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PHOTOCONDUCTIVE LAYER FOR RECORDING ELEMENT
AND METHOD OF PRODUCING SAME
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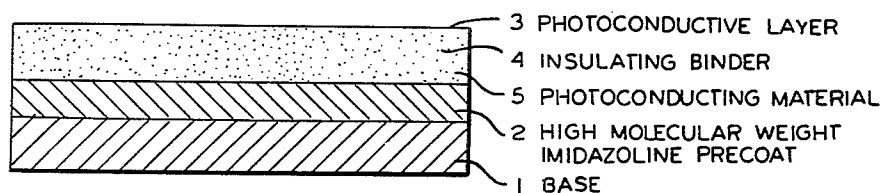


FIG. 1

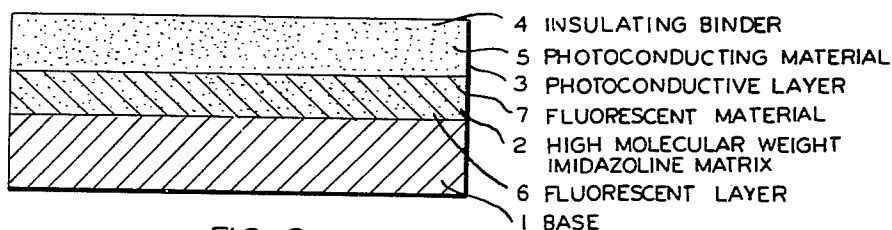


FIG. 2

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PHOTOCONDUCTIVE LAYER FOR RECORDING ELEMENT AND METHOD OF PRODUCING SAME

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15 Claims. (Cl. 96—1)

This invention relates to the general art of electrophotography and electroradiography and particularly to a new and improved electrostatic recording element and a method of producing same. More specifically, the invention relates to an electrophotographic member having a backing or support rendered electrically conductive by means of certain surface active compounds.

In the art of producing images or visible records by electrophotographic methods, a base plate or support is coated with a layer of photoconducting material which is then electrostatically charged in the dark. The charged layer is next exposed to light beneath a pattern such as a negative photographic film, positive film or a mask or other suitable light image whereupon a latent electrostatic image is formed upon the photoconductive surface. Such a latent image is produced by the dissipation of the electric charges in proportion to the intensity of light to which any given area of the photoconductive layer is exposed. Development consists in dusting an electrically charged powder on the coating in the dark which adheres to the areas of high electrostatic charge (corresponding to low exposure) while the powder clings only slightly or not at all in the neutralized or discharged areas (corresponding to high exposure). The image can then be transferred to a suitable receiving material in order to obtain a positive or negative print as the case may be.

In addition to light, other types of actinic radiations are also capable of producing electrostatic latent images on a charged surface of a photoconductor and in this connection mention is made of ultraviolet light, X-rays, gamma rays and the like. When electrophotographic plates are used in conjunction with X-rays, the process is known as "electroradiography."

In electrophotographic processes generally described above, the recording element is commonly constructed in two different ways. In one arrangement, a layer or film of the photoconductive material is applied directly to a conductive metal backing member as exemplified by the type of construction known in the art as a "xerographic plate." Alternately, the photoconductor may be employed in the form of minute particles dispersed in an electrically insulating binder and applied to a suitable backing member.

Of the two methods, the latter offers advantages in economy and convenience over the xerographic plate, as is evident from the following comparison. The manufacture of xerographic plates is, at best, a costly and highly technical process. The metal plates must be specially treated in order to assure a scrupulously clean surface after which the selenium photoconducting layer is applied by an evaporation technique. This operation must be carried out under the most vigorously controlled conditions, particularly as regards to the rate of evaporation of the selenium and the even distribution and proper thickness of the selenium coating. The fact that the entire undertaking must be conducted under high vacuum greatly contributes to the cost of manufacture.

Furthermore, the use of xerographic plates is attendant

with several disadvantages, chief among which is the need for making a transfer copy since the original electrophotographic recording element would be too bulky and expensive and generally unsuitable as a material for permanent prints. Because the selenium photoconducting layer is very thin and also very soft, it is easily abraded or scratched during ordinary service and such defects are transferred to the final prints produced therefrom. Furthermore, such plates exhibit a fatigue effect after continued usage. This property or characteristic can be attributed to incomplete neutralization of the electrostatic charge on exposure to light resulting in a certain amount of permanent residual background charge. As a consequence, the residual charge attracts some of the developing powder giving rise to images and prints displaying darkened or foggy backgrounds. Although the plates may be rejuvenated by subjecting them to an electrostatic charge opposite in sign to the original charge so as to neutralize the residual background charge, this requires extra time and steps which are undesirable in commercial installations.

