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3,240,595

## ELECTROPHOTOGRAPHIC MATERIAL

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1 Claim. (Cl. 96—1)

This application constitutes a division of our copending application Serial No. 85,474, filed January 30, 1961.

The present invention relates to electrophotographic material and electrostatic recording materials consisting of an electroconductive backing and a photoconductive layer which contains an organic polymeric photoconductive substance or which consists of an organic polymeric photoconductive substance.

Electrophotographic materials are already known which consist of a support and a photoconductive layer containing as photoconductor an inorganic substance such as selenium or zinc oxide or an organic substance such as anthracene, benzidine or a certain type of heterocyclic compound.

Electrostatic recording materials are already known comprising a photoconductive layer, such as antimony trisulphide, overcoated with an insulating layer, such as polystyrene.

Electrophotographic processes involve the electrical charging in the dark of an electrophotographic plate or sheet comprising a coating of photoconductive insulating or semiconductive material on a conductive support or on an insulating support provided with a conductive layer, so that the coating carries a fairly uniform positive or negative charge. The plate or sheet is then image-wise exposed whereby the illuminated areas of the surface are discharged and the electrostatic latent image is obtained. This latent image is then rendered visible e.g. by depositing thereon a finely divided electrostatically attractable material such as a powder, yielding a powder image. In the electrostatic recording methods an obtained electrostatic pattern of the light signals can be read by a suitable playback head.

For carrying out the above described electrophotographic process, involving electrically charging in the dark a photoconductive layer and subsequently image-wise exposing the same to light so that the illuminated areas of the layer are discharged, photoconductive layers are required which on the one hand possess a high dark resistivity so that they can easily accumulate an electric charge, and on the other hand possess a sufficiently high photoconductivity to enable them easily to deliver the accumulated charge on exposure.

It is known that some groups of polymeric substances can retain in the dark a high electric charge for a considerable period of time, but lose this charge on exposure to an electromagnetic radiation of suitable wave-length.

Polymeric photoconductive substances are e.g. described in our corresponding United States patent applications Nos. 11,128; 11,129, now Patent No. 3,155,503, and 11,130, now Patent No. 3,131,060, all filed February 26, 1960.

Now we have found that electrophotographic materials suitable for use in a wide variety of electrophotographic reproduction methods and electrostatic recording methods can also be obtained by using in the manufacture of the photoconductive layer a polymeric substance or substances obtained by reacting at least one halogen containing polymeric substance (the term "polymeric substance" here

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including homo- and co-polymers) with at least one aromatic or heterocyclic compound and/or a polymeric substance or substances obtained by reacting at least one compound containing at least one reactive halogen atom with at least one polymer containing aromatic or heterocyclic nuclei.

The exact structure of these reaction products is not known. A possible explanation of the mechanism of reactions leading to the formation of similar reaction products has been proposed by Ph. Teyssié and G. Smets, J. Polymer Sci., XX, 351 (1956). Although many facts seem to support the views of the authors, the present invention is not dependent on any particular theory of the reaction(s) involved in the preparation of the materials used.

A representative although not limitative list of polymeric reaction products particularly suitable for use in the manufacture of a photoconductive layer according to the present invention, is given below:

- 20 Reaction product of polyvinylchloride and anthracene
- Reaction product of polyvinylchloride and fluorene
- Reaction product of polyvinylchloride and naphthalene
- Reaction product of polyvinylchloride and toluene
- Reaction product of polyvinylchloride and N-methylphenothiazine
- 25 Reaction product of polyvinylchloride and carbazole
- Reaction product of polyvinylchloride and phenothiazine
- Reaction product of polyvinylchloride and N-ethylcarbazole
- 30 Reaction product of polyvinylchloride and phenoxathiine
- Reaction product of polyvinylchloride and acridine
- Reaction product of polyvinylchloride and lophine
- Reaction product of after-chlorinated polyvinylchloride and anthracene
- 35 Reaction product of chlorinated natural rubber and anthracene
- Reaction product of after-chlorinated polyvinylchloride and naphthalene
- Reaction product of chlorinated natural rubber and naphthalene
- 40 Reaction product of polyvinylbenzylbromide and N-ethylcarbazole
- Reaction product of poly(p-isoprenylbenzylbromide) with N-ethylcarbazole
- 45 Reaction product of the copolymer of vinylchloride and styrene with naphthalene
- Reaction product of polystyrene with methylenechloride and fluorene
- Reaction product of polystyrene with methylenebromide and fluorene
- 50 Reaction product of polystyrene with 1,2-dibromoethane and fluorene
- Reaction product of polystyrene with chloroacetylchloride and fluorene
- 55 Reaction product of polystyrene with chloroacetylchloride and N-ethylcarbazole
- Reaction product of polystyrene with 9-bromofluorene
- Reaction product of polystyrene with a chlorine containing carbazole derivative
- 60 Reaction product of polystyrene with 9-ethyl-3-chloro-carbonylcarbazole.

