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ELECTROPHOTOGRAPHIC PROCESS AND ELEMENT COMPRISING N,N,N',N', TETRASUBSTITUTED -P- PHENYLENEDIAMINES

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Fig. 1.

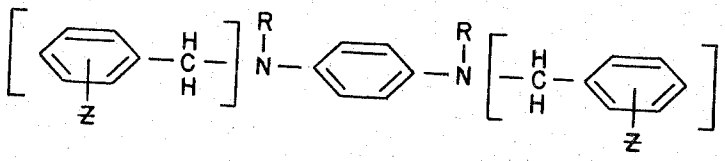
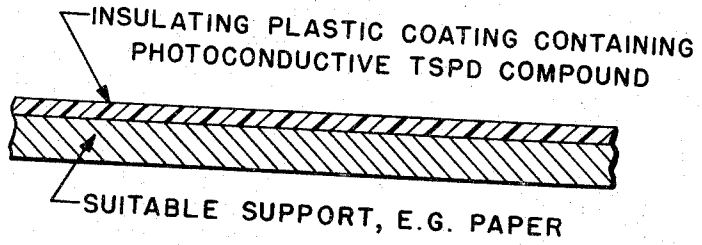


Fig. 2.



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ELECTROPHOTOGRAPHIC PROCESS AND ELEMENT COMPRISING N,N,N',N', TETRASUBSTITUTED-p-PHENYLENEDIAMINES

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This application is a continuation-in-part of S.N. 353,869, filed Mar. 23, 1964, and now abandoned.

The present invention relates to photographic reproduction, and more particularly to an electrophotographic process utilizing the photoconductive properties of a certain class of organic compounds, the N,N,N',N', tetrasubstituted-p-phenylenediamines (referred to hereinafter as TSPD compounds).

In an electrophotographic process, the electrophotographic plate consists of a coating of a photoconductive insulating layer containing the photoconductive compound carried on a relatively more conductive support such as paper, aluminum foil, or plastic film. When used, the photoconductive insulating layer is first electrically charged as with a corona discharge so that the coating has a uniform positive or negative charge on its surface. The plate is then exposed to a light image which activates the photoconductive compound. The charge density remaining at any point on the photoconductive insulating layer is inversely proportional to the intensity of illumination at that point during the exposure. The non-visible charge pattern or image is thereafter developed with an electrostatically attractable toner in a known manner. The developed image, composed of colored pigment, together with a thermoplastic resin, is subsequently fixed by heating, or in the case of liquid toners by the air oxidation of the drying oils.

In recent years, many investigations have been made with respect to the nature of suitable photoconductive materials. Most notable among the photoconductive substances hitherto used in electrophotographic process have been inorganic materials such as zinc oxide and selenium.

The present invention is based on the finding that the TSPD compounds are excellent photoconductive materials for use in the preparation of electrophotographic plates. These compounds have good photoconductivity and are particularly suitable for the preparation of lithographic plates as well as reproduction papers for use in desk type office copying devices or in electrophotographic printing. The compounds of this class are, in general, easily prepared, stable compounds with a long shelf life and are soluble in most common resin binder-solvent systems so that they can be readily applied to a supporting substrate.

The nature of this invention will become clear from the following description and examples, made with reference to the drawings attached to and forming a part of this specification.

In the drawings:

FIG. 1 illustrates the class of photoconductive TSPD compounds of interest, and

FIG. 2 schematically depicts the electrophotographic plate of this invention.

The TSPD compounds are used according to this invention in association with clear resinous film-forming polymeric binders having high dielectric characteristics such as a polystyrene, polyvinyl chloride, polyvinyl acetate, polyvinylidene chloride, polyvinyl acetal, polyvinyl ether, polyacrylic ester, or any other natural or synthetic polymeric substance having the proper electrical characteristics. The organic photoconductor and resinous polymer are dissolved in a sutiable organic solvent such as benzene, toluene, methyl ethyl ketone, methyl isobutyl ketone, chloroform or methylene chloride. Mixtures of two or more photoconductive substances can be used, as well as mixtures of two or more mutually miscible solvents which will utilize with the greatest efficiency the solubilities of both the photoconductor and the resinous binder. The solvent solutions are coated on a suitable carrier and, when dried, form a solid solution which is transparent, or will at least admit some radiant energy.

