a matter of fact, the film which is made for strict electrophotographic use according to the disclosure of said U.S. patent is completely suitable for use herein. The modulating structure 10 comprises a substrate 14 which is a sheet of polyester about a fraction of a millimeter in thickness and readily available commercially as manufactured by such chemical manufacturing companies as Celanese, DuPont, Kale and the like. It is flexible and transparent and quite stable. As described in said U.S. patent, there is an ohmic layer 16 deposited on the upper surface of the substrate 14 by sputtering techniques, this ohmic layer being preferably of the order of 100 to 300 Angstroms in thickness and also being transparent. It is preferably formed of indium tin oxide in the ratio of nine to one, respectively.

The photoconductive layer 18 also is deposited by sputtering and is laid down in a thoroughly bonded condition onto the surface of the ohmic layer as a thin film of the order of 3000 to 10,000 Angstroms thick. Even thinner films could be employed. The layer 18 is required herein to be transparent to a degree which does not substantially block the radiant energy that is intended to be projected through it, for example visible and ultra violet light, and yet it should be capable of absorbing sufficient of the radiant energy to cause the selective release of carriers. The degree of absorption of the radiant energy can be between 15 and 30%. The ohmic layer and substrate should absorb as little of the radiant energy as possible.

The preferred material for the layer 18 is pure cadmium sulfide for many reasons, not the least important of which is its panchromaticity. A fall off of response in the red end of the visible spectrum can be compensated for by selective doping if desired. When deposited the cadmium sulfide is crystalline in composition with crystallites that are very uniform and highly ordered in a vertical direction, that is perpendicular to the plane of the substrate surface. The crystallites are hexagonal, about 600 to 800 Angstroms in diameter, result in a highly dense deposit with the boundaries between crystallites very tight. The surface of such a deposit is electrically anisotropic and has a surface resistivity of the order of 10^{20} ohms per square due to the formation of a barrier layer. Dark decay is such that normal use of such a film enables it to be charged and not imaged for hours thereafter. This characteristic is nonetheless of sufficient speed to require certain precautions to be taken in the event that the electrophotographic medium of the invention is not going to be developed immediately after imaging, as will be explained hereinafter.

The dark resistivity of the photoconductive layer 18 is about 10^{13} ohm centimeters laterally in the bulk and its light resistivity in the same dimension is about 10^{8} ohm centimeters. This dimension, described as "laterally" is parallel to the plane of the surface of the substrate. This ratio of 10^{5} is of importance in the bulk of the photoconductive layer because of the manner in which the material is used herein. The same ratio exists between the resistivity of the cadmium sulfide layer 18 in light and darkness transversely in the bulk, that is perpendicular to the plane of the surface of the substrate. This is an important characteristic in order to assure the production

and transport of substantial numbers of carriers and the differentiation between those portions which are affected by photons and those which are not.

When the modulating structure 10 has been completed or prepared a dielectric layer 20 of insulating material is deposited thereon. This layer is preferably about 1000 to 3000 Angstroms thick and may be formed of an inorganic material that is capable of being sputtered so that the same equipment may be used to sputter the same as used for the ohmic layer 16 and the photoconductive layer 18. Several chemicals can be used including insulating silcon oxides such as SiO_2 and SiO, silicon nitride (Si_3N_4), aluminium oxide (Al_2O_3) and the like. The deposit of the layer 20 should be carried out in such a manner as to provide complete and intimate bonding. Sputtering will assure this as could vapor deposit if feasible for the particular substance.

After the dielectric layer 20 has been laid down, the resulting article is ready to be used. A key consideration is the fact that there is required to be an electrode 22 serving as a capacitor plate which must be used in order to provide the fixed field for moving the carriers, this electrode 22 being removable. The storage structure 12 includes the electrode 22, although the electrode 22 and the dielectric layer 20 are separable and need not even be brought together until the electrophotographic medium is ready for use. It is important that the electrode be in place when the medium is being used to produce an image; hence its inclusion as part of the storage structure.

