

[54] ZINC OXIDE-BINDER MEDIUM
CONTAINING MICROSCOPIC CAVITIES

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Related U.S. Application Data

[63] Continuation of Ser. No. 121,430, March 5, 1971,
abandoned, which is a continuation-in-part of Ser.
No. 724,459, April 26, 1968, Pat. No. 3,595,691.

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252/501, 117/37 R, 117/41, 117/119.6

[51] Int. Cl. G03g 5/06, G03g 5/08

[58] Field of Search 96/1.5, 1.8; 252/501

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UNITED STATES PATENTS

3,245,786 4/1966 Cassiers et al. 96/1.8

3,255,039	6/1966	Dalton	117/2.5
3,347,702	2/1968	Clancy	96/1.8 X
3,378,370	4/1968	Brancato	96/1.8
3,391,022	7/1968	Saito	117/211

Primary Examiner—Roland E. Martin, Jr.
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[57] ABSTRACT

Photoconductive zinc oxide particles are contained in an electrically insulating binder medium in the proportion of about 0.5 to 10 to 1, the layer being characterized in that the photoconductive layer is porous and contains myriad interconnected microscopic cavities extending at random throughout the entire layer, said cavities being in direct communication with the ambient atmosphere and with surface areas of photoconductive particles contiguous thereto so that myriad air-photoconductive interfaces exist in said layer.

17 Claims, 5 Drawing Figures

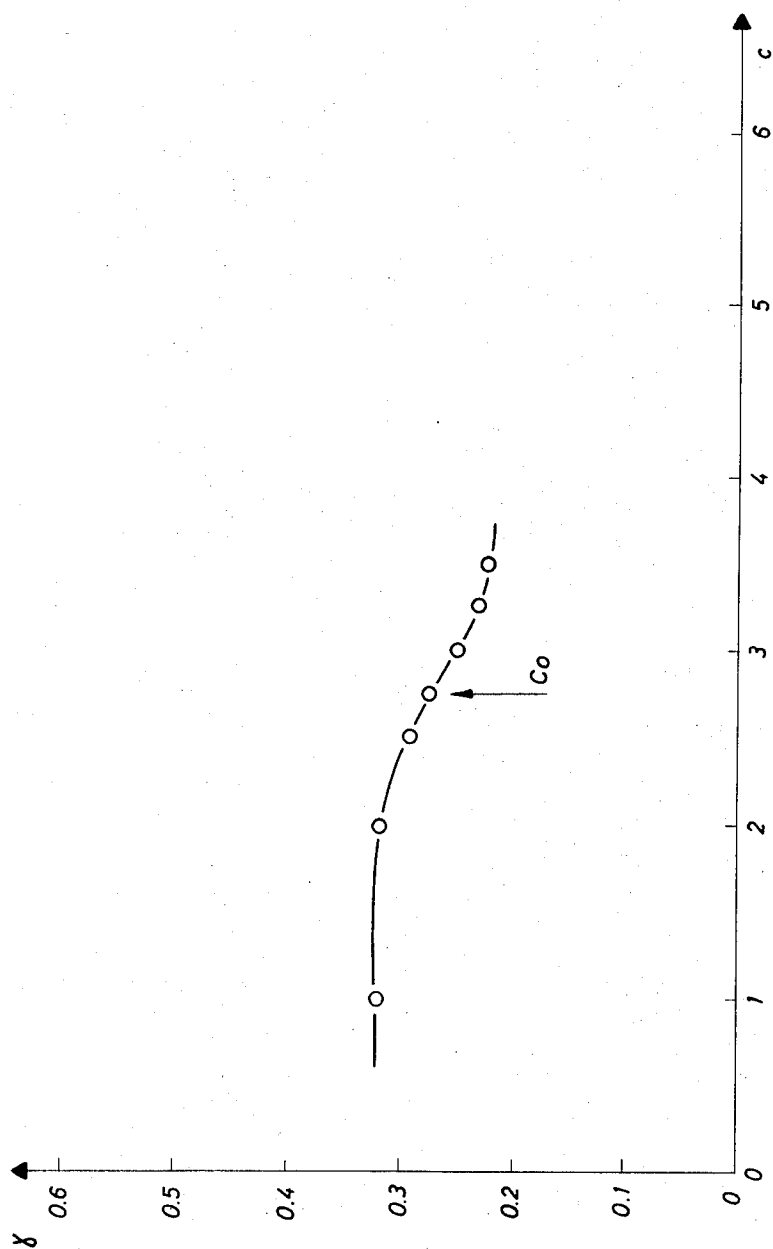
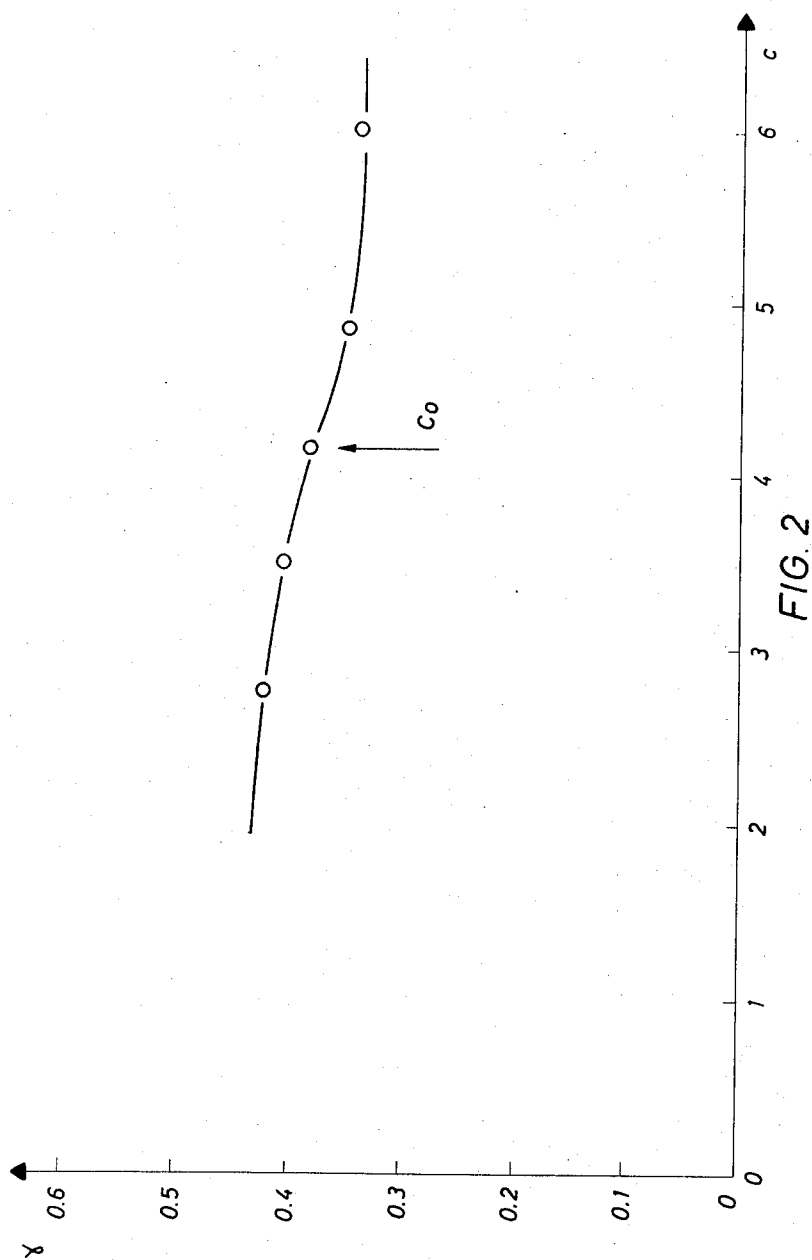


