United States Patent Office

3,708,294
Patented Jan. 2, 1973

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3,708,294
PROCESS FOR PREPARING A PHOTOCONDUCTIVE FIBER SHEET

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No Drawing. Filed June 29, 1970, Ser. No. 50,899
Claims priority, application Japan, July 2, 1969, 44/52,266
Int. Cl. G03g 5/04
U.S. Cl. 96—1.6 7 Claims

ABSTRACT OF THE DISCLOSURE

A photoconductive fiber sheet is produced by dyeing with a sensitizing coloring matter a fiber sheet made of organic high polymer fibers capable of acting as a Lewis base against a Lewis acid and forming a charge transfer complex with the Lewis acid and then treating the fiber sheet with the Lewis acid.

This invention relates to a process for preparing a photoconductive fiber sheet which fulfills multipurpose applications.

Conventional electrophotographic photosensitive members generally comprise a supporting body and a photconductive layer laid thereon, in which the photoconductive layer consists either solely of a photoconductive substance or of a photoconductive substance and a binder resin. Therefore, to prepare the photosensitive member, a photoconductive substance or, when required, a mixture of the photoconductive substance and a binder resin was coated on one surface of a support such as a metal plate, paper, etc. by an ordinary layer forming method. However, the conventional process for preparing a photosensitive member as stated above has drawbacks as described below.

First, the solution or suspension system, which mainly contains the photoconductive substance, permeates into the supporting body. Moreover, the photoconductive layer has a weak mechanical strength. These factors have caused the photosensitive member to have a short service life and a low sensitivity to light. For example, as to the above-mentioned binding agent, since the supporting body and the photoconductive layer are usually different substances, peeling of the photoconductive layer is often caused by external force or, due to nonuniformity in adhesiveness, partial unevenness in photosensitivity is produced which results in the so-called "fog." Furthermore, as a result of the permeation of the above-mentioned solution or suspension system containing the photoconductive substance into the supporting body, the thickness of the photoconductive layer becomes substantially uneven and consequently gives a photosensitive member which has a partially different dark resistance. This also results in the drop of photosensitivity. Still further, since the mechanical strength of the above-mentioned photoconductive layer is generally weak and its surface is easily damaged by the repeated rubbing when the layer is used in the electrophotographic copying process, the service life of the photosensitive member is reduced remarkably.

Since the conventional photosensitive member had many drawbacks as mentioned above, even if the selective use or processing of the supporting body or the method of forming photoconductive layer have been improved by the introduction of advanced technique, such defects have been hardly eliminated.

However, advancement of the study of organic photoconductive material is remarkable, and now there is known a photoconductive body of film form and a photconductive body of sheet form made by weaving organic photo-

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conductive material. Moreover, there are known many kinds of Lewis acids which act as particularly effective sensitizers forming organic photoconductive materials. Such film form or sheet form organic photoconductive bodies are almost free from the above-mentioned defects. On the contrary, it is expected that the transparent photoconductive body, when woven, has a wide variety of applications as a particularly endurable photoconductive body. However, since organic photoconductive materials are, in general, low in sensitivity, they have the drawback that they always require the addition of a sensitizing agent. In other words, no film form or sheet form photoconductive bodies are offered today without sensitizing agents and since effort must be made in the application of the sensitizing agent, not only are technical devices but also economical processes for preparing photoconductive bodies as well as simple processes of preparation are much hindered. This is proved by the fact that the practical values of organic photoconductive bodies are still far lower than those of inorganic ones.

The first purpose of this invention is to offer a process by which the still insufficient practicality of organic photoconductive bodies can be drastically increased.

It is, of course, possible to obtain a highly sensitive, easy handling, and excellently durable photoconductive sheet by making various kinds of sensitizing agents coexist with the organic photoconductive material to impart a high photosensitivity and then making the said material into fiber form and weaving it into cloth. However, when a fusion spinning method is employed for producing the fiber, almost all sensitizing agents undergo decomposition and sublimation under the high temperature fusion spinning conditions. Consequently, not only cannot the expected sensitizing effect be obtained, but also some sensitizing agents fail to give the sensitizing effect at all. It should be noted that the more excellent a substance is as sensitizing agent, the less withstandable the substance is against high temperature condition. When a wet spinning method is used in the process for obtaining a fiber form photoconductive body, it is necessary for both the organic photoconductive material and its sensitizing agent to be soluble to particular solvents and insoluble to other particular solvents.