On the other hand, electrophotographic plates wherein the photoconductor is dispersed in an electrically insulating binder can be produced which do not possess the disadvantages associated with the aforementioned xerographic plates. The light-sensitive layer containing the dispersed photoconductor may be coated directly on a convenient base material such as paper, exposed to light through a pattern and the resulting electrostatic image developed to yield a print immediately usable without resorting to a transfer process at any time. Such electrostatic recording elements are easy to manufacture and do not require expensive and elaborate processing equipment. Furthermore, since the original recording material becomes the final print, all the disadvantages attendant to the use and manipulation of intermediate plates are automatically eliminated.

Up to the present time, however, electrophotographic recording plates wherein the support comprised a non-metallic backing were limited in their scope and application because of rather high background fog. This situation is due to the poor electrical conductivity of a non-metallic support which retards conduction of the neutralized electrical charges away from the exposed areas of the plate. Consequently, a certain residual background charge remains which attracts the developing powder to produce the foggy images previously mentioned.

It is believed to be manifest that the art is in need of an electrophotographic recording member capable of yielding fog-free prints directly which is, at the same time, economical to manufacture and which is easy to use and operate.

It is, therefore, an object of this invention to provide an electrophotographic recording element wherein the photoconductive material is coated on a non-metallic conductive backing.

Another object of the invention is to provide a method for coating the base of an electrophotographic recording element with a composition which will increase the electrical conductivity of said base plate.

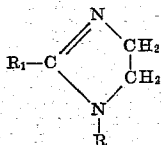
A further object of the invention is to provide a method for the production of electrostatic images directly on a suitable recording material without having to subsequently transfer the first image to a receiving material.

Other objects and purposes of the invention will be apparent as the description proceeds.

It has now been found that an improved, efficient and economical electrophotographic plate can be produced by treating a non-metallic base plate material with a surface active high molecular weight imidazoline in order to render said base plate relatively conducting after

which a layer of photoconducting composition of the type wherein the photoconductor is dispersed in an electrically insulating binder is applied to the so treated base plate.

The high molecular weight imidazoline of the type suitable for practicing the invention can be represented by the following general formula:



wherein R represents an alkyl or alkenyl group of from 1 to 5 carbon atoms and R₁ represents an organic grouping of at least 10 carbon atoms, i.e., an alkyl radical, e.g., decyl, undecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, etc.; an alkenyl radical, e.g., decenyl, undecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl, octadecenyl, nonadecenyl, etc.

Such compounds are known in the chemical art and in this connection reference is made to U.S.P. 2,404,300. According to this patent, 1,2-disubstituted imidazolines as depicted formulistically above can be prepared by reacting ethylenediamine with a long chain acylating agent and treating the resulting N-acylethylenediamine with calcium oxide in order to effect ring closure to the 2-substituted imidazoline. The latter product is then alkylated with an alkylating agent of from 1 to 5 carbon atoms to yield a 1,2-disubstituted imidazoline.

Typical 1,2-disubstituted imidazolines which can be used in practicing the invention include:

- 1-isopropyl-2-undecylimidazoline
- 1-amyl-2-hendecylimidazoline
- 1-methyl-2-decylimidazoline
- 1-ethyl-2-dodecylimidazoline
- 1-isopropyl-2-dodecylimidazoline
- 1-allyl-2-dodecylimidazoline
- 1-methyl-2-dodecylimidazoline
- 1-methyl-2-tridecylimidazoline
- 1-methyl-2-tetradecylimidazoline
- 1-methyl-2-pentadecylimidazoline
- 1-methyl-2-hexadecylimidazoline
- 1-methyl-2-(1-hendecenyl)imidazoline
- 1-allyl-2-(1-tridecenyl)imidazoline
- 1-ethyl-2-hendecylimidazoline

Typical backing or plate materials whose conductivity can be increased according to the present invention include paper, cloth, wood, plastic, leather and the like. We prefer to use paper as a support for our electrophotographic images since it is economical, readily obtainable as well as convenient to handle, store and file.

In general, the invention comprises precoating a non-metallic support such as paper with the aforesaid high molecular weight imidazolines. Over the precoating layer is then applied a second coating of a photoconducting material of the type wherein the photoconductor is suspended in the form of minute particles in an electrically insulating binding material having an electrical resistivity of about 10¹² to 10¹⁹ ohms centimeter. The resulting electrophotographic plate can then be electrostatically charged and developed in the manner commonly employed in the art. The so obtained prints are free of background fog and the use of a paper base in lieu of the usual metallic backing member results in the prints being immediately usable without resorting to any transfer processes.

The manner of preparing electrophotographic plates wherein the photoconductor is suspended or dispersed in an electrically insulating binder is described in the prior art and in this connection reference is made to U.S.P.

2,663,636. Briefly, such a process comprises mixing and grinding together, in a ball-mill or other suitable comminuting equipment, a photoconducting material together with a solvent and a binder material having an electrical volume resistivity of about 10¹² to 10¹⁹ ohms centimeter for a period of time sufficient to effect reduction to the desired particle size.

Our invention is particularly valuable when incorporated in electrophotographic elements having a built-in intensifying screen of the type described in U.S. copending application Serial No. 751,968, filed July 30, 1958. An electrophotographic element of the latter type comprises a paper support having coated thereon a fluorescent intensifying layer or screen which is then overcoated by a second layer of a photoconductor dispersed in an electrically insulating binder. Ordinarily, such a multiple coating tends to yield images having a fairly high fog background since the neutralized electric charges in the light exposed areas do not conduct away as easily as in the electrophotographic elements which do not contain the fluorescent layer. However, such a double layer coating can be made to yield images with little or no fog-forming background by dispersing particles of the fluorescent material in the above described high molecular weight imidazolines. Since the fluorescent particles are dispersed in a conducting environment, electrophotographic recording elements embodying this feature allow for easy dissipation and removal of the electric charges with the subsequent production of electrophotographic prints and fog-free background.

In the accompanying drawing, Figs. 1 and 2 represent sectional views of an electrophotographic member constructed in accordance with our invention.

In Fig. 1, a base plate 1 of paper has precoated thereon a layer 2 of a high molecular weight imidazoline described above which, in turn, is overlaid with a photoconductive insulating layer 3 comprising an electrical insulating binder 4 having dispersed therein particles of a photoconducting material 5.

In Fig. 2, 1 is a base or backing support; 6 represents a fluorescent layer comprising a high molecular weight imidazoline matrix 2 having imbedded or dispersed therein particles of a fluorescent material 7; and 3 is a photoconductive layer in which the photoconducting material 5 is dispersed or distributed throughout an electrically insulating binder 4.

Examples of photoconductors which we can employ for the purpose described herein include zinc oxide, sulfur, anthracene, anthraquinone, lead oxide, lead iodide, cadmium sulfide, cadmium selenide and the like.

In some instances, it may be desirable to incorporate sensitizing dyes in electrostatic recording elements in order to alter the spectral response of a particular photoconductive material. Thus, a sensitizing dye may be selected for the purpose of increasing the speed of the spectral response of a photoconductive material by extending or increasing the characteristic or inherent absorption of the photoconducting material itself. Or, a dye may be selected for the purpose of sensitizing the photoconducting material to a different portion of the spectrum and thus extend the band of frequencies to which the photoconducting material will respond. Among the dyes which have been suggested as sensitizers for use in electrophotography are the phthalein type dyes such as Rose Bengal, the triphenylmethane dyes such as malachite green and methyl green, the cyanine dyes such as cryptocyanine, acridine orange, as well as many others.

It has been our observation that the electrical conductivity of the backing plate or support, after treatment with a high molecular weight imidazoline, should have above the same value or higher as that of the photoconductor under the influence of the exciting radiation. However, regardless of the theory, the fact remains that a non-metallic base plate treated in the above manner results in an electrophotographic recording member

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which yields images having little or no fogged backgrounds.

The coating compositions containing a high molecular weight imidazoline are prepared by dissolving the appropriate imidazoline in an appropriate solvent and the resulting mixture coated on a non-metallic base of the type previously described. In some instances, it may be desirable to add various adjuncts to the composition in order to facilitate the coating operation. To this end, mention may be made of incorporating various dispersions of wax or wax-like materials, the function of which is to retard slippage by reducing the coefficient of friction when such coatings are wound on magazines or spools. It may also be desirable to add spreading agents to the coating compositions, the purpose of which is to effect even distribution of the coating compositions on the base or support in order that the layers of uniform thickness will ensue.

In the interest of uniformity, all coatings were made on paper and all the electrical measurements were carried out under identical conditions of temperature, humidity and illumination.

The invention is illustrated by the following examples. It is to be understood, however, that no limitations are placed on the invention by such examples.

Example 1

A paper base was coated with the following composition:

1-isopropyl-2-undecylimidazoline -----g-- 1-20
Toluene -----ml-- 800-1200

and then allowed to dry. The resistivity of the paper base coated in such a manner was 2.61×10^{10} or less ohms centimeter. This compares to 1.5×10^{11} ohms centimeter for the untreated paper.

A second coating consisting of a dispersion of a photoconductor in a binder was prepared as follows: 20 g. of zinc oxide, 16 g. of silicone resin and 20 g. of toluene were placed in a porcelain ball-mill of one quart capacity half filled with 0.5 in. porcelain balls and milled for about two hours. The mixture was then coated by applicator roller method on the above subbed paper base and allowed to dry. The thickness of the photoconductive layer was about 10 microns. An electrostatic charge was placed on the plate and exposed to radiation to effect discharge of the plate. The residual surface charge was then measured using a dynamic electrometer. A second electrophotographic plate was prepared as above except the paper base was not treated with the high molecular weight imidazoline. On charging and exposing, the residual surface charge on the second plate was much higher than in the case of the first plate.

As a consequence of the low residual surface charge remaining on the electrophotographic member having the base treated as above, the resulting prints obtained therefrom are free of background fog.

The silicone resin was obtained on the commercial market as "GE Silicone Resin SR-82," a product of the General Electric Company, Pittsfield, Mass.

The zinc oxide photoconductor was purchased commercially as "French Process Florence Green Seal Pigment Grade," a product of the New Jersey Zinc Sales Company, Inc., New York, New York.

The 1-isopropyl-2-undecylimidazoline was prepared by acylating ethylenediamine with lauroyl chloride and the resulting N-lauroylethylenediamine cyclized to 2-undecylimidazoline using calcium oxide. The latter product was then alkylated with isopropyl halide to yield the desired 1-isopropyl-2-undecylimidazoline. For more detailed directions concerning the synthesis of such compounds, reference is made to the previously cited U.S.P. 2,404,300.

Example 2

The same procedure was followed as given in Example

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1 excepting that the zinc oxide photoconductor was sensitized to the green portion of the spectrum with Rose Bengal dye. 0.01 gram of sensitizer was added to the zinc oxide dispersion during the ball-milling stage.

Example 3

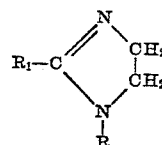
15 grams of zinc sulfide (copper and cobalt activated) and 20 g. of the 1-isopropyl-2-undecylimidazoline solution of Example 1 was ball-milled for two hours. The resulting dispersion of fluorescent agent was then coated on a metal base using the applicator roller method. The thickness of the layer amounted to about 10 microns. A photoconductive layer of the type described in Example 2 was next applied over the first layer and allowed to dry. The resulting electrophotographic recording element containing an intermediate fluorescent layer interposed between the base and photoconductive layer is particularly valuable in the field of radiography wherein the exciting radiation are X-rays. In operation, the element is first electrostatically charged in the usual manner and then exposed to an X-ray pattern or image. At the exposed areas, the electrostatic charges comprising the latent image are neutralized. In addition to the direct discharge of the latent image, the X-rays causes the fluorescent layer to emit light which neutralizes more of the electrostatic charges. Thus, the combination of a fluorescent substance and photoconductor operate in a synergistic manner to increase the efficiency of the system.

Example 4

The same procedure was employed as given in Example 3 excepting that the metal base was replaced by a paper base coated with the 1-isopropyl-2-undecylimidazoline of Example 1.

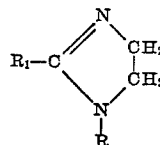
We claim:

1. An electrophotographic member comprising a base having applied thereon a pretreatment of a surface active high molecular weight imidazoline of the following formula:



wherein R_1 represents an organic grouping of at least 10 carbon atoms and being selected from the class consisting of alkyl and alkenyl radicals and R represents an organic grouping of from 1 to 5 carbon atoms and being selected from the class consisting of alkyl and alkenyl radicals and a photoconductive insulating layer thereover comprising a photoconductor uniformly dispersed in an electrically insulating binder having an electrical resistance higher than that of the base plate and photoconductor.