FIG. 1



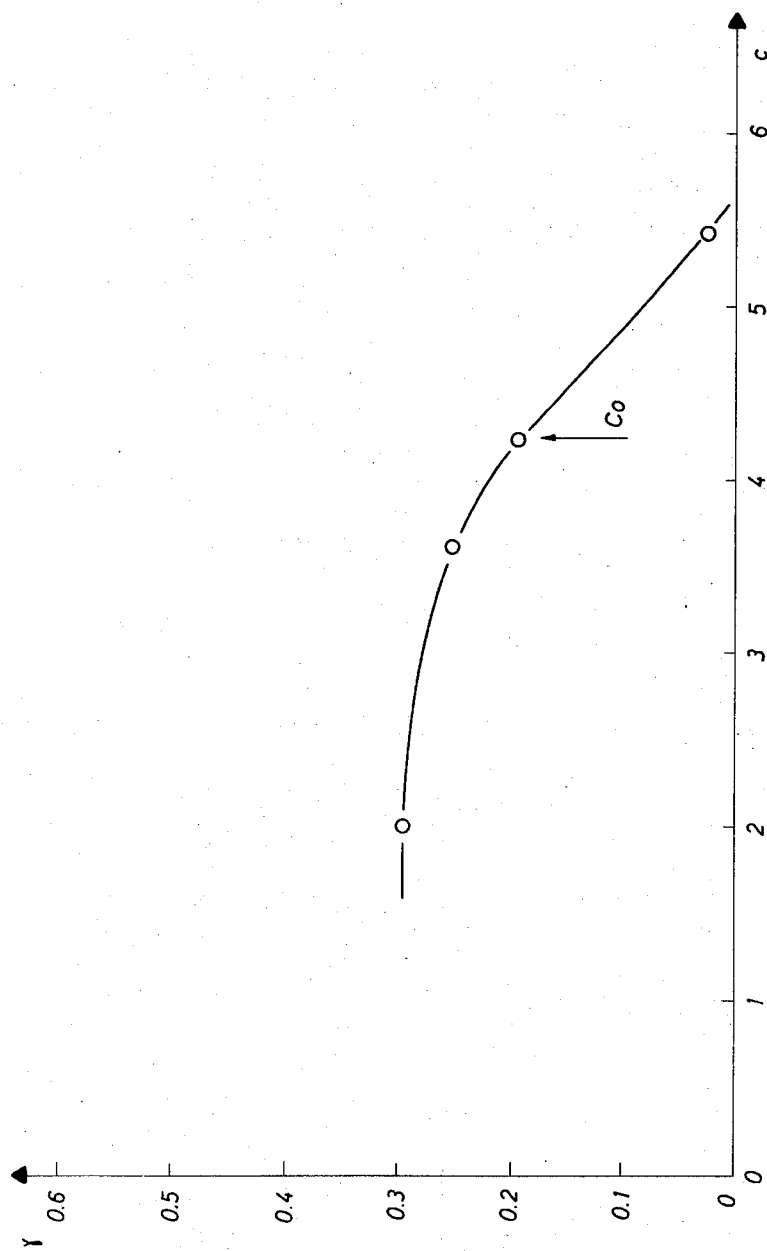


FIG. 3

SHEET 4 OF 4

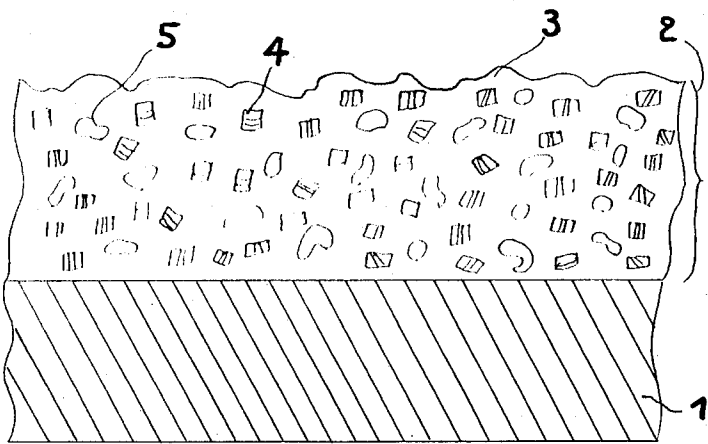


FIG. 4

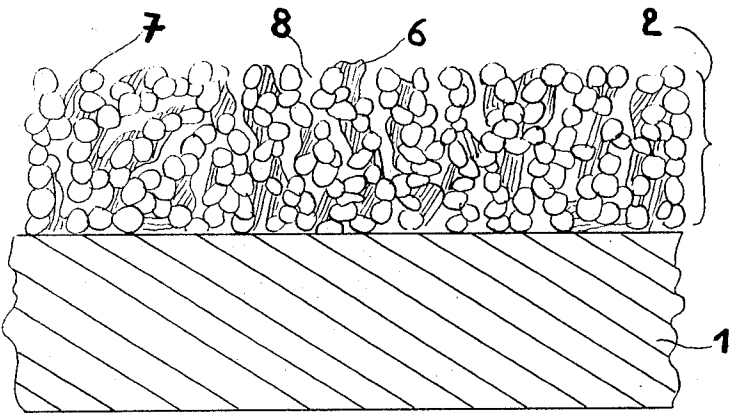


FIG. 5

ZINC OXIDE-BINDER MEDIUM CONTAINING MICROSCOPIC CAVITIES

The present application is a continuation of application Ser. No. 121,430, filed Mar. 5, 1971, now abandoned, which in turn is a continuation-in-part of application Ser. No. 724,459, filed Apr. 26, 1968, now U.S. Pat. No. 3,595,691.

The present invention relates to improved photoconductive recording materials that are suited for use in electrophotography.

A known type of electrophotographic recording plate or sheet comprises a relatively conductive backing which is coated with a photoconductive insulating composition prepared by intimately mixing and grinding together a photoconductive insulating pigment, a binder of high electrical resistivity, and one or more solvents for the binder.

In known photoconductive binder coatings, photoconductive zinc oxide is normally used as the dispersed photoconductive substance since it has a high photosensitivity, susceptibility to spectral sensitization, and a bright white colour. The binder has normally an electric resistivity and binding power as high as possible. Therefore binding agents with optimal mechanical and electrical properties at the same time are elected.

The photoconductive substance together with the binder and other additives, constitutes a paint which can be applied to a suitable support, e.g. of paper, by conventional coating techniques such as brush-, spray-, knife- or dip-coating.

It is known from Angew. Chem. 72 (1960) No. 19/20, p. 730-738, that the production of charge carriers and the dissipation of charges on a zinc oxide-containing photoconductive layer depend on the chemisorption and desorption of oxygen, and that it is possible to reduce the conductivity in the dark of the zinc oxide/binder coating by a decrease in contact points between the separate zinc oxide grains. For obtaining a highly water-repellent and highly insulating recording layer a silicon resin can be used as binding agent.

Disadvantages associated with such binding agent include a somewhat low inherent sensitivity (i.e., dischargeability by exposure to light), requiring intense exposures of the recording layer, and difficulty in providing spectral sensitization. Moreover, the molecular weight of the binding agent is usually not sufficiently high as to prevent sticking, and special care therefore must be taken during drying to prevent sticking.

It is known from the U.S. Pat. No. 3,347,702 to produce photoconductive recording layers of improved speed containing air voids.

