

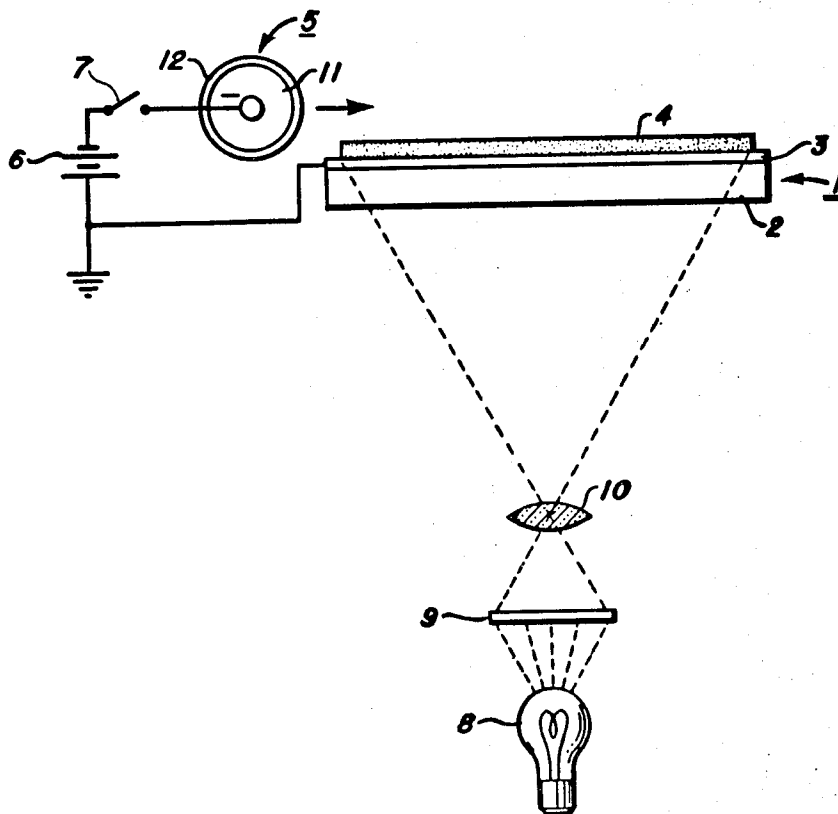
July 23, 1974

R. J. GRUBER ET AL

3,825,422

IMAGING PROCESS

Filed Oct. 26, 1972



1

3,825,422

IMAGING PROCESS

Robert J. Gruber and Bernard Grushkin, Pittsford, N.Y.,
assignors to Xerox Corporation, Stamford, Conn.

Filed Oct. 26, 1972, Ser. No. 300,958

Int. Cl. G03c 5/06

U.S. Cl. 96—1 PE

8 Claims

ABSTRACT OF THE DISCLOSURE

Vanadyl and titanyl phthalocyanine compounds as electrically photosensitive pigments in photoelectrophoretic imaging.

BACKGROUND OF THE INVENTION

The invention relates in general to imaging systems. More specifically, the invention concerns the use of vanadyl and titanyl phthalocyanine in photoelectrophoretic imaging systems.

