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3,583,869

ELECTROPHOTOGRAPHIC COPYING PAPER CONTAINING POLY-N-VINYL-3-AZO CARBAZOLE

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Int. Cl. G03g 5/00
U.S. Cl. 96—15 3 Claims

ABSTRACT OF THE DISCLOSURE

Poly-N-vinyl-3-azo carbazole which is obtained by the coupling between poly-N-vinyl carbazole and a diazo compound selected as desired from various diazo compounds is extremely suitable as a photoconductive material for use in electrophotographic copying papers. An electrophotographic copying paper which is prepared by coating this poly-N-vinyl-3-azo carbazole on a support paper sheet which transmits ultraviolet rays therethrough can be utilized as the material for preparing a second original for the copying process which uses diazotype copying papers.

BACKGROUND OF THE INVENTION

(a) Field of the invention

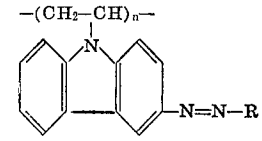
The present invention is concerned with an electrophotographic copying paper which is provided, on one surface thereof, with a light-sensitive layer which contains an organic photoconductive material. More particularly, the present invention is related to an electrophotographic copying paper which is provided, on one surface thereof, with a light-sensitive layer which contains poly-N-vinyl-3-azo carbazole as the photoconductive substance.

(b) Description of the prior art

As the photoconductive substances for use in the conventional electrophotographic copying papers, those inorganic substances such as zinc oxide, selenium and sulfur; and those organic substances such as anthracene, anthraquinone, oxadiazol and poly-N-vinyl carbazole which is a polymer having a high molecular weight, are known. A light-sensitive layer which is formed on the support of a copying paper and which is prepared with such an organic substance as described above to serve as the photoconductive substance is, in general, superior in the ability of transmitting ultraviolet rays as compared with the light-sensitive layer of a copying paper which is formed with an inorganic substance to serve as the photoconductive substance. Therefore, an electrophotographic copying paper which is obtained by the employment of an organic photoconductive substance is of an advantage that it can be used also as the copying paper which is intended for the preparation of a secondary original adapted for the copying process which utilizes diazotype copying papers. Those organic photoconductive substances which have been used in the past, however, are poor in their sensitiveness to light. In addition, these conventional organic photoconductive substances have a further inconvenience that it is difficult to uniformly disperse them in a mixture which is prepared for use in the coating of the supports.

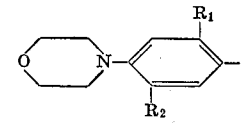
SUMMARY OF THE INVENTION

It is, therefore, the object of the present invention to provide an electrophotographic copying paper having, on one surface thereof, a light-sensitive layer which contains such a polymer as is expressed by the following chemical formula to serve as the photoconductive substance:

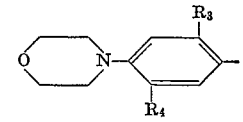


wherein R represents a residual radical of a diazo compound.

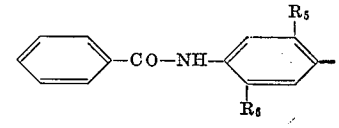
Some of these residual radicals of the diazo compounds which are expressed by the aforesaid chemical formula will be shown as follows:



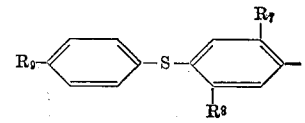
wherein R_1 and R_2 are selected from the group consisting of —H, —OCH_3, —OC_2H_5, —OC_3H_7 and —OC_4H_9.



wherein R_3 and R_4 are selected from the group consisting of —H, —CH_3, —OCH_3, —OC_2H_5, —OC_3H_7 and —OC_4H_9.



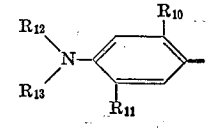
wherein R_5 and R_6 are selected from the group consisting of —H, —OCH_3, —OC_2H_5, —OC_3H_7 and —OC_4H_9.



wherein:

R_7 and R_8 are selected from the group consisting of —H, —OCH_3, —OC_2H_5; and

R_9 is selected from the group consisting of —H and —CH_3.



wherein:

R_{10} and R_{11} are selected from the group consisting of —H, —OCH_3, —OC_2H_5, —OC_3H_7 and —OC_4H_9;

R_{12} is selected from the group consisting of —CH_3 and —C_2H_5; and

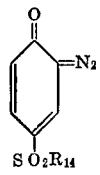
R_{13} is selected from the group consisting of —$CH_2C_6H_5$ and —C_2H_5.