In order to prepare such photoconductive recording layers a coating composition containing solid photoconductive particles and a single polymeric binding agent is applied in the form of an emulsion, the discontinuous and continuous phases being formed of immiscible liquids which exhibit a difference in vapor pressure at the temperature at which drying of the coating takes place.

The coatings which are applied as emulsion films are dried in a manner to retain the original emulsion structure in the dried film so that the film-forming binder remains in the form of a continuous film containing at randomly distributed non-interconnected (isolated) air voids corresponding with the discontinuous phase of said emulsion.

In other film coating methods mentioned for obtaining that result use is made of a foam or a liquid containing a volatile blowing agent. The air voids are at least 0.5 micron in size.

It has now been found an improved electrophotographic recording material containing solid photoconductive particles and an electrically insulating binder medium, characterized in that the recording layer is porous and contains interconnected microscopic air voids or cavities at random throughout the entire layer and incorporates the photoconductive particles including agglomerates thereof sticking together with a binder medium that only partly covers the photoconductor surfaces so that an air-photoconductor interface in said layer exists.

By the term "microscopic" is meant that the cavities are not discernable to the unaided eye. It is preferred that the average width of the cavities is below 20 microns and preferably is in the range from 2 to 12 microns.

The voids of interconnecting type can be produced by the use of a mixture of polymeric binding agents that are substantially incompatible in the solid dry state. In the manufacture of a recording layer containing such mixture of binding agents the binding agents are applied in a common solvent or solvent mixture wherein they are differently soluble and wherein the photoconductive particles and/or agglomerates thereof are applied in dispersed state.

According to a preferred embodiment of the present invention the binder medium of the recording layer contains at least two polymers characterized by:

- a. insolubility in water at pH 7,
- b. differential solubility in the solvents used in the coating of the layer, but not offering any noticeable turbidity in said solution when applied together therein,
- c. substantial absence of mutual solubility in the solid state whereby when said polymers are precipitated from a liquid in which they were both dissolved they form a polymer mass containing macroscopic heterogeneities, which are detectable by the unaided eye (The said precipitation occurs by evaporating said liquid).