Since both the organic photoconductive material and the sensitizing agent must be so chosen as to fulfill this said requirement, the sensitizing agents used are usually assigned with a heavy limitation.

From another point of view, since the organic photoconductive materials to be made in a fiber form are usually polymers, selection of soluble and insoluble solvents is normally a very difficult matter and, for this reason, the wet spinning method has limitation in its function. As a result, iits not an easy task to obtain an optimum combination of organic photoconductive material and sensitizing agent in the wet spinning method. Further, a wet spinning method can not be applied to some materials. In addition, in almost all wet spinning processes a heat curing is essential at the final stage so that the use of sensitizing agents encounters a difficulty as in the case of the melt spinning method.

Such unfavorable limiting factors become a technical "barrier" in forming a fiber form sheet and in many cases this "barrier" increases greatly the manufacturing cost of the fiber sheet.

From a different point of view, demand for photosensitive fibers is markedly limited as compared with that for usual fibers. Nevertheless it is commercially inevitable to produce continuously various kinds of photosensitive fibers different in photosensitivity, spectrum characteristic and fiber property in a comparatively small scale production. A large quantity production of such material at one time is obviously so economical that a continuous small scale production of various kinds of photosensitive fibers does not favor commercial production and shelf life of the produced material.

Another object of this invention is to offer an extremely economical process for preparing a photoconductive fiber sheet by improving the conventional photoconductive fiber sheet forming technique, by assuring a high photoconductivity, and by admitting a free selective use of sensitizing agent, etc.

A further object of this invention is to offer a process for preparing a photoconductive fiber sheet having an excellent performance in multicolor reproduction process.

A still further object of this invention is to offer a process for preparing a photoconductive fiber sheet in which the photoconductivity is given in the form of a pattern.

This invention relates to a process for preparing a photoconductive fiber sheet which comprises dyeing a fiber sheet made of an organic high polymer material as the main material with a sensitizing coloring matter and then treating it with Lewis acid. Here the organic high polymer material is a substance which has the property of assuming the property of a Lewis base against the Lewis acid and forming with it a charge transfer complex. The fiber sheet is a paper or cloth made or woven from fibers composed of an organic high polymer material. The technical feature of this invention may be explained by two factors. One is to dye the fiber sheet with a sensitizing coloring matter and the other is the joint use of a sensitizing coloring matter and a Lewis acid as the sensitizing agent.

Therefore, the greatest feature of this invention is that quite an excellent sensitizing effect for the photoconductivity of the sheet is obtained by treating the fiber sheet with a sensitizing coloring matter and by further treating it with a Lewis acid. Simultaneously, since the dyeing step can be effected on the sheet after it is formed, it is not required to choose a particular kind of high polymer material and a spinning method in order to prepare a fiber sheet. In other words, it is possible to form a fiber sheet by using a most desired material with a most suitable method.

Moreover, since the dyeing is accomplished, in principle, by only applying a sensitizing coloring matter to the said sheet under appropriate conditions, a sensitizing coloring matter which is expected to have the highest sensitizing effect can be used at will.

The sensitivity of the fiber sheet dyed in such a way is increased remarkably by treating it with a Lewis acid.

The characteristics of the photoconductive fiber sheet obtained according to the present invention are remarkably excellent as compared with those of conventional photoconductive fiber sheets obtained by adding a sensitizing agent preliminarily. The photoconductive fiber sheet is free from various disadvantages such as loss of the sensitizing agent caused by decomposition or sublimation, and lowering of photosensitivity caused by detrimental substance produced by decomposition. Therefore, the sensitivity of the photoconductive fiber can be increased to a practical level. In addition, the sensitizing agent, particularly a Lewis acid, is liable to cause deterioration of the physical property of the fiber itself during the melt spinning process while in the present invention the sensitizing agent is not present in the spinning process. In view of the excellent sensitivity characteristics of the photoconductive fiber sheets produced by the present invention, it is considered that the sensitizing agent is uniformly absorbed to the fiber in an appropriate amount.