The poly-N-vinyl-3-azo carbazole which is expressed by the aforesaid chemical formula can be readily prepared by coupling poly-N-vinyl carbazole to a diazo compound. For example, it can be prepared by causing a reaction between a monochloro benzene solution of poly-N-vinyl carbazole and a methanol solution of a diazo compound in the presence of, for example, potassium hydroxide.

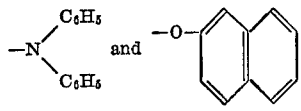
The diazo compounds which are suited for the object of the present invention are prepared by using the following substances including:

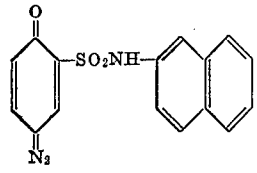
2-methyl-4-ethylaniline
4-methyl-benzylaniline
2,5-diethoxy-4'-methoxy-benzoylaniline
4-morpholinobenzene
2,5-dimethoxy-4-toluylmercaptobenzene
Triphenylamine
1,3-bis[naphthoquinone (1)-sulfonyloxy (5)]-hydroxy (5)-benzene and
4,4'-bis[naphthoquinone (1)-sulfonylaniline].

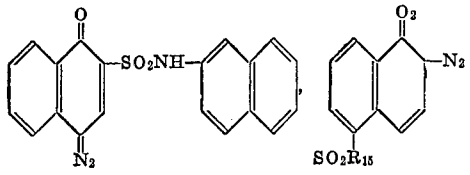
Furthermore, a photoconductive substance of the present invention can be prepared also by causing a reaction between a compound expressed by any one of the following chemical formulas and poly-N-vinyl carbazole:



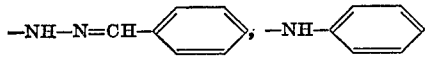
wherein R_{14} is selected from the group consisting of

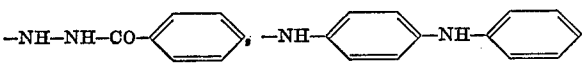


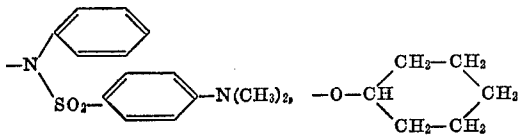


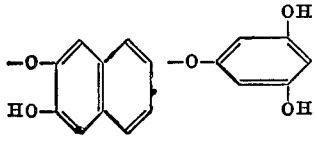


wherein R_{15} is selected from the group consisting of









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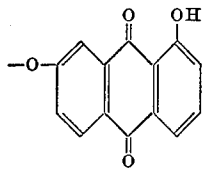
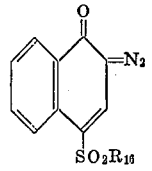
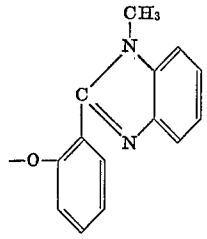




wherein R_{16} is selected from the group consisting of



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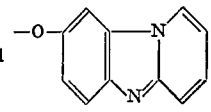
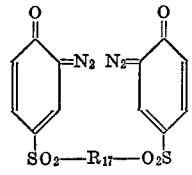
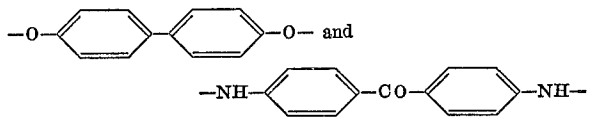
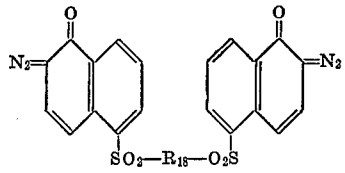


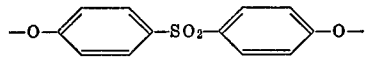


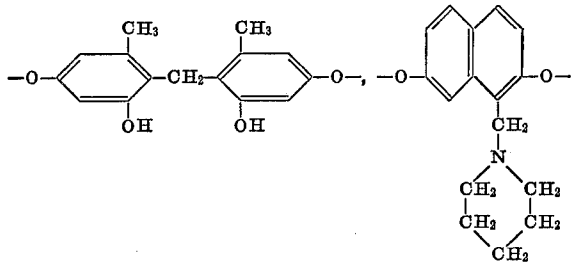
wherein R_{17} is selected from the group consisting of