The reaction products listed hereinbefore can be prepared by application of the Friedel-Crafts reaction wherein aluminum chloride serves as the catalyst.

According to a first preferred embodiment of the preparation a halogen substituted homo- or copolymer containing reactive halogen atoms such as polyvinyl chloride is reacted with an aromatic or heterocyclic compound in the presence of a Friedel-Crafts catalyst such as aluminum chloride.

According to a second preferred embodiment of the preparation an aromatic or a heterocyclic compound con-

taining a reactive halogen atom is reacted with a polymer or a copolymer containing aromatic or heterocyclic nuclei.

According to a third preferred embodiment of the preparation an organic compound containing two reactive halogen atoms is reacted with an aromatic or a heterocyclic compound and a polymer or a copolymer containing aromatic nuclei.

It is to be noted that the degree of polymerization of the halogenated polymers is not critical and can vary between wide limits. As far as the copolymers are concerned, it is further to be noted that the content of halogenated groups is not critical and can vary between wide limits, taking into account the properties of the compounds used in the preparation of the copolymers and the required electrophotographic and/or mechanical properties.

The preparation of some polymeric reaction products for use according to the invention, including some of those listed above, is described hereinafter by way of example.

#### PREPARATION 1

1 mol of a polyvinylchloride and 1 mol of an aromatic product such as fluorene, naphthalene, toluene are brought into 1250 cm.<sup>3</sup> of dichloroethane. Whilst stirring, 1 mol of aluminum chloride is added at once. The reaction is slightly exothermic and the temperature is maintained below 25° C. After stirring at room temperature for 20 hours the reaction mixture is poured into a fourfold excess of methanol. The polymer precipitate formed is purified by washing with methanol. The polymer is further purified by dissolving in a suitable solvent such as benzene, chloroform, tetrahydrofuran etc. filtering and precipitating again in methanol, ether or hexane. The intrinsic viscosity of the reaction products formed has been measured at 25° C. in tetrahydrofuran and ranges around 0.08 dl./g. The analysis and viscosity results of some of the synthesized reaction products are given hereinafter by way of example.

Reaction product of polyvinylchloride and fluorene intrinsic viscosity: 0.13 dl./g.

*Analysis.*—Calculated: C, 93.76%; H, 6.24%. Found: C, 93.28%; H, 6.26%.

Reaction product of polyvinylchloride and naphthalene intrinsic viscosity: 0.06 dl./g.

*Analysis.*—Calculated: C, 93.50%; H, 7.75%. Found: C, 92.4%; H, 5.94%; Cl, 0.6%.

Reaction product of polyvinylchloride and toluene intrinsic viscosity: 0.10 dl./g.

*Analysis.*—Calculated: C, 91.53%; H, 8.47%. Found: C, 90.14%; H, 8.25%; Cl, 1.02%.

#### PREPARATION 2

1 mol of an halogen containing heterocyclic compound, 1 mol of polystyrene and 1 mol of aluminum chloride are reacted in a suitable solvent such as carbon tetrachloride or tetrachlorethane. The reaction can also be carried out with 1 mol of polystyrene, 2 moles of a heterocyclic compound and 1 mol of a compound containing two reactive halogen atoms such as methylene chloride, methylene bromide, 1,2-dibromoethane and monochloroacetylchloride. The preferred reaction medium in this case is carbondisulphide. Purification of the resulting polymer proceeds in the same way as described under Preparation 1. A preparation of a particular polymer according to this method is described hereinafter.