In general, photoelectrophoretic imaging, as used herein, refers to those systems wherein electrically photosensitive particles dispersed in an insulating carrier liquid are exposed to imagewise light and an electrical field resulting in particle migration in image configuration. One such process which is capable of producing one color or more or natural full color images in one step is described in detail and claimed in U.S. Pats. 3,383,993 to Yeh; 3,384,488 and 3,384,565 to Tulagin and Carreira; 3,384,566 to Clark, all issued May 21, 1968. In such an imaging system, electrically photosensitive particles are dispersed in a relatively non-conductive liquid carrier. The suspension is placed between electrodes, subjected to a potential difference and exposed to an image. As these steps are completed, selective particle migration takes place in image configuration. Where the electrical field is applied between electrodes, which are in contact with the imaging suspension, normally images made up of particles are formed on one or both electrodes. In a monochromatic system, particles of only one color need be used, but particles of many colors may be used if desired to provide a range of monochrome colors which may be reproduced. In a polychromatic system, images of more than one color may be formed by utilizing particles of more than one color which have spectral response curves which do not have substantial overlap thereby providing for color separation. In a preferred embodiment for subtractive full color imaging yellow particles are used responsive mainly to blue light, cyan particles are used which are responsive mainly to red light and magenta particles are used which are responsive mainly to green light. Thus, when the suspension is exposed, for example, to areas of the original to be copied which are red, the red light causes the cyan particles to migrate leaving the yellow and magenta which combined appear red. Further, where white light impinges the suspension, all particles migrate leaving a clear area which when transferred to white paper appears white. Similarly, where no light impinges the suspension, all particles remain which form a dark brown or black area.

The critical component of such an imaging system is the electrically photosensitive particles. They must have intense and pure colors to form pleasing highly saturated images. For monochrome images, the particles should have high photosensitivity, and it is often desirable that they be panchromatic so as not to be "blind" to one area of the spectrum. The requirements for subtractive polychrome particles are more severe in that not only must they have intense and pure colors but their spectral response curves must be well-defined and not overlap the spectral response curves for particles of other colors.

2

Further, the photoresponse of a given particle must be to approximately the same intensity of exposure as the other particles to provide color balanced images. For example, in a subtractive system, if the particle is too photoresponsive or has too broad a spectral response, the final image will be deficient in that color. Conversely, where the particle is too slow, the image formed will have a high background and will have poor color balance. For additive systems, the results, of course, would be reversed.

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide photoelectrophoretic imaging systems which overcome the above noted problems.

It is another object of this invention to provide a photoelectrophoretic imaging suspension having improved photoelectrophoretic imaging characteristics.

It is another object of this invention to provide new electrically photosensitive particles for use in photoelectrophoretic imaging systems.

The foregoing objects and others are accomplished in accordance with this invention by providing photoelectrophoretic imaging processes utilizing vanadyl phthalocyanine or titanyl phthalocyanine or mixtures of vanadyl phthalocyanine and titanyl phthalocyanine. The titanyl and vanadyl phthalocyanines may be substituted or unsubstituted. Phthalocyanine, which is also known as tetra-benzotetraazaporphin and tetra-benzoporphyrine, may be considered as the condensation product of four indole groups. Phthalocyanines may be metal-free or metal-containing and are very well-known. One book describing phthalocyanine compounds in detail is Moser et al., *Phthalocyanine Compounds* ACS Monograph 157, Reinhold Publishing Co. (1963).

In a preferred photoelectrophoretic imaging process, finely divided particles of electrically photosensitive particles are dispersed in an insulating carrier liquid and coated onto a transparent conductive electrode called the "injecting" electrode. A second electrode having an insulating outer surface and called a "blocking" electrode is caused to contact the free surface of the suspension. An electrical field of relatively high potential is applied across the suspension between the electrodes while the suspension is exposed through the injecting electrode to a pattern of electromagnetic radiation of wavelengths to which at least some of the particles are responsive. On completion of these steps, normally a positive image is found adhering to the injecting electrode and a negative image is formed on the blocking electrode. Apparently, the particles which are within interaction range of the conductive injecting electrode when struck by light to which they are sensitive exchange charge with the injecting electrode and are repelled by it migrating to the blocking electrode leaving behind a positive image. The particles which migrate to the blocking electrode are less able to exchange charge with the insulating surface and adhere to it forming a negative image.

The process of photoelectrophoretic imaging and the materials used are set out in detail in the above mentioned patents 3,383,993; 3,384,488; 3,384,565 and 3,384,566, the disclosures of which are incorporated herein by reference.