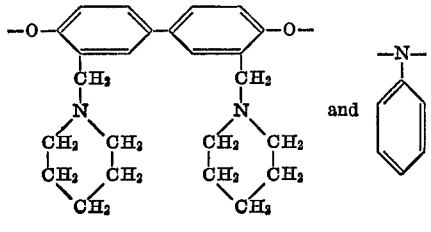




wherein R_{18} is selected from the group consisting of







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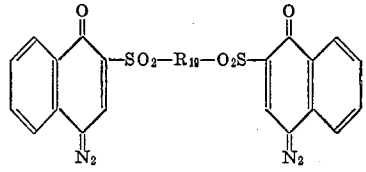
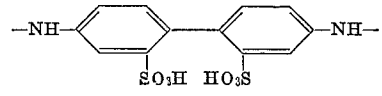
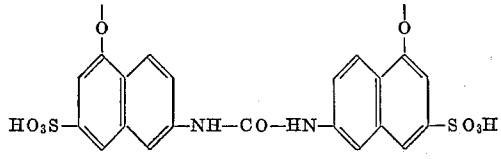


wherein R_{19} is selected from the group consisting of



and



The poly-N-vinyl-3-azo carbazole which is employed in the present invention is, in itself, of a quite superior photoconducting property, and therefore, it can be directly used as the material for the formation of a light-sensitive layer by applying the same onto one surface of a support by relying on an appropriate coating technique such as spraying, brushing or coating by means of rollers. Or, alternatively, said azo carbazole may be treated with alcohol to be refined, and then the refined substance may be dissolved in an organic solvent, and the resulting solution may be applied onto one surface of a support to form a light-sensitive layer thereon.

Also, in order to further enhance the sensitivity to light of the light-sensitive layer, it is desirable to use a sensitizing dyestuff and/or an assistant sensitizer jointly with the aforesaid photoconductive substance. As the sensitizing dyestuffs, the employment of such substance as Brilliant Green, Victoria Blue B, Methyl Violet, Crystal Violet, Acid Violet, Rhodamine B Extra, Sulforhodamine B, Fluorescein, Methylene Blue, Acridine Yellow and Acridine Orange, is suitable.

As the assistant sensitizer, the employment of such acids as acetic acid, monochloro acetic acid and dichloro acetic acid, or their salts; or metal halides such as antimony pentachloride and stannous chloride; or quinones such as p-benzoquinone and p-chloranil, is suitable.

In case the light-sensitive layer of the electrophotographic copying paper of the present invention is impressed with a positive or a negative charge by means of corona discharge, the charged copying paper will exhibit sensitivity to light having a wavelength ranging from 3600 A. to 7000 A. Therefore, a very clear copied image will be obtained by exposing the charged copying paper to light for an extremely short period of time, utilizing a tungsten lamp as the light source. It is to be noted, however, that a light-sensitive layer which has a much better sensitivity to light is obtained by including the aforesaid sensitizing dyestuff and/or an assistant sensitizer at the time said light-sensitive layer is formed. According to the present invention, the support may be made with a film or a sheet material made of a material including aluminium, zinc or copper; paper; cellulose esters such as cellulose acetate and butyl cellulose; polyolefins such as polyethylene and polypropylene; polyvinyl compounds such as polystyrol, polyvinyl chloride and polyvinlidene chloride; polyacryl compounds such as polyacrylonitrile and polymethacrylate; polyesters such as polyterephthalic acid and glycol esters; and plastics such as polyamides and polyurethanes. These films and sheet materials other than the metal sheets are used after they have been given an electroconducting treatment according to the known process. In the event that paper sheets are used as the supports, it is preferred to treat these paper sheets, prior to using the paper sheets as the supports, with, for example, an aqueous solution

of methyl cellulose or polyvinyl alcohol; or with an acetone or methyl ethyl ketone solution of a copolymer of methyl acrylate ester and acrylonitrile; or with an alcohol solution of a polyamide.

As has been stated, the present invention contemplates the provision of a novel electrophotographic copying paper having a light-sensitive layer formed on one surface of a support, said light-sensitive layer being prepared essentially with a photoconductive substance consisting of a polyvinyl azo compound. This electrophotographic copying paper obtained according to the present invention is of a number of advantages and conveniences such that the copying paper can be manufactured easily; that it is free from the fear of a reduction in its sensitivity to light during the storage lasting for an extended period of time, meaning that this copying paper has a very good shelf-life; and also that copying paper which is manufactured by the use of a transparent support can be utilized as a secondary original which is suitable for diazotype copying papers.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Example 1