2. An electrophotographic member comprising a base plate, an intermediate fluorescent layer bonded thereto, said layer comprising a fluorescent material dispersed uniformly throughout a surface active high molecular weight imidazoline of the following formula:



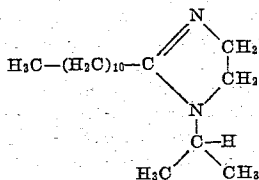
wherein R_1 represents an organic grouping of at least 10 carbon atoms and being selected from the class consisting of alkyl and alkenyl radicals and R represents an organic grouping of from 1 to 5 carbon atoms and being selected from the class consisting of alkyl and alkenyl radicals and a photoconductive insulating layer thereover comprising a photoconductor uniformly dispersed in an electrically insulating binder having an electrical re-

3. The article as defined in claim 2 wherein the photoconductor is finely divided zinc oxide.

3. The article as defined in claim 2 wherein the photoconductor is finely divided zinc oxide.

4. The article as defined in claim 2 wherein the photoconductor is dye sensitized.

5. The article as defined in claim 1 wherein the surface active high molecular weight imidazoline has the following formula:



6. The article as defined in claim 1 wherein the electrically insulating binder is selected from the class consisting of silicone resins, cellulose esters, cellulose ethers, vinyl resins, waxes and natural resins.

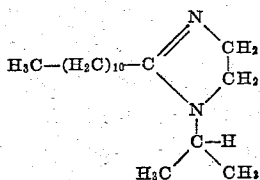
7. The article as defined in claim 2 wherein the fluorescent material is selected from the class consisting of copper activated zinc sulfide, copper and cobalt activated zinc sulfide, silver activated zinc sulfide, zinc cadmium sulfide, magnesium titanium dioxide, calcium tungstate and cesium halide.

8. The article as defined in claim 1 wherein the photoconductor is finely divided zinc oxide.

9. The article as defined in claim 6 wherein the electrically insulating binder is a silicone resin.

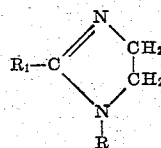
10. The article as defined in claim 7 wherein the fluorescent material is copper cobalt activated zinc sulfide.

11. The article as defined in claim 2 wherein the surface active high molecular weight imidazoline has the following formula:



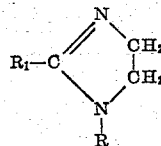
12. The article as defined in claim 1 wherein the base is paper.

13. An electrophotographic process comprising placing an electrostatic charge on the surface of an electrophotographic member comprising a base having applied thereon a pretreatment of a surface active high molecular weight imidazoline of the following formula:



wherein R_1 represents an organic grouping of at least 10 carbon atoms and being selected from the class consisting of alkyl and alkenyl radicals and R represents an organic grouping of from 1 to 5 carbon atoms and being selected from the class consisting of alkyl and alkenyl radicals and a photoconductive insulating layer there-over comprising a photoconductor uniformly dispersed in an electrically insulating binder having an electrical resistance higher than that of the base plate and photoconductor, selectively neutralizing the electrostatic charge from the surface of the charged photoconductive insulating layer by exposing said charged layer to radiation of a wave length ranging from 10^{-12} centimeters to 10^{-1} centimeters thereby creating an electrostatic latent image on the surface of the photoconductive insulating layer and developing said electrostatic latent image with electrically charged powder particles.

25 14. An electrophotographic process comprising placing an electrostatic charge on the surface of an electrophotographic member comprising a base having applied thereon a pretreatment of a surface active high molecular weight imidazoline of the following formula:



wherein R_1 represents an organic grouping of at least 10 carbon atoms and being selected from the class consisting of alkyl and alkenyl radicals and R represents an organic grouping of from 1 to 5 carbon atoms and being selected from the class consisting of alkyl and alkenyl radicals and a photoconductive insulating layer thereover comprising a photoconductor uniformly dispersed in an electrically insulating binder having an electrical resistance higher than that of the base plate and photoconductor, selectively neutralizing the electrostatic charge from the surface of the charged photoconductive insulating layer by exposing said charged layer to radiation of a wave length ranging from 10^{-12} centimeters to 10^{-1} centimeters thereby creating an electrostatic latent image on the surface of the photoconductive insulating layer and developing said electrostatic latent image with electrically charged powder particles.

15. The process as defined in claim 14 wherein the
55 exposing radiation are X-rays.

No references cited.