The photoconductive recording materials according to the present invention may contain all types of solid photoconductive particles that do not dissolve in the polymeric binding agents by means of which they are stuck or kept together in the recording layer. For that purpose are mentioned the oxides, sulfides, selenides, tellurides and iodides of cadmium, mercury, antimony, bismuth, thallium, indium, molybdenum, aluminum, lead and zinc. In addition, mixtures of these as well as arsenic trisulfide, cadmium arsenide, lead chromate, selenium and organic photoconductive pigments should be mentioned.

The photoconductive pigments are generally finely divided solid particles which tend to agglomerate when mixed into the liquid coating combination. This agglomeration is not undesirable. In formulating the coating it is desirable to disperse the photoconductive particle agglomerates only enough to give a smooth coating on the support.

Preferably inorganic photoconductive pigment particles are used the spectral response of which can be easily controlled by spectral sensitizing agents; in that respect photoconductive zinc oxide is particularly useful.

The thickness of the recording layer will depend upon practical limitations such as photosensitivity, mechanical strength and the end use of the product. A useful film thickness is e.g., in the range from 5 to 30 microns. Preferably from 15 to 35 g of solid photoconductive material is present per sq.m.

The photoconductive recording materials according to the present invention have high corona-chargeability in the dark and a surprisingly high photosensitivity even without use of spectrally sensitizing agents; this may be due to the enlarged photoconductive pigment-air contact in the recording layer.

The photoconductive recording materials according to the present invention contain preferably a porous recording layer that has been produced by a method containing the steps of:

1. dispersing photoconductive pigment particles in a solution comprising at least one organic solvent having dissolved therein a mixture of polymeric binding agents including at least two polymers characterized by:
 - a. insolubility in water at pH 7,
 - b. differential solubility in said solvent in which they are dissolved;
 - c. when dissolved in said solvent formation of a solution without any noticeable turbidity;
 - d. absence of mutual solubility in the solid state, whereby when said polymers are precipitated from a solution containing them in admixture they form a polymer mass containing macroscopic heterogeneities, which are detectable by the unaided eye,
2. coating the dispersion on a support, and
3. drying the coating at such a rate that at least a portion of one of the polymers precipitates from said solvent before the other polymer whereupon at completion of the drying, the dried coating contains at random microscopic interconnecting cavities and the pigment particles or agglomerates thereof are stuck together by means of the binding agents that still leave pigment-air interfaces.

It has been observed experimentally that the rate of drying, i.e., the rate of evaporation of the solvent(s) has an influence on the yield of the voids and that also the adsorption (adhesiveness) of the binding agents to the solid photoconductor plays a role in the formation of the cavities.

The optimal concentration of the mixture of said polymers in the solution, i.e., the concentration for obtaining maximum sensitivity of the recording layer at minimum loss in optical density, may be determined by a test in which a precipitating agent is used whereby the solubility of the polymers in the solvent is decreased, thereby simulating the effect of the drying step in the process of the invention. The optimal concentration for a given ratio by weight of the different polymers is found at maximum variation of the γ -factor, which is determined according to the ratio:

$\gamma = \text{milliliters of precipitant} / \text{milliliters of precipitant} + \text{milliliters of the solution containing the mixture of said polymers}$

The precipitant should be a liquid wherein neither or none of the said polymers is soluble and which is completely miscible with the solvent mixture wherein the said polymers are dissolved. The number of milliliters of precipitant used in the above described test corresponds with the amount necessary to reach the turbid-

ity point in the titration of a given number of milliliters of solution of the said polymers in the said solvent mixture.

FIGS. 1, 2 and 3 relate to a diagram containing the γ -factor as a function of a particular polymer mixture concentration.

FIG. 4 represents a fragmentary cross-sectional view of a recording material described in the U.S. Pat. No. 3,347,702.

FIG. 5 represents a fragmentary cross-sectional view of a recording material containing a photoconductive layer according to the present invention.

In FIG. 4 the element 1 represents a support e.g., a paper support, element 2 represents the photoconductive coating built up by the insulating continuous binding agent 3, the dispersed photoconductive solid particles 4 and the isolated air voids 5.

In FIG. 5 the element 1 likewise represents a support, element 2 represents the photoconductive coating of the present invention containing photoconductive solid particles and agglomerates stuck together by means of a solid binder medium that is not filling up the whole space between the particles and agglomerates but leaves at random interconnected air channels of microscopic size through which the air stands in direct contact with parts of the photoconductor surfaces.

The drying of the coating prepared according to the above mentioned method is preferably carried out as a two stage drying process, in which in the first drying stage the temperature is kept relatively low e.g., below 30°C, preferably in the neighbourhood of room temperature (20°-25°C), the rate at which the solvent(s) are evaporated in the said first drying stage being controlled so that the layer, before being dried in the second stage, loses solvent(s) by evaporation sufficiently to ensure at least a partial precipitation of one of the polymers due to the concentration of the solution surpassing the solubility limit of the said polymer. This aim is most easily achieved when the original dispersion is concentrated to a point just slightly less than the concentration at which the said polymer is present in a saturated solution.

In the first drying stage it is advantageous to use a slow velocity drier, preferably a laminar current drier known as a tangential current drier wherein an air current strikes parallel along the coated layer. The rate of evaporation produced by such a drying system is less than that produced by a high-velocity drier (impinging air current drier), wherein air perpendicularly impinges from nozzles to the coated layer.

In the second drying stage, wherein advantageously but not necessarily an impinging air current drier is used, the temperature of the impinging air may be raised well above room temperature, for instance up to 10° to 20°C below the boiling point of one of the solvents.