A chlorine containing carbazole derivative is prepared by refluxing for 16 hours. 25 g. of N-hydroxypropyl carbazole with 25 cm.<sup>3</sup> of thionylchloride and 50 cm.<sup>3</sup> of toluene. The reaction product is precipitated in hexane, redissolved in tetrahydrofuran and finally precipi-

tated in water. After filtration, the reaction product is dried under vacuum. Yield: 11.6 g.; chlorine content: 15.1%.

10 g. of the thus obtained chlorine containing carbazole derivative, 4.3 g. of polystyrene and 5.35 g. of aluminum chloride in 200 cm.<sup>3</sup> of carbontetrachloride are stirred at room temperature for 48 hours. The reaction product is precipitated in methanol, redissolved in tetrahydrofuran and freed from insoluble impurities by centrifuging. The polymer is finally reprecipitated in methanol, filtrated and dried under vacuum. Yield: 10.6 g.

The present invention includes electrophotographic materials comprising a suitable electroconductive backing in intimate surface contact with a photoconductive layer consisting of or containing (e.g. consisting mainly of) at least one of the reaction products as hereinbefore defined.

For the preparation of the electrophotographic material according to the present invention various techniques can be applied when coating the support with a photoconductive layer.

In practice it is preferable for the polymeric substance or substances involved, either alone or together with other additives such as those described more specifically hereinafter first to be dissolved or dispersed in a suitable organic solvent such as for instance benzene, acetone, methylenechloride, dimethylformamide, tetrahydrofuran, chloroform, carbontetrachloride or in a mixture of two or more of such solvents. The solution or dispersion thus obtained is uniformly spread on a surface of a suitable support, for instance by centrifuging, spraying, brushing or coating, whereafter the layer formed is dried in such a way that a uniform photoconductive layer is formed on the surface of the support.

Photoconductive layers, consisting wholly or mainly of one or more reaction products of one or more halogenated homo- or copolymers and one or more aromatic compounds, and/or of one or more reaction products of one or more halogenated monomers and one or more aromatic polymers, firmly adhere to supports which they are applied.

The thickness of the photoconductive layers is not critical, but is open to choice within a wider range according to requirements in each individual case. Good results are attained with photoconductive layers of a thickness between 1 and 20  $\mu$  preferably between 5 and 10  $\mu$ . Layers which are too thin do not have a sufficient insulating power and layers which are too thick require extensive exposure-times.

Photoconductive layers according to the present invention may contain, in addition to one or more halogen containing reaction products, one or more other photoconductive monomeric or polymeric compounds with similar or different photo-electric, mechanical or other physical properties.

The photoconductive layers according to the present invention may contain besides one or more of the polymeric substances according to the present invention still one or more other photoconductive monomeric or polymeric compounds with similar or different photoelectric, mechanical or other physical properties.

In this way, there are prepared several mixtures of one of the polymeric substances, according to this invention, with substances such as those disclosed in our corresponding United States patent applications Nos. 11,128; 11,129 and 11,130. In this respect particularly favourable results are attained with layers consisting of 67 to 99% of a reaction product or products according to the present invention and 1 to 33% of one or more of the vinyl polymers or vinyl copolymers referred to in the specification of our United States patent application Serial No. 11,130 filed February 26, 1960.

Further, according to the present invention a compound or compounds which cause an increase of the general

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sensitivity and/or of the sensitivity to electromagnetic rays from a particular part of the spectrum can also be present in the photoconductive layers, and for this purpose sensitizing compounds may be selected irrespective of whether or not they themselves possess photoconductive properties.

Suitable compounds for increasing the general sensitivity and/or the sensitivity to electromagnetic rays from the visible part of the spectrum are e.g. the sensitizing substances described in United States copending application Serial No. 11,129. These compounds are preferably used in an amount of 0.1 to 5% in respect of the weight of the polymeric photoconductive substances used.

Finally, there can be present in the photoconductive layer other monomeric or polymeric compounds which confer desired properties on the photoconductive layer and/or on the composition wherefrom this layer is formed. Thus, e.g., plasticizers such as dibutylphthalate, dimethylphthalate, dimethylglycolphthalate, tricresylphosphate, triphenylphosphate, monocresyldiphenylphosphate etc. may be added to the polymeric substance or substances used in the photoconductive layer in amounts of 10 to 30% of the reaction product weight.

Other additives, well known in the art, of surface coating, which may be used, include pigments, and agents controlling viscosity, free flow, aging and thermal stability, oxidation and/or gloss. In selecting such additives, preference is given to those substances which do not markedly impair the dark resistivity of the photoconductive layer.

An important feature of the reaction products according to the present invention is their ability to improve the sensitivity of the polymeric materials proposed as photoconductors in the United States patent application Serial No. 11,129 particularly when incorporated into a photoconductive layer in amounts varying between 0.5 and 5% in respect of the weight of the said polymeric material.

The reaction products according to the invention are preferably employed in the photoconductive layer of electrophotographic materials wherein the said layer is united with or at least held in intimate surface contact with a backing or support in the form of an electrically conductive plate or sheet member or in the form of an insulating plate or sheet with an electrically conductive layer in contact with the photoconductive layer. An electrically conductive member or layer is a plate, sheet or layer the specific resistivity of which is lower than that of the photoconductive layer, i.e., in general lower than  $10^9$  ohm/cm. Conductive materials the specific resistivity of which is lower than  $10^5$  ohm/cm. are preferably used.

Suitable backings or supports in the form of an electrically conductive plate or sheet or in the form of an insulating plate or sheet provided with an electrically conductive layer are described in the United States patent application Serial No. 11,129.

Electrophotographic materials according to the present invention can be used in any of the different techniques whatever which are based on the exposure and the discharge of an electrostatic charge provided in or on a photoconductive layer.

The electrostatic charging of the photoconductive layer, the exposure, the transfer of the latent image, if any, the development, the transfer of the powder image, if any, the fixation of the powder image can be carried out as described in the United States patent application Serial No. 11,129.

The present invention is not limited in regard to the particular way in which the new electrophotographic materials are used, and the method of charging, the exposure technique, the transfer (if any), the developing method, and the fixing method as well as the materials used in these steps can be chosen according to requirements.

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Electrophotographic materials according to the present invention can be applied in reproducing techniques using different kinds of radiations, not only electromagnetic radiations as hereinbefore referred to but also nuclear radiations. For this reason, it should be pointed out that although materials according to the invention are mainly intended for application in processes involving an exposure, the term "electrophotography" wherever appearing in the description and the claims is used broadly, and includes both xerography and xeroradiography.

The present invention includes also electrostatic recording materials.

The following examples illustrate the present invention without limiting, however, the scope thereof.

#### Example 1

A 90 g./sq.m. paper support coated with a 10 g./sq.m. baryta layer, is coated with a 6% solution of Hostalit CAM (trade mark for a terpolymer of vinyl chloride, vinyl acetate and maleic anhydride manufactured by Farbwerke Hoechst A.G., Frankfurt (M)—Höchst) in methylene chloride. The thus formed material is coated with a 10% solution in methylene chloride of the reaction product of polyvinylchloride and anthracene. After complete drying the photoconductive layer obtained is negatively charged with a corona device whereafter it is exposed reflectographically for 6 sec. with a 100 watt-lamp at a distance of 10 cm. The development of the latent image formed is carried out with a suitable triboelectrical powder. The powder image thus obtained is brought into contact with a thin wax bearing sheet. The wax melts when heated and makes the powder adhere to the sheet. After stripping off the latter a clear, legible and contrasty image is obtained.

#### Example 2

A 10 g./sq.m. baryta layer is coated on a 90 g./sq.m. paper stock. This layer is coated with a thin rubber layer from a 0.5% aqueous rubber dispersion. Hereupon is coated a 10% solution of the reaction product of polyvinylchloride and phenoxathine in chloroform. When the material obtained is thoroughly dried it is charged by means of a corona device and exposed for 6 seconds through a diapositive with a 100 watt-lamp at a distance of 10 cm. The electrostatic latent image thus obtained is developed by treating it with a suitable developing powder. After fixing the powder image in known way a very contrasty image is obtained.

#### Example 3

The metal side of an aluminum paper sheet is coated with a layer from the following solution.

|                                                                                    |                     |
|------------------------------------------------------------------------------------|---------------------|
| 10% solution of the reaction product of polyvinyl chloride and fluorene in acetone | 50 cm. <sup>3</sup> |
| 10% solution of Hostalit CAM (registered trademark) in methylene chloride          | 50 cm. <sup>3</sup> |
| Rhodamine B (C.I. 45,170)                                                          | 10 mg.              |

The material obtained after quick drying is positively charged with a corona device whereafter it is contact-exposed for 60 sec. through a diapositive with a 100 watt-lamp at a distance of 10 cm. When using a suitable reversal toner a directly legible image is produced which is fixed in known way by heat. A very contrasty image is obtained.

#### Example 4

A 90 g./sq.m. paper stock is coated with a Hostalit CAM (registered trade-mark) layer. On this support is coated a 10% solution of the reaction product of polyvinylchloride and naphthalene in methylene chloride. After drying this coated material for 1 day under normal circumstances it is charged by means of a corona apparatus. After exposure for 6 seconds through a negative to a 100 watt lamp at a distance of 10 cm. an electrostatic latent image is obtained. This image is de-

veloped by means of a suitable powder and fixed by heat. A very contrasty image is obtained.

#### Example 5

An electrically conductive glass plate is coated with a layer from the following solution.

10% solution of the reaction product of polyvinylchloride and N-ethylcarbazole in dimethylformamide ----- 50 cm.<sup>3</sup>  
10% solution of Hostalit CAM (registered trade-mark) in methylene chloride ----- 50 cm.<sup>3</sup>  
Rhodamine B (C.I. 45,170) ----- 10 mg.

After drying this material for 15 h. at 50° C. it is charged by means of a corona device and contact-exposed for 1 second through a diapositive to a 100 watt-lamp at a distance of 10 cm. After development with a suitable developing powder and fixing by heat a very contrasty reproduction of the original is obtained.

#### Example 6

An aluminum plate of 250 g./sq.m. is coated with a 10% solution of the reaction product of Rhenoflex (registered trade-mark) and anthracene in a mixture of dimethylformamide and methylene chloride (50/50). After drying for 24 hours this material is negatively charged by means of a corona apparatus and exposed for 4 minutes to a 75 watt-lamp through a miniature diapositive which is 10 times enlarged. By using a suitable developing powder a vigorous and contrasty image is obtained which is finally fixed by heat.

#### Example 7

A 90 g./sq.m. paper stock is coated with a 10 g./sq.m.

baryta layer. On this support the following solution is coated.

Polyvinylcarbazole ----- 4 g.  
Methylene chloride ----- 100 cm.<sup>3</sup>  
Friedel-Crafts reaction product of poly(4-vinylbenzylbromide) and N-ethylcarbazole ----- 0.5 g.

The layer is charged by means of a corona device and reflectographically exposed for 2 seconds with a printed original to a 100 watt-lamp at a distance of 10 cm. The latent electrostatic image formed is treated with a suitable developing powder yielding a contrasty and vigorous image. By transferring the powder image onto a sheet of writing paper in well known way, a directly readable copy is obtained which is fixed by heat and which can be stored for an unlimited period of time.

We claim:

An electrophotographic copying process which comprises exposing an electrostatically charged photoconductive insulating layer comprising a polymeric substance obtained by reacting (A) polystyrene, (B) an organic compound containing two reactive halogen atoms, selected from the group consisting of methylene chloride, methylene bromide, 1,2-dibromoethane, and chloroacetylchloride and (C) a compound selected from the group consisting of fluorene and N-ethylcarbazole in the presence of a Friedel-Crafts catalyst to a light image whereby the light struck area is discharged and developing said image of electrostatic charges with an electroscopic material.

No references cited.

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