Next, the representative substances used in this invention are listed below:

(1) As for organic polymers which form the fiber sheet: Polymers having aromatic rings or heterocyclic rings such as polyethylene terephthalate, polyester of bisphenol A and terephthalic acid, polyester of 9-ethylcarbazole-3,6-dibutanic acid and ethylene glycol, aromatic polyamides, polydiphenylene oxide, polybenzimidazole, polybenzoxazole give favorable results in this invention. Other polymers that can be used in this invention are: Phenolformaldehyde resins, epoxy resins, polycarbonates, melamine resins, polyimides, polyurethanes, aromatic silicon resins, polystyrene, poly (2-vinyl quinoline), poly-(3, 3′-dimethyl-diphenylene-4,4′), polyvinylxylene, poly (2-vinyl-naphthalene), polyindene, polyvinylimidazole, poly (3-vinyl-pyrene). As representative examples of Lewis acids, the following compounds give very favorable results: Anthraquinone-β-carboxylic acid ester, anthraquinone-β-carboxylic acid-sec-amyl ester, 2-nitrofluorenoncarboxylic acid-n-butyl ester, and anthraquinone-β-carboxylic acid-n-butyl ester. Furthermore, the following compounds may be used:

(1) Nitro compounds such as 1,3,5-trinitrobenzene, picric acid, picryl chloride, 3,5-dinitrosalicylic acid, 1,4-dinitronaphthalene, 9-nitro-anthracene, 2,7-dinitroanthraquinone, 3,6-dinitrocarbazole, and 5-nitrobarbitalic acid.

(2) Cyanic compounds such as acetic cyanide, tetracyanethylene, dicyanonaphthalene, and 9-cyano-anthracene.

(3) Acids such as acetodicarboxylic acid, fumaric acid, maleic acid, dibromomaleic acid, malonic acid, muconic acid, phthalic acid, cinnamic acid, and phenylphosphonic acid derivatives.

(4) Carboxylic anhydrides such as phthalic anhydride, tetra halogenated phthalic anhydride, hexabromonaphthalic anhydride, and chrycene-2,4,8,9-tetracarboxylic anhydride.

(5) Esters such as ethylenetetracarboxylic acid tetraethyl acetylester, terephthalic acid dimethylester, nitroterephthalic acid dimethylester, phthalic diester, and anthracene-9-carboxylic methylester.

(6) Halogen compounds such as 1,5-dichloronaphthalene, tetrabromo-p-xylene, triphenylchloromethane, octachloronaphthalene, 9-bromo-anthracene, and 9,10-dichloroanthracene.

(7) Quinones such as benzoquinone, 1,4-naphthoquinone, anthraquinone, 1,2-benzanthraquinone, aromatic 1,2-quinones, and chloranil.

(8) Keto compounds such as pyrene-3-aldehyde, benzil, benzoin, 2-nitroindandione-1,3, 9-propyonylanthracene, and xanthone.

(9) Azo compounds such as acridine, azophenanthrene, and 1-azo-pyrene.

The sensitizing coloring matters used in this invention are common spectrum sensitizers and are not limited by any other conditions. Some of the examples of sensitizing coloring matter other than those disclosed in the examples shown later are Rhodamine B, Malachite Green Chloride, Crystal Violet, Rhodamine G extra. Malachite Green Oxalate, Rose Bengal, Erythrosine, Alizarin Red, Brilliant Green, Rhodamine 6G, Methylene Blue, and Acridine Yellow.

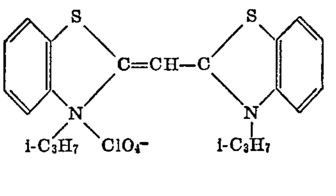
Description will be given to the embodiment of this invention. A sheet can be formed by employing an ordinary paper making or spinning process. A typical process comprises firstly dissolving or, in particular cases, suspending the source material for sheet forming in an appropriate solvent, agitating, adding a hardener or softener, when required, and, in the case of dry spinning, the resulting solution is ejected through a spinnerette and then the solvent is evaporated by means of hot air to form a fiber. In the case of wet spinning, the solution is ejected through the spinnerette, and introduced to a coagulating solution to form a fiber. The fiber thus made is beaten and then made into paper, or the above-mentioned fiber is woven into cloth to form a sheet. The sheet may be formed optionally by employing a hitherto known method. It is also allowed to add various kinds of additives such as sizing agents, electric resistance controlling agents, plasticizers, and other resins in order to make the property of the sheet more favorable. The dyeing of the fiber sheet with sensitizing coloring matter is effected by using under such conditions as heating a solution prepared by dissolving or dispersing the sensitizing coloring matter in an appropriate solvent. In this invention, it is particularly preferable and simple to carry out the dyeing simultaneously with the treatment with a Lewis acid. When treatment with the Lewis acid is effected separately, it is preferable to dissolve the Lewis acid in an appropriate solvent in which the sheet is not soluble and treat the sheet with the resulting Lewis acid solution. However, when the Lewis acid in its normal state is in a liquid form, the acid can be used as it is.

Furthermore, in the stage of Lewis acid treatment, the sheet is preferably required to have an affinity to the Lewis acid solution or liquid Lewis acid sufficient to wet the surface of the sheet and some degree of hygroscopicity. According to this invention, the dyeing treatment and Lewis acid treatment are carried out after forming a fiber sheet. Therefore, this invention is, of course, applicable to any desirable combination of an organic polymer for forming a fiber sheet, sensitizing coloring matter, and Lewis acid. The fiber sheet is only a material in this invention, and the actual photoconductive fiber sheet can be formed by treating the material normally only once. This enables various kinds of sheets to be made freely and very economically. According to another embodiment of this invention, the photoconductive fiber sheet is obtained by using two or more kinds of sensitizing coloring matters so as to impart a panchromatic photosensitivity over the visual spectrum wavelength region to offer a photosensitive sheet which is suited to forming color copy image. According to a further aspect of this invention, the fiber in the stage previous to the fiber sheet is divided, for example, into three blocks. Each block is dyed separately with a sensitizing coloring matter so as to impart a photosensitive wavelength characteristic corresponding to red, blue and green (Lewis acid treatment may be carried out during this step), and then the same quantity of the fibers having the above-mentioned different photosensitive wavelength characteristics respectively is collected together to be woven into cloth. The photoconductive fiber sheet thus obtained can also offer a photosensitive sheet suitable for color copy image formation. According to a still further aspect of this invention it is possible to form a photoconductive fiber sheet having sensitized photoconductive patterns by first dyeing the fiber sheet with a sensitizing coloring matter and then treating it with Lewis acid in such a way that the treated portion forms a pattern during treatment. In this case the photoconductive fiber sheet offers a photosensitive sheet capable of accepting electrostatic printing as shown in the example described later. Examples of this invention are given below. It should be understood, however, that these are given for illustrating this invention, but not for limiting this invention.

EXAMPLE 1

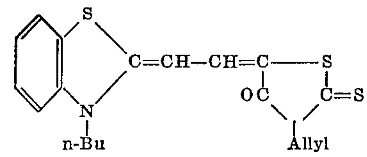
Copolymer of 9-vinylcarbazole and laurylmethacrylate (copolymerization molecular ratio 85:15) was melted and spun into fiber at about 260° C. On the other hand, the following three dye baths i.e. dye bath [I], dye bath [II], and dye bath [III], were prepared separately.

Dye bath [I]: Methanol solution containing a sensitizing coloring matter which affords photosensitive wavelength characteristic mainly corresponding to blue spectrum and a Lewis acid. The Lewis acid is anthraquinone-β-carboxylic acid-n-butylester (the same compound is used in the dye baths [II] and [III]) and the sensitizing coloring matter is a substance represented by the following structural formula.



Dye bath [II]: Methanol solution containing a sensitizing coloring matter affording photosensitive wavelength characteristic mainly corresponding to red spectrum and the Lewis acid as used in dye bath [I]. The sensitizing coloring matter is diphenylamine blue.

Dye bath [III]: Methanol solution containing a sensitizing coloring matter affording photosensitive wavelength characteristic mainly corresponding to green spectrum and the Lewis acid as used in dye bath [I]. The sensitizing coloring matter is a substance represented by the following structural formula



The above-mentioned fiber was divided into 3 equal groups. One of the groups was subjected to treatment with the dye bath [I], the second group with the dye bath [II], and the remaining group with the dye bath [III] and each was treated with the Lewis acid simultaneously with the dyeing. In this way, 3 kinds of fibers having photosensitive wavelength characteristics corresponding to blue, red, and green, respectively were prepared. These fibers were mixed and woven into cloth by an ordinary method. Next, a multicolor reproduction was carried out by using the cloth thus woven. The above-mentioned cloth was first subjected to a charging process and then a color original film was laid on the cloth in close contact, and exposure was made by a light source of 150 W. tungsten lamp at a distance of 30 cm. The exposure was made in three steps: First through a blue filter, followed by immediate development with yellow toner, then through a green filter followed by immediate development with magenta toner, and finally through a red filter followed by cyan toner development. Exposure time was 3 seconds for each step. As the result, a very clear color image was obtained. Nearly the same result was obtained when the constituents of the above-mentioned dye baths [I], [II], and [III] were prepared by sensitizing coloring matter and the Lewis acid treatment was carried out later.

EXAMPLE 2

A copolymer of 3-chloro-9-vinylcarbazole and ethyl acrylate (polymerization molecular ratio 85:15) was melted and spun at about 270° C. and the resulting fiber was woven into cloth. The cloth was subjected to treatment with the mixture of dye baths [I], [II], and [III] of Example 3 to produce a photoconductive cloth. Then, the cloth thus produced was used for reproduction under the same conditions as in Example 3. A clear color image was obtained was an exposure time of 2.5 seconds.

EXAMPLE 3

45 g. of Epikote 1001 (Trade name, supplied by Shell Petroleum Co., epoxy resin) and 0.8 g. of resin hardener, m-phenylenediamine were dissolved in 100 ml. of tetrahydrofuran. The resulting solution was injected into water at a rate of 20 ml. per second with stirring to separate the fine fibers in a rather lump form. The fine fibers were then collected and made into paper of about 5 μ in thickness, final heating being at 100° C. for 10 minutes. The surface of the paper was treated with a mixture of the dye baths [I], [II] and [III] used in Example 1, dyed with sensitizing coloring matters and then treated with a Lewis acid. Next, the paper thus prepared was charged by a charging device to which was applied a high voltage of about 5.5 kv. to obtain a uniform negative charge of about 1,000 v. on the electrostatic image forming surface. Then, a positive original film was laid on the above-mentioned paper in close contact and, by an exposure device having a 150 watt tungsten lamp as a light source was placed at 10 cm. away from the film, an exposure was made for

about 4 seconds. The film was then developed by dipping it into a positive liquid developer. A good positive image with fidelity to the original was obtained. When, in the above example, the above-mentioned paper was first subjected to a dyeing process by means of a dye bath containing only the sensitizing coloring matter, instead of a simultaneous application of the dyeing process and the Lewis acid process, and next subjected to the Lewis acid processing and, in this Lewis acid processing, a piece of aluminum foil cut into a pattern form was laid on the surface of the paper in close contact and then a Lewis acid (anthraquinone-β-carboxylic acid-n-butylester) solution was applied to the paper covered with the aluminum foil. Thus, a paper having photoconductivity along the pattern cut in into aluminum foil was obtained. Then, this paper was charged under the same condition as above followed by whole surface exposure made by the exposure device having a 150 w. tungsten lamp as the light source for about 3.5 seconds at a distance of 100 cm. The paper was then developed by a magnet brush method using a positively charged toner, and fixed by heat. As a result, a clear negative image which followed the pattern was obtained. Furthermore, the photoconductive paper that followed the above-mentioned pattern was wound around an aluminum metal drum, and visual image obtained by conducting the above-mentioned charging, whole surface exposure and development was subjected to copy image forming process which transfers the image to paper. It was found that a clear pattern image was allowed to be transferred to the paper more than 5000 times.

What is claimed is:

1. A process for preparing a photoconductive fiber sheet which comprises preparing a fiber sheet comprising an organic high polymer material; treating said sheet with a Lewis acid capable of reacting with said material to form a photoconductive charge transfer complex and dyeing said sheet with a spectral sensitizing coloring matter.

2. A process according to claim **1** in which the dyeing and the Lewis acid treatment are simultaneous.

3. A process according to claim **1** in which the fiber sheet is a paper sheet made of fibers of the organic high polymer.

4. A process according to claim **1** in which the fiber sheet is a cloth sheet made by weaving fibers of the organic high polymer.

5. A process according to claim **1** in which the spectral sensitizing coloring matter is a mixture of two or more coloring matters having different absorption spectrum characteristics so as to impart a panchromatic photosensitive property for the visual spectrum wavelength region to the fiber sheet.

6. A process according to claim **1** in which the photosensitizing coloring matter is a mixture of a spectral sensitizing coloring matter capable of imparting to the fiber sheet a photosensitive wavelength characteristic mainly corresponding to red spectrum, a spectral sensitizing coloring matter capable of imparting to the fiber sheet a photosensitive wavelength characteristic mainly corresponding to blue spectrum, and a spectral sensitizing coloring matter capable of imparting to the fiber sheet a photosensitive wavelength characteristic mainly corresponding to green spectrum.

7. A process for preparing a photoconductive fiber sheet which comprises preparing a fiber sheet comprising an organic high polymer material, treating said sheet with a Lewis acid capable of reacting with said material to form a photoconductive charge transfer complex and dyeing said sheet with a spectral sensitizing coloring matter wherein the treatment with the Lewis acid is carried out in such a manner that the region treated with said Lewis acid forms a photoconductive pattern capable of accepting electrostatic printing.

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U.S. Cl. X.R.

96—1.5; 252—501