The use of phthalocyanine compounds generally in photoelectrophoretic imaging, is disclosed and claimed in U.S. Pat. 3,615,558 to L. Carreira and V. Tulagin, issued Oct. 26, 1971. In this patent substituted and unsubstituted, metal-containing and metal-free phthalocyanines are disclosed and claimed. There is, however, no disclosure as to the specific use of vanadyl or titanyl phthalocyanines in photoelectrophoretic imaging and the unexpected results obtainable therewith.

The carrier liquid for the imaging suspension of this invention may comprise any suitable insulating material. Typical insulating materials include liquids or materials which may be converted to a liquid at the time of particle migration. Typical insulating liquids include: decane, dodecane, tetradecane, kerosene, molten paraffin, molten beeswax or other molten thermoplastic material, mineral oil, silicone oils such as dimethyl polysiloxane, fluorinated hydrocarbons and mixtures thereof. Mineral oil and kerosene are preferred because of their excellent insulating qualities.

Alternatively, the particles may be pre-coated on one of the electrodes in a solid binder such as Piccotex polystyrene resin available from Pennsylvania Industrial Chemical Co. or eicosane wax for ease of handling and storage. The binder is melted or dissolved by a dielectric solvent such as those listed above prior to imaging so that the particles are free to migrate. Other typical solvent-soluble dielectric binder materials include hydrogenated rosin esters such as Stabelite Esters 5 and 10 available from Hercules Powder Co., phenolformaldehyde resins such as Amberol ST-137-X available from Rohm and Haas, and Piccotex 75 and 100 and Piccopale 70 SF available from Pennsylvania Industrial Chemical Co.

It is desirable to use particles of a relatively small size because small particles provide a more stable suspension and provide images of higher resolution than would be possible with larger particles. Particles of less than one or two microns in average cross section are preferred although particles up to about 5 to 10 microns may be used.

The concentration of particles dispersed in the liquid depends on a number of variables including operating conditions, the density of the final image desired, the use to which the image is to be put, the solubility of added dispersants and other factors generally known to those skilled in the art of ink or plastic coating formulation.

The transparent conductive substrate may comprise any suitable material. Typical transparent conductive materials include conductively coated glass, such as aluminum or tin oxide coated glass or transparent plastic materials such as polyester films overcoated with similar materials and cellophane.

The insulating surface for the blocking electrode may be paper, cloth, rubber, plastics, both thermosetting and thermoplastic, and other insulating materials.

The vanadyl and titanyl phthalocyanines may be prepared by conventional methods. Preferred methods for preparing these compounds for photoelectrophoretic imaging are shown in the following Examples.

EXAMPLE I

Vanadyl phthalocyanine is prepared as follows: a mixture of 247 grams of phthalic anhydride, 247 grams of urea, 3 liters of chloronaphthalene and 100 grams of vanadium trichloride is refluxed at 255° C. for 45 minutes, cooled to 25° C. and filtered. The solid is washed with 300 ml. of ethanol, then slurried in 100 ml. of ethanol for 2 hours and filtered. The wet pigment is then thoroughly washed at 70° C. using first, 2 liters of 10% sodium hydroxide, then 2 liters of 20% HCl and then 2 liters of deionized water. The wet cake is air dried then vacuum dried at 65° C.

7.5 grams of the thus prepared crude vanadyl phthalocyanine is dissolved in 40 ml. of concentrated sulfuric acid then filtered through a coarse fritted funnel and sprayed into one liter of water and again filtered using a medium porosity funnel. The material is extensively washed in water including a wash with 750 ml. of water containing 18 ml. of concentrated ammonium hydroxide. The vanadyl phthalocyanine is air dried and then vacuum dried at 65° C.