The average width of the interconnecting microscopic cavities of the dried layer can be influenced by prolonging or shortening the time of the first drying stage. A prolongation of this period increases the average width of the cavities and increases the sensitivity of the material, whereas shortening of this period gives rise to a less porous material having a lower sensitivity.

A possible explanation of the formation of the interconnecting microscopic cavities produced according to the invention, in zinc oxide containing layers is that the most soluble polymer reticulates upon drying during

the second drying stage when it comes into contact with the first precipitated binding agent.

Particularly suitable binding agent systems for preparing recording materials according to the present invention can be found in the combination of polymers with different electrophilic character, e.g., a combination of polymers wherein one type (Group A) contains groups having the properties of a Lewis base (i.e., substances that provide unshared electron pairs available for co-ordination), e.g., ether groups, amino groups, or halogen atoms and an other type (Group B) which comprises groups with co-ordinated electron pairs, thus a neutralized Lewis base or acid, e.g., an ester group, or groups having the properties of a Lewis acid (i.e., substances capable of co-ordinating with unshared electron pairs), e.g., carboxylic anhydride groups such as maleic anhydride groups.

Polymers, which illustrate the nature of the binding agents suited for use in combination according to this invention, are illustrated in the following table, without however, limiting the invention thereto.

Group A

poly(vinyl ether) compounds e.g., copoly(vinyl methyl ether maleic anhydride);
cellulose ether compounds e.g., ethylcellulose and ethylallylcellulose;
vinyl acetal polymers e.g., poly(vinyl-n-butyral);
halogen-containing polymers e.g., vinyl chloride polymers and copolymers e.g., copoly(vinyl chloride/vinyl acetate) e.g., in a weight ratio of 80/20, copoly(vinyl chloride/vinyl acetate/maleic anhydride), e.g., in a weight ratio of 85/14/1 a copolymer of vinylchloride, vinylacetate, and a minor amount (less than 5 mole %) of an unsaturated bivalent dicarboxylic acid and/or its anhydride e.g., maleic acid, citraconic acid and itaconic acid, a copolymer of vinylchloride/vinylidene chloride and minor amounts (less than 5 % by weight) of maleic anhydride and acrylonitrile e.g., a copolymer containing these monomers in a weight ratio of (58/39/2/1), copoly(ethylene/vinylsulfonylchloride/vinylchloride), chlorinated rubbers e.g., chlorinated natural rubber, chlorinated polypropylene.

Group B

aliphatic esters derived from poly(vinyl alcohol) e.g., poly(vinyl acetate) and copolymers of vinyl acetate with higher (C₁₂-C₁₈) aliphatic carboxylic esters of vinyl alcohol e.g., copoly(vinyl acetate/vinyl laurate) (80/20 by weight);
homopolymers and copolymers of acrylate and methacrylate esters e.g., polymethylacrylate, polyethylacrylate, poly(methyl methacrylate), poly(isobutyl methacrylate), copoly(styrene/butylacrylate), and copoly(n-butylmethacrylate/isobutyl methacrylate).

In the mixture of above-cited polymers more than two binding agents may be present.

In the preparation of the electrophotographic recording materials according to the present invention it is important to use a solvent or solvent mixture wherein both types of polymers are sufficiently differently soluble and wherefrom preferably the polymer with the Lewis base groups first precipitates upon evaporation of the solvent(s). In this connection preferably use is made of a solvent mixture containing at least two miscible solvents, one of which has a higher vapour pressure

at the drying temperature than the other and wherein the solvent having the highest vapour pressure is a good solvent for the polymer with the Lewis base groups, whereas the solvent having a lower vapour pressure is a better solvent for the other polymer.

The photoconductive dispersion can be coated according to standard techniques e.g., by dipping, by pouring, the pigment-binder mixture onto the support to be coated, or by applying the mixture with a dip-roller.

The dried recording layer may have a thickness ranging from 1 to 30 microns, preferably from 5 to 15 microns, and the proportion of pigment to binder may be within the range between 0.5 and 10 parts, preferably between 1 and 3.5 parts of pigment calculated on 1 part by weight of binder. The ratio of polymer(s) of group (A) and polymer(s) of group (B) is chosen taking into account the need for a sufficient mechanical strength and a light-sensitivity as high as possible.

A preferred electrophotographic material, the recording element of which is prepared by the above described steps, contains a mixture of ethylcellulose and copoly(vinyl acetate/vinyl laurate) (80/20) as binder in a weight ratio of 4:1 to 1:4.

A suitable combination of solvents for the binder composition containing ethylcellulose and copoly(vinyl acetate/vinyl laurate) (80/20) contains approximately 83 parts by volume of sym.-dichloroethane, 7 parts by volume of ethanol and 10 parts by volume of a solvent containing a ketone group e.g., cyclohexanone or ethyl methyl ketone.

The photoconductive recording layers prepared according to the present invention may contain, in addition to the photoconductive substance(s) and the binder, spectrally sensitizing agents and colour correction dyes e.g., those described in the U.K. Pat. Nos. 1,020,504, 1,142,509, 1,183,044, 1,198,994, 1,199,062 and 1,200,901.

Further they may contain compounds increasing the dark-resistivity of photoconductive zinc oxide e.g., the acid compounds described in the Belgian Pat. No. 612,102. Particularly suited in that respect is acid butyl phosphate and tetrachlorophthalic anhydride. When selecting coating aids e.g., dispersing agents, preferably those are chosen, which reduce the dark-resistivity of the photoconductive layer the least possible.

The supports or base materials are chosen in view of the specific charging, exposing, recording, developing and/or transfer technique wherein the recording material is to be used.

In electrophotographic recording techniques wherein the photoconductive layer is electrostatically charged, the support preferably has an electric volume resistivity considerably lower than that of the recording layer. Suitable supports are described in the U.K. Pat. Nos. 1,020,504 and 995,491.