In Figure 1 the electrode 22 is a thin plate or band of some metal such as aluminum, copper, steel or the like. It is laid on top of the dielectric layer with an intervening film 24 of conductive material. This film 24 is required to provide the physical conductive interface or connection between the electrode 22 and the dielectric layer 20 and should be as thin as possible. In Figure 1 the film is formed of a liquid which could be as simple as a saline solution so that it conducts properly, possibly containing a wetting agent of some kind that is miscible with the saline solution so that the surface tension of the liquid is lowered for better wetting and intimate contact. One of the liquids which could also be used is a conductive organic solvent such as the type of liquid polymer used to make paper conductive when producing zinc oxide paper for electrophotographic use. One example is Merck Conductive Polymer 261 sold by Merck & Co., Rahway, New Jersey, in aqueous solution.

In order to use the electrophotographic medium 10, 12 a d.c. voltage source 26 in the form of a simple battery or the like is connected between the electrode 22 and the ohmic layer 16 by means of the leads 28 and 30, there being a switch 32 in the lead 28. The lead 30 can be at ground potential which is convenient for making connection with the ohmic layer 16. A pattern of radiant energy such as a light scene as indicated by the arrows 34 is projected through the bottom surface of the substrate and through the substrate 14, the ohmic layer 16 and the photoconductive layer 18. The switch 32 is closed for the time that exposure is to be made, this time being of the order of microseconds or even nanoseconds if desired or required. During this period of time there will be a selective movement of carriers which, in the case that the photoconductive layer is cadmium sulfide or other N-type material, will comprise electrons. These electrons will move toward the ohmic layer 16 leaving the interface between the photoconductive layer 18 and the dielectric layer 20 more positive where increments were subjected to the impingement of radiant energy and less positive, that is, remaining negative where increments were not subjected to radiant energy. In other words, if the radiant energy 34 comprises visible light, the light increments at the surface of the photoconductive layer 18 would be positive while the dark increments could be negative. They could be neutral as well assuming that there was absolutely no movement of electrons at all.

It can be realized that in the case of normal use of the modulating structure 10 as an electrophotographic film, the film would be charged negative on its surface, the projected light would cause transit and recombination of the electrons so that the light increments would become positive while the dark increments would remain negative. This, then would form the latent image in the same manner as in the case of the electrophotographic medium described herein except that a substantially greater number of carriers would be available in the case of the invention.

One can consider the electrical effect as described by saying that positive charges move toward the interface between the photoconductive layer 18 and the dielectric layer 20 but the fact of the matter is that in the case of N-type material such as cadmium sulfide there are no mobile holes as such. These immobile "holes" may be considered positive energy states whose conditions are affected by the movement of the carriers, which in this case comprise electrons. In Figure 6, the effect of closing the switch is illustrated in the electrophotographic medium in two zones, one being light and the other darkness.

In the light zone, there are shown two positive charges at 40 which seem to move from the ohmic layer 16 toward the dielectric layer 20 to come to rest at 42 on the bottom of the layer. As a result of their presence, an equal and opposite charge is induced through capacitor action on the opposite surface of the dielectric layer 20 indicated by the negative charges 44. In actuality, however, the movement was that of the only mobile carriers, namely the electrons. Thus, two electrons 46 are shown moving toward the ohmic layer 16. The effect of this movement was to leave more positive increments in the interface between the photoconductive layer 18 and the

dielectric layer 20, believed to be in the barrier layer of the photoconductive layer 18.

Where there is darkness, we see the positive charges at 48 and the negative charges at 50 which have not moved. Assuming that these negative charges 50 were linked to positive charges 52 and thereby neutralized, there would be no charge at all at the interface and hence none on the surface of the dielectric layer in the dark zone. Relative to the high negative charge at 44 the uncharged increment in darkness is positive, but whatever the situation, there is a substantial charge gradient between the dark and the light increments which will be stored because the dielectric material has infinite resistivity on its surface as well as throughout its bulk with no leakage, normally.

After exposure, the electrode 22 is lifted off the dielectric layer 20 and by capillary action because of the film 24 being quire thin (of the order of a few hundred Angstroms, ideally) most of the liquid of the film 24 will also be lifted off. A blast of air can blow off that which remains, which being nominal, has no effect.