EXAMPLE II

To a 1-liter flask, fitted with a thermometer and set up for distillation, is added 12.3 grams (0.08 mole) of titani-

um trichloride, 20 grams (0.16 mole) of o-phthalonitrile and 375 ml. of alpha-chloronaphthalene. The flask is heated under a blanket of nitrogen while being stirred with a magnetic stirrer. When the temperature is at approximately 170°, an orange-red liquid begins to distill. The temperature is raised steadily to 255° C. (reflux) and is maintained at 255° C. for one hour. The product is then cooled to room temperature. After filtering, the solid is washed with dry benzene and 375 ml. portions of anhydrous ether. The solid is then dried under vacuum to give 20.7 grams of TiCl_2Pc . A mixture of 1.8 grams of TiCl_2Pc , 1 liter of 95% ethanol, and 20 ml. of pyridine is refluxed with stirring for 3.5 hours. After cooling to room temperature, the reaction mixture is filtered and the solid washed with 200 ml. of ethanol. In this manner, there is obtained 14.2 grams of a blue solid whose infrared spectrum is similar to that reported for $(\text{TiOPc})_x$.

The crude titanyl phthalocyanine thus prepared is acid pasted by dissolving 6.8 grams of TiOPc in 100 ml. of concentrated sulfuric acid then, after one hour, the sulfuric acid solution is carefully poured onto 1 liter of crushed ice, filtered, and washed with 100 ml. of deionized water until it is no longer acidic. The resulting wet cake is slurried for one hour two times in the following solutions at 70° C.: water, dilute ammonium hydroxide, and finally again, water. The pigment is then air dried overnight followed by vacuum drying at 65° and 20 mm. for 24 hours. 4.9 grams of acid pasted TiOPc is obtained.

EXAMPLE III

In a 500 ml.-3 necked flask, fitted with a condenser stirrer and heating mantle, is placed 10 g. (0.064 mol) of vanadium trichloride, 25 g. (0.172 mol) of 1,3-diminoisindole and 250 ml. of chloronaphthalene. The mixture is slowly heated to reflux over a 1 hour period and then held at reflux for an additional .5 hours. After filtering at 65° C., the solid is washed with 300 ml. of acetone, then slurried in 500 ml. of ethanol overnight followed by two slurrings in 10% sodium hydroxide for 2 hours at 70° C. and twice in 20% hydrochloric acid also for 2 hours at 70° C. The solid is further washed with deionized water and dried at 65° under vacuum to give 18.2 g. (48.8%) of vanadyl phthalocyanine.

This reaction can be carried out in ethylene glycol, quinoline or other suitable high boiling solvent. The reaction also can be carried out using vanadium tetrachloride or vanadium oxychloride.

EXAMPLE IV

0.55 mole of vanadium tetrachloride and 0.5 mole of metal free phthalocyanine in 3 liters of trichlorobenzene is heated to reflux for 5 hours. The mixture is then cooled and filtered. The solid is washed with acetone, ethanol and then a 10% sodium hydroxide, 10% hydrochloric acid, and finally water. After drying the crude product is dissolved in concentrated H_2SO_4 (1 gram in 50 ml. acid) and poured into water. An 80% yield of vanadyl phthalocyanine is recovered.

EXAMPLE V

The experiment of Example IV is repeated except disodium phthalocyanine is used providing a 90% yield of vanadyl phthalocyanine.

EXAMPLE VI

0.4 mole of phthalonitrile and 0.1 mole of V_2O_5 are heated to 285° C. in the absence of solvent for 3 hours, then cooled and slurried in benzene, acetone, isopropanol, 10% NaOH, 10% HCl, then water and dried. A 40% yield of vanadyl phthalocyanine is obtained.

BRIEF DESCRIPTION OF THE DRAWING

The advantages of this improved method of PEP imaging will become apparent upon consideration of the detailed disclosure of this invention, particularly when con-

sidered in conjunction with the accompanying drawing wherein:

The Figure is a side sectional view of a simple exemplary photoelectrophoretic imaging system in accordance with this invention.

The sizes and shapes of the drawings should not be considered as actual sizes or even proportional to actual sizes because many of the elements have been purposely distorted in size to more fully and clearly describe the invention.

Referring now to the Figure, there is seen a transparent electrode generally designated 1, which in this exemplary instance, is made up of a layer of optically transparent glass 2 overcoated with a thin optically transparent layer 3 of tin oxide, commercially available under the name NESA glass. This electrode will be referred to as the injecting electrode. Coated on the surface of injecting electrode 1 is a thin layer 4 of finely divided photosensitive particles dispersed in an insulating liquid carrier. The term "electrically photosensitive," for the purposes of this application, refers to the properties of a particle which, when brought into interaction range of the injecting electrode, will migrate away from it under the influence of an applied electric field when it is exposed to radiation to which it is responsive. Liquid suspension 4 may also contain a sensitizer and/or a binder for the particles which is at least partially soluble in the suspending or carrier liquid. Adjacent to the liquid suspension 4 is a second electrode 5, "blocking electrode" which is connected to one side of potential source 6 through switch 7. The opposite terminal of potential source 6 is connected to the injecting electrode and ground so that when switch 7 is closed, an electrical field is applied across the liquid suspension 4 between electrodes 1 and 5. An image projector made up of light source 8, a transparency 9 and a lens 10 is provided to expose the suspension 4 to a light image of the original transparency 9 to be reproduced. Alternatively, the image may be light reflected off of an opaque picture or document. Electrode 5 is in the form of a roller having a conductive central core 11 connected to potential source 6. The core is covered with a layer of an insulating material 12. The suspension is exposed to the image to be reproduced while a potential is applied across the blocking and injecting electrodes by closing switch 7 and causing roller 5 to roll across the free surface of suspension 4 during imagewise exposure. On completion of roller traverse, a positive image is found on electrode 1 and a negative image is found on surface 5.

During roller traverse, the roller is pressed into virtual contact with the injecting electrode surfaces. Gaps of up to about one mil. are used. Voltages of from about 300 to 5,000 volts are used in the apparatus as shown in the Figure.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following Examples further specifically illustrate the improved photoelectrophoretic imaging system using the compositions of this invention. Parts and percentages are by weight unless otherwise indicated. Examples VII and VIII are carried out in an apparatus of the general type illustrated in the figure with the imaging suspension coated on the conductive surface of a NESA glass plate through which exposure is made. The NESA glass surface is connected to a source of high D.C. potential and ground. The other terminal of the source of high potential is connected to a steel roller about one inch in diameter having a $\frac{3}{4}$ " layer of polyurethane having a resistivity of about 5×10^8 ohm. cm. forming a $2\frac{1}{2}$ inch roller. A paper sheet is placed over the plastic to receive migrating particles. The particles are dispersed in the liquid carrier and ball milled until the average particle size is less than about one micron and a stable suspension is formed. The roller is moved across the plate sur-

face at a rate of about 3 inches/second and the image is projected using a conventional tungsten lamp. The transparency may be black and white or color as indicated.

EXAMPLE VII

About 7 parts of vanadyl phthalocyanine made as in Example I are dispersed in about 100 parts Sohio Odorless Solvent 3440. This mixture is coated onto the NESA glass plate to a thickness of about 2 mils. Roller potential is about 2500 volts, the roller being biased negative with respect to the injecting electrode. Exposure is made through a 0.30 neutral density step wedge filter to measure the sensitivity of the suspension to white light and then Wratten 29, 61 and 41b filters are individually superimposed over the light source in separate tests to measure the sensitivity of the suspension to red, green and blue light, respectively. The reciprocal of spectral sensitivity is given in microwatts/cm.², being the result of a curve of optical density plotted against the intensity of exposure in microwatts/cm.², the time of exposure being held constant. This is the method used to determine the photographic "speed" of the photosensitive material. Sensitivity to blue light was found to be 200 mw./cm.², to green light 100 mw./cm.², to red light 18 mw./cm.² and 18 mw./cm.² to white light.