A paper support of the glassine type is used preferably.

The photoconductive layer of an electrophotographic material prepared according to the present invention can be used in recording systems wherein prior to the image-wise exposure an electric charge is non-differentially applied according to known methods.

The material can, however, also be used in recording techniques wherein the exposure step precedes the

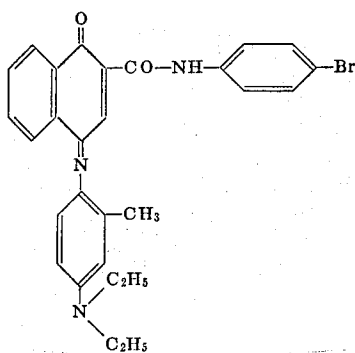
charging step. Such techniques are described e.g., in the U.K. Pat. Nos. 1,033,479 and 1,033,420.

The following examples illustrate the present invention without however limiting it thereto. The percentages are by weight if not otherwise indicated.

EXAMPLE 1

The following mixture was ground in a sand mill at a rate of 24 litres per hour:

- 7.5 g of Vinnapas B100/20VL, which is a copoly(vinyl acetate/vinyl laurate) (80/20) sold by Wacker Chemie GmbH, Burghausen, W.-Germany,
 - 7.5 g of Piloform BL 18, a poly(vinyl-n-butyral) sold by Wacker Chemie GmbH, Burghausen, W.-Germany,
 - 208.5 ccs of sym.-dichloroethane,
 - 30 ccs of cyclohexanone,
 - 17.5 ccs of ethanol,
 - 3.25 ccs of a 10 % solution of acid butyl phosphate in ethanol,
 - 3.25 ccs of a 10 % solution of tetrachlorophthalic anhydride in ethanol,
 - 75 g of photoconductive zinc oxide prepared by oxidation of zinc vapour.
- The following sensitizing dyes were then thoroughly blended with the milled composition:
- 3 ccs of a 0.25 % solution in ethanol of Orange Acridine Brillante EZ, sold by Francolor, Brussels, Belgium (C.I. 46,005),
 - 3.4 ccs of a 0.20 % solution in ethanol of a compound corresponding to the following structural formula:



- 3.75 ccs of a 1 % solution in ethanol of Eriochrome Cyanine R (C.I. 43,820) sold by Geigy, Basel, Switzerland.

The resulting dispersion was coated onto a glassine type paper support at a rate of 30 g per sq.m. by means of a dip-coating device.

The drying of the coated layer proceeded in the following manner; in the first drying stage the coated material was transported through a tangential current drier (air speed 2 m/sec) at 20°C over a period of 5 seconds. In the second drying stage the coated material was led till dry through an impinging air current drier (air speed 8 m/sec) at a drying temperature of 60°C. A mechanically very strong recording layer, which exhibited interconnecting microscopic cavities of an average width of approximately 4 μ was obtained.

The accompanying Table contains the relative sensitivity values of a recording layer as described in the

present example and of recording layers differing therefrom by the presence of only one binder of the mentioned composition.

Binder	Relative sensitivity
(A) Plioform BL 18 (trade name)	1
(B) Vinnapas B100/20VL (trade name)	4
Mixture of (A) and (B) as described in the example	12

The γ-factor depending on the concentration of the mixture of polymers (A) and (B) in the used solvent mixture is shown in FIG. 1 of the accompanying drawings, in which the concentration is shown on the abscissa and the γ-factor on the ordinate.

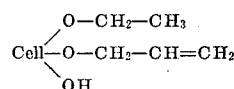
The concentration (C) is expressed by the grams of copoly (vinyl acetate/vinyl laurate) (80/20) dissolved in 100 ccs of the solvent mixture used in coating the zinc oxide dispersion of example 1, together with the necessary grams of the other polymer (B) to maintain the weight ratio of the polymers as described above, viz. 1:1.

The value C₀ shown in the curve of FIG. 1 stands for the grams of copoly(vinyl acetate/vinyl laurate) (80/20) used in the present example viz. 2.75 g per 100 ccs of the solvent mixture used in the present example.

For determining the γ-value n-hexane was used as precipitant.

EXAMPLE 2

The constituents of the binder described in example 1 were changed in quantity and nature: 3.75 g of Vinnapas B100/20VL (trade name) were used instead of 7.5 g and the poly(vinyl-n-butyral) was replaced by 3.75 g of a cellulose derivative corresponding to the following structural formula:



(degree of substitution (DS) 2.25 for the ethyl groups and 0.06 for the allyl groups).

When coating and drying as described in Example 1, analogous results were obtained.

EXAMPLE 3

1.275 litre of a 20 % solution of Vinnapas B100/20VL (trade name) in sym.-dichloroethane was mixed with a solution of 120 g of "Ethylcellulose K 50" in 3.705 liters of sym.-dichloroethane, 290 ccs of ethanol, and 600 ccs of cyclohexanone. The type of ethylcellulose used is sold by Hercules Powder Co. Inc. Wilmington, Del., U.S.A. A 5 % solution of this type of polymer in a mixture (80/20 parts by volume of toluene and ethanol possesses at 25°C a viscosity range of 40-52 cps) (degree of substitution of ethyl groups: 2.28-2.38).

The following compounds were then added:

acid butyl phosphate, 10 % solution in ethanol	65 ccs
tetrachlorophthalic anhydride, 10 % solution in ethanol	65 ccs
zinc oxide as used in Example 1	1,500 kg.

The mixture was well blended whereafter the whole

dispersion was sand milled at a rate of 24 litres/hour.

The resulting dispersion was spectrally sensitized with 60 ccs of a 0.25 % solution in methanol of Orange Acridine Brillante EZ (C.I. 46,005) sold by Francolor, Brussels, Belgium and 75 ccs of a 1 % solution in methanol of Eriochrome Cyanine R (C.I. 43,820) sold by Geigy A.G. Basel, Switzerland.