To 100 gr. of 5% monochloro benzene solution of poly-N-vinyl carbazole was added 2 cc. of 5% methanol solution of a double salt of p-diazo-2,5-dimethoxy-1-p-toluylmercaptobenzene and zinc chloride. After stirring the resulting mixed solution, the latter was added with 0.2 cc. of 5% methanol solution of potassium hydroxide. This mixed liquid was allowed for reaction therebetween at a temperature ranging from 45° C. to 50° C. for 10 minutes, while stirring the same. Thus, a solution for use in the formation of a light-sensitive layer was prepared. This solution was applied onto one surface of a tracing paper which had been priorly given an electroconducting treatment, and the same was dried, with a result that an electrophotographic copying paper was obtained. After imparting the light-sensitive layer of the electrophotographic copying paper thus obtained an electrostatic sensitivity to light by impressing said light-sensitive layer with a negative charge by corona discharge, the charged light-sensitive layer of the copying paper was exposed, for 2.5 seconds through a positive original placed thereon, to light coming from a light source which was a tungsten lamp of 100 watts which was disposed at a distance of 30 cm. from said light-sensitive layer. The exposed copying paper was developed according to a known wet type development method. As a result, a very clear copied image was obtained. This copied image was found to be a faithful reproduction of the original image. It was also noted that this copy was quite suitable for use as the secondary original for diazotype copying papers.

Example 2

To 100 gr. of 5% monochloro benzene solution of poly-N-vinyl carbazole was added 3 cc. of 5% methanol solution of a double salt of p-diazo-1-morpholino benzene and zinc chloride. After stirring this mixed solution, the latter was added with 0.2 cc. of 5% methanol solution of potassium hydroxide. After allowing the resulting mixed liquid to react therebetween at a temperature ranging from 45° C. to 50° C. for 10 minutes while stirring the liquid, the latter was added further with 0.5 cc. of 5% methanol solution of Methylene Blue FZ and also with 1.5 cc. of 10% methanol solution of aluminum nitrate, followed by a thorough stirring. Thus, a solution for use in the formation of a light-sensitive layer was prepared. This solution was applied onto one surface of a cellulose acetate film which had been priorly given an electroconducting treatment, and the same was dried, with a result that an electrophotographic copying paper was obtained. For comparison, a control electrophotographic copying paper was manufactured by first preparing a solution for the formation of a light-sensitive layer by

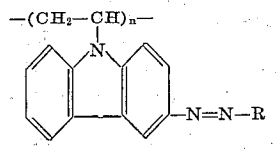
adding the methanol solutions of Methylene Blue FZ and aluminium nitrate, respectively, to poly-N-vinyl carbazole, and then applying this solution onto one surface of a support similar to the one used in this instant example, and then drying the same. These two copying papers were then processed in the same way as that described in Example 1, and thus, copied images were produced. The sensitivities of these two copying papers were compared based on the effects of the two copies obtained. It was found that the copying paper of the present invention had a light-sensitivity which was 1.5 times higher than that of the control copying paper.

Example 3

To 100 gr. of 5% monochloro benzene solution of poly-N-vinyl carbazole was added 4 cc. of 5% methanol solution of p-diazo-diphenylaniline. After stirring the resulting mixture, the latter was added with 0.2 cc. of 5% methanol solution of potassium hydroxide. While stirring the mixed liquid, the latter was allowed for reaction at a temperature ranging from 45° C. to 50° C. for 15 minutes. Thereafter, the resulting liquid was added further with 0.5 cc. of 5% methanol solution of Methylene Blue FZ and also with 1.5 cc. of 10% methanol solution of aluminium nitrate, followed by a thorough stirring. Thus, a solution for use in the formation of a light-sensitive layer was prepared. This solution was applied onto one surface of a tracing paper having priorly been given an electroconducting treatment, and the same was dried, with a result that an electrophotographic copying paper was obtained. This copying paper was then subjected to a process in a manner similar to that described in Example 1 to form a copied image. The copied image thus obtained was noted to be a very clear one. The exposure to light in this example used a tungsten lamp of 100 watts as the light source which was disposed at a distance of 100 cm. from the light-sensitive layer and the exposure lasted for 3 seconds.

What is claimed is:

1. An electrophotographic copying paper comprising a support and a light-sensitive layer formed on one surface of said support and containing, in said layer, a photoconductive substance, wherein said photoconductive substance is poly-N-vinyl-3-azo carbazole expressed by the chemical formula:



wherein R represents a residual radical of a diazo compound.

2. An electrophotographic copying paper according to claim 1, wherein said support is made with a material having a property of transmitting ultraviolet rays.

3. An electrophotographic copying paper according to claim 1, wherein said light-sensitive layer further contains at least one of the agents selected from the group of sensitizing dyestuffs and assistant sensitizers.

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U.S. Cl. X.R.

260—88.3, 152, 164; 252—501