Since the dielectric material is an electrical insulator as explained, the charges are captured just as they would be in an efficient capacitor or on the surface of an efficient insulator. These charges are selectively distributed in accordance with the distribution of radiant energy projected through the medium. Furthermore, they will remain in place as an integrated image for long periods of time—as much as several months without deteriorating. Thus, several of the articles could be kept in a camera and exposed over a period of time with the images lasting until the articles are removed from the camera for processing.

The thinness of the medium and including the dielectric layer, render the same quite flexible and capable of being stored in a cartridge in rolled form and dispensed therefrom, being moved into position to be exposed and the electrode 22 laid onto the dielectric layer 20. The liquid 24 could be automatically dispensed from the same cartridge as the article is dispensed from the cartridge.

In the development of the latent charge image any suitable technique can be used. This includes the reading of the information by electron beam, toning the surface and fixing the developed image directly onto the surface to make a transparency, toning the image and transferring the toner, etc. In cases where the development is not effected immediately, precautions can be taken to prevent the image from being altered by drifting those carriers in the photoconductor which persist after the switch 32 has been opened. This will be explained below in connection with Figure 5.

There is some criticality in the timing of the switch 32 which is to be considered in building apparatus for the use of the medium 10, 12. It is essential that the latent charge image be formed in the most efficient manner and this requires a condition where the maximum of carriers reach the interface between the dielectric layer 20 and the photoconductive layer at the same time. If the electric current is cut off by opening the switch 32 before that condition occurs, the image will not be fully formed; if the electric current is permitted to flow after that condition occurs, carriers will continue to be moved after the image has formed and the image will be swamped. If the switch 32 is held in closed position long enough, the entire image will be lost in fog since the entire surface of the photoconductor will pick up charge without discrimination as a condenser fully charged. Once the exposure has been completed, the switch 32 is opened, the two electrodes are momentarily grounded and the latent image retained on the dielectric layer 20.

The thinness of the photoconductive layer 18 of the modulating structure 10 is such that there is an extremely short transit time. This time as a general rule will be microseconds or nanoseconds. Thus, the average time of transit of the carriers is chosen to be the time that the switch 32 is closed and this will be the time of exposure. There will only be one length of duration for a given image which is the optimum, this length of duration varying with the conditions of exposure, that is, the intensity of the radiant energy, the spectral response of the photoconductor, the relative intensity of the different parts of the pattern, and perhaps other factors such as temperature and the like. Good results can be expected, however, with variations of an order either way.

In order to achieve this precise time, the switch 32 is preferably operated by automatic means, such as electronic switching circuits. The radiant energy is sampled by means of photoresponsive device, for example, and provides a signal that is compared with a reference signal to achieve a third signal that operates the switch. This technique and apparatus for practicing the technique are disclosed in U.S. Patents 3,864,035 and 3,880,512. Application of this technique to the instant invention is explained in connection with Figure 4 hereinafter.

In Figure 2 there is illustrated a modification of the invention which differs from that of Figure 1 only in the construction of the electrode 22 and the film 24 and the resulting change in the method of the invention.

The dielectric layer 20 is here shown with a film 60 that is the equivalent of the film 24 but is of metal. By using any of the conductive low melting point metals known as fusible alloys, such as for example Wood's metal, intimate contact can be ensured between the electrode 62 and the dielectric layer 20 if the film 60 is molten before the exposure is made. Thus, the electrode 62 may be arranged to have a bond or strip of the solid metal led along its lower surface much in the form of a shoe with a band on it. When the article comprising the substrate 14, ohmic layer 16, photoconductive layer 18 and the dielectric layer 20 is ready to be used, it is placed in position and the shoe-electrode 62 brought into position on

the upper surface of the dielectric layer 20. Heating elements 64 contained in the shoe-electrode 62 are energized electrically melting the metal on the bottom of the shoe-electrode 62 to form the liquid film 60. This film 60 establishes completely intimate contact between the shoe-electrode 62 and the surface of the dielectric layer 20. Whether the liquid metal solidifies slowly thereafter or not is of no consequence so long as the intimate contact is retained. If desired, the heating elements 64 can be kept energized during the exposure step.