The dispersion was coated within 8 hours after completing the formula at a rate of 35 g of solids per sq.m. The drying proceeded in two stages as in example 1: the first drying stage in a tangential drier at 25°C with an air rate of 2 m/sec. for 20 sec. and the second drying stage in an impinging air drier at 50°C with an air velocity of 8 m/sec. through the nozzles. The layer was thoroughly dried in this zone.

The dried layer possessed the characteristic structure with interconnecting microscopic cavities.

The γ -factor as a function of polymer concentration is shown in FIG. 2.

The concentration (C) is expressed by the grams of copoly(vinyl acetate/vinyl laurate) (80/20) dissolved in 100 ccs of the solvent mixture used for coating the zinc oxide dispersion of example 3, together with the necessary grams of the other polymer to maintain the ratio of the polymers as in example 3.

The value C_0 shown in the curve of FIG. 2 stands for the grams of copoly(vinyl acetate/vinyl laurate) (80/20) used in example 3, viz. 4.2 g per 100 ccs of the solvent mixture used in that example.

For determining the γ -value, n-hexane was used as precipitant.

EXAMPLE 4

In example 3 the ethylcellulose was replaced by "Ethylcellulose G50" (sold by Hercules Powder Co. Inc., Wilmington, Del., U.S.A.) having a viscosity range of 40-52 cps in a 5 % by weight concentration at 25°C in a mixture of toluene/ethanol (80:20 parts by volume) and having a degree of substitution of ethyl groups: 2.21-2.28.

The results were entirely similar to those obtained according to the procedure of example 3.

EXAMPLE 5

2.4 kg of "Ethylcellulose N7" (trade name of an ethylcellulose sold by Hercules Powder Company Inc., Wilmington, Del., U.S.A.) was dissolved in 80 litres of

2.58 litres of a 10 % solution in ethanol of acid butyl phosphate,

2.58 litres of a 10 % solution in ethanol of tetrachlorophthalic anhydride,

7.8 kg of "Ethylcellulose N7" (trade name) dissolved in 39 litres of sym.-dichloroethane,

2.4 litres of a 0.25 % solution of Orange Acridine Brillante EZ (C.I. 46,005) in methanol,

3 litres of a 1 % solution in methanol of Eriochrome Cyanine (C.I. 43,820),

21 litres of ethyl methyl ketone.

The composition was coated at a rate of 32 g of solids per sq.m. of glassine type paper base, which is inherently sufficiently resistant to penetration of the solvents used.

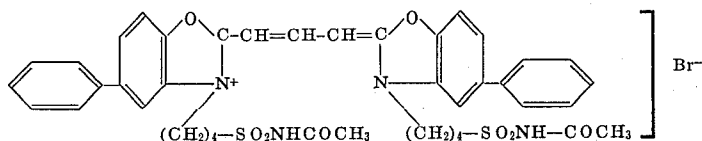
The drying time in the first drying stage was 10 seconds at a tangential air rate of 4 m/sec. at 20°C. In the second drying stage the temperature was raised to 70°C.

The sensitivity of this material was four times higher than that of the corresponding material obtained with the exclusive use of an impinging air drier working at 80°C.

EXAMPLE 6

18.88 litres of sym.-dichloroethane were mixed with 1.664 litres of ethanol and 11.136 kg of a 20 % solution of Vinnapas B100/20VL (trade name) in sym.-dichloroethane. After thorough stirring 3.20 litres of ethyl methyl ketone and 1.024 kg of Hostalit M 131 (trade name of a copolymer of vinyl chloride (87 mole %), vinyl acetate and minor amounts (less than 1 mole %) of an anhydride of an unsaturated dicarboxylic acid, a 20 % solution in ethyl acetate at 20°C has a viscosity of 120 cps, the polymer is sold by Farbwerke Hoechst, Frankfurt a/Main, W.-Germany). 0.256 litre of a 10 % solution of monobutyl phosphate in ethanol and 0.320 litre of a 10 % solution of tetrachlorophthalic anhydride in ethanol together with 9,600 kg of photoconductive zinc oxide as used in example 1 were added to the resulting solution.

The whole dispersion was mixed and then sandmilled at a rate of 24 litres per hour, whereupon 34 ccs of a 1 % solution in a 50:50 mixture of dimethylformamide and methanol of the sensitizing dye with the following structural formula:



sym.-dichloroethane (a 5 % by weight solution of this type of ethylcellulose in a mixture of toluene and ethanol (80:20 parts by volume) possesses at 25°C a viscosity range of 6-8 cps; degree of substitution of ethyl group 2.50-2.66.

The resulting solution was diluted with 3 litres of ethanol and 3 litres of cyclohexanone. Subsequently 60 kg of zinc oxide as used in Example 1 were added while mixing. The whole dispersion was fed through a homogenizer till all agglomerates were sufficiently broken. The following compounds were then added to the dispersion:

58.8 litres of sym.-dichloroethane,

8.6 litres of ethanol,

10.2 kg of Vinnapas B100/20VL (trade name) dissolved in 20.4 litres of sym.-dichloroethane,

and 63 ccs of a 1 % solution of Bromophenol blue in methanol were added. The coating and drying procedure of example 5 was then followed with comparable results.

The γ -factor as a function of polymer concentration is shown in FIG. 3.