EXAMPLE VIII

The experiment of Example VII is repeated except that the titanil phthalocyanine prepared as in Example II is used in place of the vanadyl phthalocyanine. Sensitivities were determined to be 200 mw./cm.² to blue light, 100 mw./cm.² to green light, 20 mw./cm.² to red light and 20 mw./cm.² to white light.

It has been found through extensive testing that the sensitivity to red light is greater for the vanadyl and titanil phthalocyanines than for the metal free or copper phthalocyanines shown in the prior art. Further, the absorption of the green and blue wavelengths for the vanadyl and titanil phthalocyanines is less than that of metal free or copper phthalocyanine. The vanadyl and titanil phthalocyanines are superior cyan colorants for use in polychromatic imaging. The vanadyl and titanil phthalocyanines provide a larger range of green reproduction than do prior art pigments. Those characteristics are extremely important for a full color subtractive imaging process where accurate color separation and reproduction are required.

The improvements obtained were further confirmed in full color subtractive imaging using their vanadyl phthalocyanine or titanil phthalocyanine in combination with a yellow pigment and a magenta pigment as shown in Examples XI through XVI of U.S. Pat. 3,615,558, the disclosure of which is incorporated herein by reference.

Although specific components and proportions have been described in the above Examples, other suitable materials, as listed above, may be used with similar results. In addition, other materials may be added to the pigment compositions to synergize, enhance or otherwise modify their properties. The pigment compositions where desired, for example, may be coated with a plastic.

Other modifications and ramifications of the present invention will occur to those skilled in the art upon a reading of the present disclosure. These are intended to be included within the scope of this invention.

What is claimed is:

1. A method of photoelectrophoretic imaging which comprises the steps of:

- (a) forming a layer of an imaging suspension, said imaging suspension comprising finely divided electrically photosensitive particles dispersed in an insulating carrier liquid;
- (b) subjecting said layer of a suspension to an electric field; and,
- (c) exposing said suspension to a pattern of activating electromagnetic radiation to which at least a

portion of said particles are sensitive until an image is formed, said particles comprising a pigment, said pigment selected from the group consisting of vanadyl phthalocyanine and titanyl phthalocyanine and mixtures thereof.

2. The method of claim 1 wherein said particles comprise vanadyl phthalocyanine.

3. The method of claim 1 wherein said particles comprise titanyl phthalocyanine.

4. The method of claim 1 wherein said suspension comprises particles of more than one color, said particles of one color having a photosensitive response which does not substantially overlap the photosensitive response of particles of a different color.

5. The method of claim 1 wherein said particles comprise vanadyl phthalocyanine responsive mainly to red light, a yellow particle responsive mainly to blue light and a magenta particle responsive mainly to green light.

6. The method of claim 1 wherein said particles comprise titanyl phthalocyanine responsive mainly to red light, a yellow particle responsive mainly to blue light and a magenta particle responsive mainly to green light.

7. The method of claim 1 wherein said electrical field is applied between an electrode having a conductive surface and an electrode having an insulating surface.

8. The method of claim 1 wherein said electrical field is applied between a transparent conductive electrode and an electrode having an insulating surface and said exposure is made through said transparent conductive electrode.

References Cited

UNITED STATES PATENTS

3,615,558	10/1971	Carreira	96-488
3,647,659	3/1972	Keller et al.	96-13
3,616,395	10/1971	Carreira	96-13
3,384,565	5/1968	Tulagin et al.	96-13
3,664,941	5/1972	Jelto	96-13

RONALD H. SMITH, Primary Examiner

J. L. GOODROW, Assistant Examiner

U.S. Cl. X.R.

96-88

DESCRIPTION OF THE INVENTION

The present invention relates to a method of forming a latent image on a photosensitive surface. The method comprises the steps of: (a) providing a photosensitive surface having a conductive layer and an insulating layer; (b) applying an electrical field between the conductive layer and the insulating layer; (c) exposing the photosensitive surface to light; and (d) developing the latent image. The method is particularly adapted for use in the field of microphotography and is a significant improvement over the prior art.