The exposure takes place by closing the switch 32 for a time duration that ideally is the average transit time for the carriers to pass through the photoconductive layer 18 and reach the dielectric layer 20 and thereafter the film 60 is permitted to solidify. The shoe-electrode 62 can have conduits or manifolds 66 capable of carrying coolant therein to cause the molten metal film 60 to solidify. The electric current in the heating elements 64 has in the meantime been discontinued. After the film 60 solidifies, the shoe electrode 62 is lifted off the upper surface of the dielectric layer 20. It has been found that the film 60, if it does not come off directly with removal of the shoe-electrode 62, is easily and cleanly capable of being peeled off the surface of the dielectric layer 20 since it has very low affinity for the insulating surface of 20, certainly much less than it has for the metal of the shoe-electrode.

The bottom of the shoe-electrode 62 can be made out of the fusible alloy and used over and over again, the alternate melting and solidifying having no effect on the efficiency of the apparatus. An alternate form would be a heating pot disposed above or slightly to the rear of the location where the electrophotographic medium is to be exposed. The pot deposits a layer of the fusible alloy onto the surface of the dielectric layer. Exposure takes place by means of a slit and the electrophotographic medium is moved away from the pot carrying the thin layer of solidified metal with it, this layer thereafter being raised as by tilting the remaining part of the medium downward, it being quite flexible, and fed back into the pot.

From the above discussion, one can appreciate that since there is no preliminary charging, there is no need to keep the electrophotographic medium in darkness and hence no need for a shutter or any structure to provide for blocking light at any time. In a suitable imaging device such as a camera or duplicator the projected pattern can be directed against the bottom of the substrate 14 at all times. Nothing will happen until the switch 32 is closed and only so long as it is closed. This is an ideal situation because it permits the apparatus for using the electrophotographic medium 10, 12 to be extremely simple.

In Figure 3 there is illustrated a simple diagram showing the theoretical equivalent of the structure according to the invention. The dielectric layer 20 acts as a condenser 67 to store charge which will run into the condenser depending upon the values of the other elements of the system. The condenser 68 and variable resistor 70 represent the effect of light and darkness on the photoconductive member, changing the impedance of which provides the selective pattern of carriers. The voltage of the source 26 moves these carriers at a rate and to the extent that is permitted by the relative impedance of the elements.

As pointed out above, the ideal exposure time is related to the degree of radiant energy to which the electrophotographic medium is exposed. The properties of the medium must also be taken into consideration. In Figure 4 there is illustrated a block diagram which represents apparatus for carrying out the mandate of the requirement that the time of exposure be as nearly equal as possible to the average transit time of the carriers produced.

The switch 32 in this case is an electronic switch which is operated by a timer driver circuit 70 that turns it on and off through line 71 at a particular time depending upon the nature of the signal on the control line 72 coming out of the comparator 74. There is a photoresponsive device 76 which intercepts a small portion of the radiant energy 34 to sample it. This is a transducer which produces a change in current or voltage that appears on the channel 78 leading to the control signal device 80. This control signal device can be adjusted for various conditions to provide a first signal at 82 that is fed to the comparator 74. A reference signal that can be adjusted for various conditions of the electrophotographic medium is produced in a circuit 84 and applied to the comparator 74 through the line 86.

This circuitry merely is suggestive and can readily be worked out to achieve the desired end, namely—to provide a timing signal that will close the switch 32 for a time duration that will give the best exposure for the conditions of the incident radiant energy 34. This is done in U.S. Patent 3,880,512 in a slightly different manner. In that patent, the average light of an image or scene is used to control the degree of charge of an electrophotographic film or the charging level is fixed and the amount of light varied. Herein, the time of exposure is controlled in the preferred version since there is no charging of the film, the field and carrier driving voltage being constant. The adjustments required are made for the particular characteristics of the photoconductor and to be certain to get the desired comparison signal from the photoresponsive device sampling the radiant energy.

In the apparatus of Figure 4, the process may be started manually by a switch or push button 88 that turns on the power supply 91 through the line 92, this power supply energizing all of the electrical components of the apparatus through suitable connections, generally and symbolically indicated at 94. The apparatus will turn itself off by means of the timer driver 70 that times the

duration and turns the switch 32 on and off at the appropriate instants.

An alternate form of circuitry would have the blocks shown in Figure 4A, all other parts of the apparatus being the same as in Figure 4. Here, instead of varying the duration of exposure, a suitable fixed duration is chosen which is within the range expected for the particular kind of photoconductor and the conditions under which it will be used, and instead the d.c. voltage is varied for the changes in radiant energy. Thus, the switch 32′ is a fixed time duration closing switch. When energized it will automatically close for a fixed time and then automatically open, the exposure taking place during this fixed duration. The comparator 74 receives the same signals and make a comparison to provide an output signal on the line 72′ which now extends to a driver 70′ that in turn automatically adjusts the voltage of the variable d.c. supply 26′ through the channel 71′. The same effect is achieved, that is, the exposure duration is adjusted to be as close as possible in time to the average transit time of the carriers. For higher intensities of radiant energy the voltage will be lower than for lower intensities of radiant energy. The driver 70′ can simply furnish power to a small motor driving the slider of the potentiometer of a voltage divider.

Where the latent charge image is immediately read out by electronic scanning there is no problem with carriers that have not completed their transit, and there will always be some of those. If the image is to be stored, however, the dark decay characteristic of the photoconductive layer 18 will continue to move those slow carriers towards the surface of the layer 18. If there are enough of these drifting carriers they will cause deterioration of the latent image as they arrive. It should be recalled that the field for movement of carriers is still present internally, however slow the movement may be. Accordingly, after the image has been established and the electrode 22 has been removed, another electrode 90 is moved over the dielectric layer 20 but is spaced therefrom. A reverse voltage, i.e., having an opposite polarity relative to the voltage used during exposure is applied. Thus, for an N-type material such as cadmium sulfide the ohmic layer will now be connected to a negative terminal of a power supply while the electrode 90 is positive. Electrons will tend to flow in the opposite direction thus neutralizing those carriers as electrons which were moving towards the ohmic layer leaving positive charges. This will have no effect upon the image which is carried on the dielectric layer surface because there is no contact with the electrode 90 and there is an intervening air gap.

In Figure 5 the timer 70 represents a circuit somewhat like that of Figure 4 and is shown to represent the fact that the exposure of the medium occurs in a timed manner by connecting the voltage source 26 as indicated in Figure 1, for example. A ganged switch 92 is shown having the two poles 94 and 96 connected respectively to the negative line 28 and the positive line 30. The contacts 98 and 100 are engaged by the switch arms 102 and 104 during exposure, but as soon as the switch is thrown to the other contacts, these arms 102 and 104 engage the contacts 106 and 108, respectively reversing the polarity. The contacts 106 and 100 both connect through the line 110 to the ohmic layer 16. The contact 98 connects through the line 112 to the electrode 22. The contact 108 connects through the line 114 to the electrode 90.

The apparatus is required to move the electrode 90 into position mechanically after the electrode 22 has been removed and this can be done automatically by the same timing device 70 that operates the switch 92. The line 116 energizes a driver 118 that has a mechanical connection 120 with the electrode 90 to move the same.

A computation of the A.S.A rating of an electrophotographic article of the invention using cadmium sulfide as the photoconductive layer is made hereinafter.

A daylight scene on a cloudy day shows a highlight illumination of 200 candles/foot^2. In deep shadows, the illumination is about 1% of this value or 2 candles/foot^2.

Tests made on a typical electrophotographic film where the photoconductive material is pure cadmium sulfide of about 3500 Angstroms thickness have shown that through a lens opening of 1.8 the resistance of the cadmium sulfide will vary from 1.1×10^3 ohms/cm^2 for highlights to 1.1×10^5 ohms/cm^2 in the shadows. This test involves using the film as a photocell.

If the dielectric layer 20 has a capacitance C of 2×10^{-8} farads/cm^2, which is typical of the materials mentioned, the time constant RC will be

$$T=2.2\times10^{-5} \text{ second in highlights}$$

and

$$T=2.2\times10^{-3} \text{ second in shadows.}$$

At an exposure time of 33 microseconds, the factor t/RC (t=time of exposure) is

$$1.5 \text{ for highlights } e^{-t/RC}=.223$$

$$0.015 \text{ for shadows. } e^{-t/RC}=.985$$

During the exposure time, which incidentally has been chosen as a rough estimate of the average transit time for carriers through the photoconductor layer, the capacitor of which the structure 10, 12 is the equivalent, will charge. The voltage V attained is computed by the formula

$$V=V_o(1-e^{-t/RC})$$

where V_o is the applied d.c. voltage across the condenser plates (16 and 22) and e is the Napierian constant.

Under the assumed conditions the dielectric layer 20 will charge to

.77 V_o in the highlights

and

.015 V_o in the shadows

Using the assumptions made above, it is estimated that in order to get the same reponse from a silver halide black and white film under the light conditions given, its A.S.A. rating would have to be of the order of 30,000. No such film is known, so far as we are aware.

Incidentally, it should be clear from the above that the time of exposure, that is, charging time of the equivalent capacitor must be such that the factor of

$$\frac{t}{RC}$$

must be between zero and unity, preferably as close to unity as feasible. Transit time across the cadmium sulfide can be approximated by the mobility of the carriers multiplied by the thickness of the layer 18, assuming that the distance travelled is the full thickness.

As mentioned, the layer 18 is preferably cadmium sulfide in its pure sputtered condition. Doping with carbon, copper, or other substances will enable varying the spectral response and even increasing the quantum gain in certain cases. Other substances can also be used as the photoconductive layer, such as zinc sulfide (ZnS) and mixtures of zinc sulfide and cadmium sulfide; zinc telluride (ZnTe), arsenic trisulfide (As_2S_3); zinc selenide (ZnSe); zinc indium sulfide ($ZnIn_2S_4$); cadmium selenide (CdSe); cadmium telluride (CdTe); gallium arsenide (GaAs); and antimony trisulfide (Sb_2S_3).

Variations in thickness of the several layers can be made as well without leaving the scope of the invention. The dielectric layer 20 can be quite thin, i.e., less than 1000 Angstroms if desired. It serves additionally as a protective cover for the photoconductive layer and should be deposited very uniformly. Thick layers, i.e., 1000 Angstroms and up are easier to deposit.

It has been described above that the apparatus of the invention requires no shutter inasmuch as there will be no production of carriers until the simultaneous occurrence of the projection of the radiant energy through the electrophotographic medium and the establishment of the connection with the voltage source 26. Thus, in making an image, one need only keep the scene or pattern of radiant energy projected upon the medium and close the switch for the desired time. This is the preferred method because it eliminates the need for shutter and mechanisms to drive the shutter. It is, however, quite feasible to utilize shutters and shutter mechanisms such as for example, those which may be in the possession of the user and control the time of exposure thereby. In such case, the switch 32 would be closed for a period before the image is to be projected, remaining closed until after the image has been projected. The shutter is then adjusted to expose the film to the scene for the period of time desired, say for example, a thousandth of a second (1×10^{-3}) or less. the electrophotographic medium will otherwise remain in darkness.

The claims should be interpreted with the understanding that both of the methods may be used, that is, the shutterless preferred method and the method of exposure using a shutter. The constructed apparatus can be used in either manner.

From the above it will be seen that the invention can be used under adverse light conditions to produce images which are readily available for development. As an example, aerial cameras can make high resolution photos of the terrain at high speeds at light levels no greater than moonlight without using complex shutters and lens systems. Many other uses will suggest themselves to those skilled in this art.

Claims

1. An electrophotographic medium capable of being imaged by a particular type of radiant energy to achieve at least a latent charge image of a pattern of said radiant energy, said medium comprising: a modulating structure consisting of a substrate that is tranparent to said radiant energy, an ohmic layer of a thin film material deposited onto a surface of said substrate in a thickness to be transparent to said radiant energy, and a thin film photoconductive layer intimately bonded to the ohmic layer; a storage structure consisting of a layer of dielectric material that is highly insulating electrically, intimately bonded to the surface of the photoconductive layer opposite the ohmic layer, an electrode overlying the dielectric layer on the surface opposite the photoconductive layer and interfacing, intimately connecting conductive film between the electrode and the dielectric layer, said film being of a nature to enable ready separation of the electrode from the dielectric layer; means for extending a connection from each of said ohmic layer and electrode to a relatively low voltage d.c. source; and said electrophotographic medium capable of receiving said pattern projected against the bottom of the substrate, through the substrate and ohmic layer and into said photoconductive layer whereby selectively to release charge carriers for modulated movement through said photoconductive layer to effect the synthesization of said projected pattern onto the surface of the photoconductive layer opposite the ohmic layer and thence by induction through and onto the surface of said dielectric layer.

2. The combination according to claim 1 in which the conductive film comprises a liquid of conductive material disposed between the electrodes and the dielectric material.

3. The combination according to claim 1 in which the conductive film comprises a fusible metal alloy and the electrode includes means for enabling the heating of the electrode to melt the metal under control to establish the intimate

.77 V_o in the highlights

and

.015 V_o in the shadows

Using the assumptions made above, it is estimated that in order to get the same reponse from a silver halide black and white film under the light conditions given, its A.S.A. rating would have to be of the order of 30,000. No such film is known, so far as we are aware.

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2. The combination according to claim 1 in which the conductive film comprises a liquid of conductive material disposed between the electrodes and the dielectric material.

3. The combination according to claim 1 in which the conductive film comprises a fusible metal alloy and the electrode includes means for enabling the heating of the electrode to melt the metal under control to establish the intimate

connection, said fusible metal alloy when solidified being readily separable from said dielectric layer.

4. The combination according to claims 1 to 3 in which the modulating structure and the dielectric layer are highly flexible.

5. The combination according to claims 1 to 4 in which the combined thickness of the ohmic layer, photoconductive layer and dielectric layer is substantially less than one micron whereby to render the medium highly flexible without the electrode.

6. The combination according to claim 3 in which the electrode includes means for cooling the electrode to solidify the metal under control.

7. The combination according to any one of claims 1 to 6 in which the photoconductive layer is formed of a sputter-deposited, N-type material and the charge carriers are electrons.

8. The combination according to any one of claims 1 to 7 and a source of relatively low d.c. voltage connected to the ohmic layer and electrode and poled with regard to the type of mobile carriers producible by the photoconductive layer to provide a large number of available charge carriers for movement through the photoconductive layer and a field to drive the charges, switch means in the connection between the source and the medium adapted to be closed for a predetermined time to enable exposure of the medium to a pattern of said radiant energy, and means for enabling the projection of a pattern of said radiant energy through one of said electrode and substrate, through said photoconductive layer whereby selectively to release charge carriers for modulated movement through said photoconductive layer to effect the synthesization of said projected pattern onto a surface of said dielectric layer, said enabling means comprising circuitry for operating said switch means to close said connection and effect exposure to said pattern.

9. The combination according to claim 8 in which the switch means are adjusted so that the time of closure of the switch means in any event is approximately the average time of transit of carriers through said photoconductive layer.

10. The combination according to claims 8 or 9 in which means are provided for varying the time of closure of the switch means, said voltage source being arranged to provide a constant voltage during exposure for all conditions of said radiant energy intensity.

11. The combination according to claims 8 or 9 in which means are provided for varying the voltage of the voltage source, said switch means being arranged to be closed for a constant time of exposure for all conditions of said radiant energy intensity.

12. The combination according to any one of claims 8 to 11 and means are provided to measure the projected radiant energy which is projected to said medium to provide a first electrical signal representative of the intensity of the energy, means are provided to produce a second electrical signal as a reference which is related to electrical characteristics of the photoconductive layer, means are provided to compare the two signals to derive a third difference electrical signal, and means are provided for varying one of the time of closure of said switch means and the value of voltage of said source while keeping the other constant in accordance with the value of said third electrical signal.

13. The combination according to any one of claims 8 to 12 in which means are provided for moving a second electrode relative to the dielectric layer after exposure and removal of the first electrode and applying a d.c. voltage between the second electrode and the ohmic layer which is poled opposite to that applied during exposure whereby to neutralize slowly moving charge carriers remaining in the photoconductive layer after exposure.

14. The combination according to any one of claims 1 to 13 in which the photoconductive layer is sputter-deposited cadmium sulfide of high purity but for dopant, if any.

15. The combination according to any one of claims 1 to 13 in which the photoconductive layer is sputter-deposited cadmium sulfide of high purity but for dopant, if any, having a thickness which is between about 1000 and 8000 Angstroms; the ohmic layer is an oxide of principally indium, sputter-deposited and having a thickness between about 100 and 500 Angstroms; the substrate is polyester having a thickness that is a fraction of a millimeter; and the dielectric layer is an inorganic material of a thickness greater than about 500 Angstroms but substantially less than a micron.

16. The combination according to any one of claims 1 to 13 in which the photoconductive layer is cadmium sulfide of high purity but for dopant, if any; the ohmic layer is principally indium oxide; and the dielectric layer is an inorganic material selected from the group comprising silicon oxide, silicon dioxide, aluminum oxide and silicon nitride.

17. The combination according to claim 15, wherein the ohmic layer is sputter-deposited indium-tin oxide; and the dielectric layer is silicon nitride about 500 to 3000 Angstroms thick.

18. The combination according to any one of claims 1 to 17 in which the negative pole of the source is connected to the electrode.

19. The combination according to claim 13 in which the same voltage source is used to apply both voltages and the switch means include reversing contacts.

20. A method of producing a charge image of a pattern of radiant energy and making the same available for utilisation which comprises: forming a multilayer sandwich of materials consisting of a substrate having a thin film layer of ohmic material bonded to one surface and a thin film layer of crystalline, sputter-deposited wholly inorganic, dense, highly ordered and oriented crystallite, substantially panchromatic photoconductor material bonded to said ohmic

layer and a thin film layer of dielectric material bonded to the photoconductive layer, overlaying an electrode onto the layer of dielectric material and interposing a conductive film material between the electrode and dielectric layer to establish an intimate bond therebetween, applying a low voltage source of d.c. between the ohmic layer and the electrode for a predetermined period of time, projecting the radiant energy pattern onto the photoconductive layer for the time that said connection is established whereby to release carriers from the photoconductive layer to effect the synthesisation of a latent charge image of said pattern on the dielectric layer and removing the electrode and conductive film to uncover the dielectric layer.

21. The method according to claim 20 in which the conductive film comprises a liquid of conductive material captured between the electrode and the layer of dielectric material and in the process of overlaying and interposing, the liquid is applied.

22. The method according to claim 20 in which the conductive film comprises a fusible metal and the method includes melting the metal when the electrode is applied to establish the intimate connection, and solidifying the metal at least after exposure and stripping same off the dielectric layer at the time of removal of the electrode.

23. The method according to any one of claims 20 to 22 in which the time of projection is chosen to be approximately the average time of transit of the carriers through the photoconductive layer.

24. The method according to any one of claims 20 to 22 in which the intensity of the radiant energy is measured and an exposure time is used which has a relation to the measurement while holding the voltage applied by the d.c. source constant.

25. The method according to any one of claims 20 to 22 in which the intensity of radiant energy is measured, the exposure time is maintained at a constant value and the voltage applied to the ohmic layer and electrode is adjusted to have a relation to the measurement.

26. The method according to any one of claims 20 to 25 in which the medium is exposed to radiant energy for at least a period of time which is greater than the period of time that the connection is established and includes the latter period of time.

27. The method according to any one of claims 20 to 25 in which the medium is exposed to radiant energy only for a predetermined period of time while otherwise being retained in darkness, the connection being established for at least a period of time which is greater than the time of exposure and includes the latter time.

28. A method substantially as herein described with reference to and as illustrated in the accompanying drawings.

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