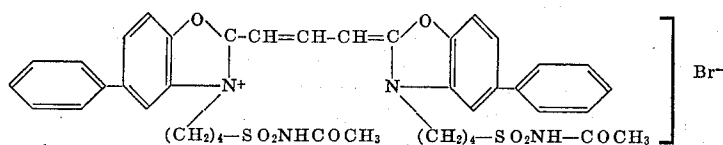
The concentration (C) is expressed by the grams of copoly (vinyl acetate/vinyl laurate) (80/20) dissolved in 100 ccs of the solvent mixture used for coating the zinc oxide dispersion of example 6, together with the necessary grams of the other polymer to maintain the ratio of the polymers used in example 6.

EXAMPLE 7

18.88 litres of sym.-dichloroethane were mixed with 1.664 litres of ethanol and 11.136 kg of a 20 % solution

of Vinnapas B100/20VL (trade name) in sym.-dichloroethane. After thorough stirring 3.20 litres of ethyl methyl ketone and 1.024 kg of IXAN SGA (trade name of a copoly(vinyl chloride/vinylidene chloride/maleic acid and corresponding anhydride/acrylonitrile) (58/39/2/1), which polymer is sold by Solvay S.A. — Belgium). 0.256 litres of a 10 % solution of monobutyl phosphate in ethanol and 0.320 litres of a 10 % solution tetrachlorophthalic anhydride in ethanol together with 9,600 kg of photoconductive zinc oxide as used in example 1 were added to the resulting solution.

The whole dispersion was mixed and then sandmilled at a rate of 24 litres per hour, whereupon 34 ccs of a 1 % solution in a 50:50 mixture of dimethylformamide and methanol of the sensitizing dye with the following structural formula:



and 63 ccs of a 1 % solution of Bromophenolblue in methanol and 20 ml of a 5 % solution of Soudan Yellow (C.I. 12,700) in sym.-dichloroethane were added. The coating and drying procedure of example 5 was then followed with comparable results.

An electrophotographic recording layer characterized by at random distributed interconnecting microscopic cavities was produced. The recording material excelled by its high photosensitivity.

We claim:

1. A photographic material suitable for electrophotographic recording of information comprising a support and a photoconductive insulating layer containing finely divided solid photoconductive zinc oxide particles or agglomerates thereof and an electrically insulating binder medium in the proportion of about 0.5-10:1, characterized in that the photoconductive layer is porous and contains myriad interconnected microscopic cavities extending at random throughout the entire layer, said cavities being in direct communication with the ambient atmosphere and with surface areas of photoconductive particles contiguous thereto so that myriad air-photoconductor interfaces exist in said layer.

2. A photographic material according to claim 1, wherein the insulating layer contains a mixture of two polymeric binding agents that are substantially incompatible in the solid dry state and that are precipitated on each other from a common solvent wherein they were differently soluble.

3. A photographic material according to claim 1, wherein the insulating layer contains microscopic cavities of an average width below 20 microns.

4. A photographic material according to claim 3, wherein the insulating layer contains microscopic cavities with an average width in the range of 2 to 12 microns.

5. A photographic material according to claim 1, wherein the photoconductive zinc oxide particles have been spectrally sensitized.

6. A photoconductive material according to claim 1, wherein the photoconductive zinc oxide particles have been treated with a substance increasing their dark-resistivity.

7. A photoconductive material according to claim 6, wherein said substance is acid butyl phosphate or tetrachlorophthalic anhydride.

8. A photographic material according to claim 1, wherein the binder medium contains at least two polymers characterized by:

- insolubility in water at pH 7,
- differential solubility in the solvent used in the coating of the recording layer without any noticeable turbidity in said solution when applied together in said solvent,
- substantial absence of mutual solubility in the solid state whereby when said polymers are precipitated from a mutual solvent solution they form a polymer mass containing macroscopic heterogeneities, which are detectable by the unaided eye.

9. A photographic material according to claim 1, wherein the insulating layer contains a polymer selected from the group consisting of polyvinyl acetals, polyvinyl ethers, cellulose ethers, halogen-containing vinyl polymers, chlorinated rubbers and chlorinated polyolefins and a polymer selected from the group consisting of aliphatic esters of polyvinyl alcohol, homopolymers and copolymers of acrylate esters and homopolymers and copolymers of methacrylate esters.

10. A photographic material according to claim 9, wherein the mixture of polymers consists of a cellulose ether and an aliphatic ester of polyvinyl alcohol.

11. A photographic material, according to claim 9, wherein an ethyl cellulose ether and a vinyl acetate/vinyl laurate copolymer is used.

12. A photographic material according to claim 9, wherein an ethyl-allyl cellulose ether and a vinyl acetate/vinyl laurate copolymer is used.

13. A photographic material according to claim 9, wherein a mixture of polymers is used consisting of a polyvinyl acetal and a vinyl acetate/vinyl laurate copolymer.

14. A photographic material according to claim 9, wherein a combination of polymers is used consisting of a copolymer of vinyl chloride, vinyl acetate, and a minor amount of a bivalent unsaturated carboxylic acid anhydride and a copolyvinyl acetate/vinyl laurate copolymer.

15. A photographic material according to claim 9, wherein a mixture of polymers is used consisting of a copolymer of vinyl-chloride, vinylidene chloride, and a minor amount of maleic anhydride and acrylonitrile and a copolymer of vinyl acetate and a C₁₂-C₁₈ carboxylic acid vinylalcohol ester.

16. A material according to claim 11, wherein the binder contains ethylcellulose and copoly(vinyl acetate/vinyl laurate) (80:20) in a weight ratio of 4:1 to 1:4.

17. A material according to claim 1, wherein the photoconductive layer is present on a glassine paper support.

**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

PATENT NO. : 3,857,708
DATED : Verhille et al.
INVENTOR(S) : Karel Eugene Verhille; Robert Joseph Noe

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

On the line following item [21] in the title of the patent insert the following line:

[30] Foreign Application Priority Data

April 26, 1967 Great Britain.....19,186/67

Signed and sealed this 29th day of April 1975.

(SEAL)

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks