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3,425,830 ELECTROPHOTOGRAPHIC RECORDING ELEMENT

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6 Claims

ABSTRACT OF THE DISCLOSURE

The present invention relates to electrophotographic recording elements comprising photoconductive pigments and a binder therefor comprising inorganic ammonia-soluble metal salts such as zinc, copper, cobalt or silver phosphate, chromates or carbonates. For most desirable results, the photoconductive pigment should be present in substantially larger proportions than the binder. The said inorganic ammonia-soluble salts should not be used in amounts substantially larger than required for binder purposes. The above specified binder may have mixed with it smaller amounts of conventional organic copolymer binders.

This application is a continuation-in-part of U.S. patent application Ser. No. 459,923 filed May 28, 1965.

The present invention relates to electrophotographic materials and process of producing same. More particularly, it relates to improved electrophotographic compositions containing an electrically insulating film-forming composition containing inorganic photoconductive particles coated with a layer of ammonia soluble inorganic metal salts.

An electrostatic printing process is a process in which a visible record, reproduction or copy is produced and which includes the conversion of a light image into an electrostatic charge pattern. Examples of such electrostatic printing process include the xerographic process generally known in the trade as Xerox and a modification thereof generally known in the trade as Electrofax.

The Xerox process may be described generally as one where a base plate of relatively low electrical resistance such as metal, paper, etc. having a photoconductive insulating surface thereon is electrostatically charged in the dark. The charged coating is then exposed to a light image. The charges leak off rapidly to a base plate in any given area that is so exposed, after such exposure the coating is contacted with electrostatic marking particles in the dark. These particles adhere to the areas where the electrostatic charges remain, forming a powder image corresponding to the electrostatic image. The powder image is then transferred to a sheet of transfer material resulting in a positive or negative print, as the case may be. A detailed description of the steps of such a process is found in U.S. Patent No. 2,297,691 issued Oct. 6, 1942, to C. F. Carlson.

Alternatively, where the base plate is relatively inexpensive as of paper, it may be desirable to fix the powder image directly to the plate itself. In such case, the process is generally known in the trade as Electrofax whereby direct electrophotographic printing is effected on the paper. The Electrofax process may be described generally as including the following steps for making a direct print. The paper is first made sensitive to light by giving it a blanket negative electrostatic charge on the coating side in the dark. One way of doing this is by ion transfer from a corona discharge. The sheet, now sensitive to light, is

exposed by any of the conventional photographic procedures. The electrostatic charge is lost or reduced in the exposed area and retained in the masked areas to form a latent electrostatic charge image on the surface of the paper. The latent image is then developed by applying a pigmented resin powder carrying a positive electrostatic charge. The powder is attracted and held by the negatively charge image areas. Finally, the powder image is fixed by melting the resin powder so it fuses to the paper surface to produce a durable light-fast image. A detailed description of the steps of such a process is given by H. G. Greig in U.S. Patent No. 3,052,539, issued Sept. 4, 1962.

The latter process eliminates the intermediate step of transferring the powder image and enables production of the image directly upon a desired surface. A photoconductive paper suitable for use in connection with such process usually comprises a backing sheet, such as paper, coated with photoconductive particles suspended in an electrically insulating film-forming binder. Such a coated printing base, while satisfactory for carrying out the Electrofax process, is also, subject to certain limitations, many of which are primarily physical in character.

The electrically insulating film forming material may be one of a number of substances such as various synthetic resinous materials having high dielectric strength. Previously used materials of this type include polyvinyl acetate, copolymers of vinyl chloride-vinyl acetate, polystyrene, silicone resins, etc., as well as resin-like materials such as methyl or ethyl cellulose and cellulose nitrate, natural resins and waxes.

The photoconductive powder may be incorporated into the selected film-forming material in various ways. For example, the selected film-forming material may be dissolved in an organic solvent and then mixed with the photoconductive powder. Or, the latter may be kneaded dry with the film-forming material heated to a sufficiently high temperature to make it plastic. Other methods may also be suitably employed.

The dispersion of the photoconductive powder in the selected dispersing agent is then applied to the base in any suitable manner as, for example, by immersing the base in an organic solvent suspension of the composite comprising photoconductive particles of film-forming composition and then removing the solvent by evaporation, or by spraying or otherwise coating one or both sides of the base with the solvent suspension and then evaporating off the solvent. Other suitable methods may also be used.

It has now been found, in accordance with the present invention, that the desired coatings of photoconductive particles can be satisfactorily obtained without the employment of the organic polymers and, in general, without the use of organic solvents which must be removed from the films before the latter can be used.

It is accordingly an object of the present invention to produce carbon-free binder systems of inorganic photoconductive particles suitable for electrophotographic and other purposes.

Other objects will become evident from the description which follows.

The photoconductive layer of the present invention consists essentially of an inorganic photoconductive material such as zinc oxide, zinc sulfide, cadmium sulfide, titanium dioxide or other inorganic photoconductive particles bonded by a relatively thin coating of an ammonia soluble inorganic binder such as a metal phosphate, chromate or carbonate of metals such as zinc, copper, cobalt, silver and others. This composition not only adheres well to various types of bases such as papers of different types, cellophane, cellulose ester sheets or films, aluminum plates or foils, woods, etc., but in addition is non-hygroscopic,

hard and durable, and in general is less subject to deterioration than photoconductive films prepared in other ways.

For most satisfactory results in producing an electrophotographic printing plate, regulated amounts of inorganic photoconductive particles and binder should be used. For example, a suspension of equal parts of photoconductive zinc oxide and binder shows slight photoconductivity. By increasing the proportion of zinc oxide to four times that of the binder, the photoconductivity is increased by as much as 100 times. It is important, therefore, to use the zinc oxide, or other photoconductive particles, and the binder in such proportions that the zinc oxide is used in predominant proportions and the inorganic binder, such as zinc phosphate, is employed only in an amount sufficient for an adhesive or binder for the photoconductive particles.

The photoconductive agent-binder composition may be prepared in various ways. For example, it may be prepared by adding a stoichiometric excess of zinc or zinc oxide to a solution of ammonia and diammonium phosphate to give the zinc ammonium phosphate complex and unreacted suspended zinc oxide. The application of this suspension to a suitable base, followed by drying, gives a glass- or enamel-like layer, which adheres well to the base.

Alternately, the binder can be prepared by reacting stoichiometric proportions of zinc or zinc oxide and diammonium phosphate in ammonia solution and then thoroughly mixing or dispersing in the resulting reaction mixture, the desired amount of zinc oxide.

The specific examples below are given for the purpose of illustrating the invention disclosed herein. It will be evident, however, that variations from the specific procedures disclosed therein will be obvious to one skilled in the art. It is understood, therefore, that any such variation which does not depart from the basic concept of the disclosed invention is intended to fall within the scope of the appended claims.

Example I

A solution containing the equivalent of 19.4% by weight of zinc phosphate was prepared by dissolving stoichiometric proportions of zinc oxide and diammonium phosphate in 20% ammonium hydroxide solution. To the resulting solution was then added 100 grams of a previously prepared slurry composed of 100 grams of photoconductive zinc oxide in 125 grams of 10% ammonium hydroxide solution. This gave a ratio of zinc oxide to zinc phosphate of approximately 5 to 1.

The above composition was then used to coat: (a) a tubsized base paper stock, (b) an aluminum sheet previously scrubbed with a steel wool pad saturated with methanol and ammonium hydroxide solution, and (c) a base paper stock coated with 22# of a 5 to 1 zinc oxide and ammonium salt of a vinyl acetate-crotonic acid copolymer containing about 5% crotonic acid.

The coated bases, prepared as above described, were dried in an oven for 4 minutes at 105° C. and resulted in dry coatings of approximately 16# per 3300 square feet. Upon testing, all three coatings were found to give good reproductions of the electrophotographically produced powder images. The adhesion of the layers was excellent and no evidence of deterioration thereof was evident under normal usage and storage conditions.

Example II

In this experiment, the operation was carried out exactly as in Example I, with the exception that ratios of 1:1, 2:1 and 3:1 of zinc oxide to zinc phosphate were employed. In all three cases, the physical properties of the dried films were quite satisfactory. However, the film containing the 1:1 ratio showed only a slight photoconductivity. Increasing amounts of zinc oxide added so that the portion of dissolved zinc oxide decreased from a ratio of one part dissolved to one part undissolved to a ratio of one part dissolved to four parts undissolved increased the

photoconductivity about 100 times, thus indicating the necessity for an adequate amount of photoconductive zinc oxide or other agent in the dried film in order to obtain satisfactory photoconductivity for good reproduction of images.

Example III

The operation of Example I was repeated using as the binder, a composition containing one part of the ammonium salt of a vinyl acetate-crotonic acid (containing 5% crotonic acid) copolymer and 1.5 parts of zinc phosphate. The resulting dried plates, upon testing, were found to image electrophotographically but showed no particular advantage over the plates made without the vinyl acetate-crotonic acid polymer.

Example IV

The operation in Example I was repeated by replacing one-half of the zinc phosphate with copper phosphate or cobalt phosphate. Upon testing, all of the dried films imaged electrophotographically but showed no particular advantage over the use only of zinc phosphate, as described in Example I.

Example V

The procedure of Example I was repeated using ratios of 1:1, 2:1, and 3:1 of zinc oxide to zinc phosphate applied to commercially available paper offset master plate, then powder imaged by electrophotography and run on a commercial offset lithographic press (Addressograph-Multigraph #1250 press). Good reproductions of the fused electrophotographic image were obtained in all cases.

Example VI

The procedure of Example I was repeated, using silver phosphate, copper phosphate and cobalt phosphate in place of zinc phosphate. The coatings were applied to commercially available offset master paper, then powder imaged and run in an offset press as in Example V. Good reproduction of the electrophotographically produced powder images was obtained in all cases.

Example VII

The procedure of Example I was repeated adding the ammonium salt of polyacrylic acid in ratios of 0.1, 0.25, 0.5 and 1 to 1 part zinc phosphate. Coatings were applied to a tubsized direct process base paper stock and to a direct process base paper stock coated with 22# of a 5 to 1 zinc oxide and ammonium salt of a vinyl acetate-crotonic acid copolymer containing about 5% crotonic acid, and also to a commercially available offset master. After drying, the resulting sheets were powder imaged electrophotographically and run on an offset press as previously described. Excellent reproductions were obtained.

Example VIII

When 0.5 gram of diammonium phosphate was added to 50 ml. of a composition obtained by mixing 24.4 grams of zinc oxide, 26.4 grams of diammonium phosphate and 150. ml. of 28% ammonium hydroxide, the resulting dried film changed from a glassy appearing film to a crystal-appearing type film, and with the loss of some rigidity using commercially available fountain solutions and etches. When 0.5 gram of ammonium carbonate and 0.5 gram of diammonium phosphate were added to a similar quantity of the original composition, the resulting dried film was no longer a film of glass-like character, but instead was a white opaque powdery material, thus indicating the critical character of the ratio of zinc oxide to ammonium salt, with best results being obtained when using above the stoichiometric amounts of zinc oxide and an excess of ammonia over the amount necessary to dissolve the zinc ammonium complex. Below this amount, the binding qualities of the compositions deteriorate rapidly.

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Example IX

In this experiment, 50 grams of zinc oxide were suspended in 50 ml. of water and to the resulting suspension was then added 10 grams of ammonium carbonate and 10 grams of 27% ammonium hydroxide solution. The coating prepared from this product had good adhesion to the base and formed a glassy, enamel like coating. The photoconductive properties were excellent.

Example X

Similar experiments were carried out in which other ammonia-soluble chromate and carbonate salts were substituted for the phosphates of the preceding examples. All were found to serve as excellent binders for the ammonia-insoluble inorganic photoconductive particles and the films prepared therewith gave excellent photoelectric reproductions.

In carrying out the above experiments, the photoconductivity was measured as a drop in resistance from the resistance in the dark to the resistance on exposure to a spotlight focused on the coated paper between the contacts on the coating with 100 volts potential applied.

Where desired to give particular properties, conventional types of binders may be used with the ammonia-soluble inorganic binders disclosed above. Other agents such as plasticizers, fillers such as barium sulfite, china clay, ochre, etc., may also be incorporated in the coatings when desired to give any particular desired result.

Because of the attractive glassy appearing surface of the films made as above described, their rigidity, relative insolubility, and excellent adhesion to a wide variety of bases, the compositions of the present invention have wide utility over previous compositions used for photoconductive coatings.

What is claimed is:

1. An electrophotographic recording element for electrostatic printing comprising a substrate carrying on at least one side thereof a dried layer comprising inorganic photoconductive particles and a binder comprising an

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inorganic ammonia-soluble metal salt selected from the group consisting of phosphates, chromates and carbonates of metals of the group consisting of zinc, copper, cobalt and silver, the ratio of said photoconductive particles to said binder being at least 1:1.

2. The electrophotographic recording element of claim 1, wherein the ratio of said photoconductive particles to said binder is of the order of approximately 5:1.

3. The electrophotographic recording element of claim 1, wherein said binder additionally comprises an amount of a vinyl acetate-crotonic acid copolymer containing 5-7%, by weight, crotonic acid which is less than the amount of inorganic ammonia-soluble metal salt.

4. The electrophotographic recording element of claim 1, wherein said binder comprises additionally an amount of a polyacrylic acid salt which is less than that of the inorganic ammonia-soluble metal salt.

5. The electrophotographic recording element of claim 1, wherein the photoconductive particles are selected from the group consisting of zinc oxide, zinc sulfide, cadmium sulfide and titanium dioxide.

6. The electrophotographic recording element of claim 1, wherein said inorganic ammonia-soluble binder is selected from the group consisting of zinc phosphate, silver phosphate, copper phosphate, cobalt phosphate and zinc carbonate.

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