The electrophotographic plate or sheet of this invention comprises a support carrying a photoconductive insulating layer which layer consists of a suitable resinous binder and at least 10 weight percent of the TSPD compound having the formula illustrated in FIG. 1 of the drawings. R in the formula is preferably a benzyl radical as illustrated or an alkyl radical of 3 to 4 carbon atoms, preferably one that is branched. The Z radicals in the formula are chosen to be essentially innocuous to the photoconductive properties of the compound, although some radicals can be used in the Z positions to improve some other property such as solubility. Preferred radicals in the Z position are methyl and halogen radicals. The benzyl radicals are preferably substituted only once.

It is to be noted that the phenylene ring is unsubstituted as substitution would tend to destroy photoconductivity because of steric hindrance of the planar configuration of the amine groups.

The preferred compounds are white and have a melting point in the range of 50° to 160° C. They are soluble to the extent of at least 2.5 grams in 100 milliliters of chloroform at 25° C.

Symmetrical N,N,N'N' tetrabenzyl - p - phenylenediamine is a preferred example of the TSPD compounds because of its ease of preparation and excellent properties. However, the alkyl derivatives will produce a photoconductive coating that responds excellently to ultra-violet light without the need of adding sensitizers to the coating.

The TSPD compounds can be prepared by condensing the appropriate alkyl halide and paraphenylenediamine in solution with heating. The chloro alkyl halides are preferred. It is important to note that the TSPD compound is the reaction product of a primary aryl diamine and an alkyl halide and is not the reaction product of a secondary diarylamine and an aryl halide. The latter reaction besides being difficult and expensive gives phenyl instead of benzyl derivatives.

The TSPD compounds when dissolved in a layer of insulating resin, which layer is electrostatically charged and exposed to light having a wave length in the range of 3500 to 4200 A., will produce electrostatic latent images as previously described. Excellent images can be obtained by a short exposure under a photographic transparency using a carbon arc or mercury-vapor lamp. The insulating layer will hold a charge of 100 to 400 volts for from 0.1 to 10 minutes.

The spectral sensitivity of the electrophotographic plates can be shifted into the visible region and the sensitivity increased by the addition of dyes, to such an extent that images can be formed using a low wattage tungsten lamp. This spectral sensitivity is obtained in a known manner by adding to the photoconductor-resin mixture a small amount of a dyestuff such as Crystal Violet, Cryptocyanine, Pinacyanole, Orthochrome T, Rhodamine B, or Sulforhodamine. See also page 8 of British Patent No. 895,001 (1962) for additional suitable compounds as well as Belgian Patent No. 626,527 based on U.S. Ser. No. 163,016 filed Dec. 29, 1961, now U.S. Patent No. 3,265,496 which patent also lists additional suitable plastic binders and supports. Water soluble quaternary ammonium and oxonium dyes are preferred.

The invention is further illustrated in the following specific examples, without being limited thereto:

Example I

N,N,N'N', tetrabenzyl-para-phenylene diamine was prepared and purified as follows: Potassium hydroxide was dissolved in ethanol. 76 grams of benzyl chloride and 10.8 grams of p-phenylenediamine where mixed in a 500 ml. Erlenmeyer flask with the alcohol solution (containing 9 grams of KOH). The flask was heated on a steam bath and a vigorous but controllable reaction took place. An additional 27 grams of KOH in ethanol was added over a 15-minute period, along with enough extra ethanol to keep the system mobile. The reaction product was crystallized after ¾ of an hour by cooling and adding water. The crystals were filtered and washed thoroughly with water and 30–60° petroleum ether, which removed large amounts of blackish material. The washed crystals were dried, dissolved in chloroform and decolorized with carbon black, followed by filtration through a Celite filter pad. The solution was then heated and ethanol was added to precipitate the compound as white needles (M.P. 145.5–146.0° C.). The first crop was 36.3 grams, a 77.6% yield (theoretical yield was 46.8 grams).

A coating composition is prepared by mixing 1 part by weight of the TSPD compound, 0.0007 part by weight of a sensitizing dye such as Rhodamine B Base; 3 parts by weight of a resinous binder such as Butvar B–76 (a polyvinyl butyral resin; Shawinigan Resins Corp.) and 20 parts by weight of $CHCl_3$ as a solvent. This coating solution is applied to a suitable paper or foil substrate for example, Silkote Offset, a high quality printing paper manufactured and sold by the S. D. Warren Paper Company. The amount applied is 2–15 pounds (dry weight) per ream (500 sheets 25 x 38"), preferably in the range of from 4–6 pounds. The coated paper is either air dried or even dried to remove the solvent carrier.

To make a print, the coated paper is either positively or negatively charged under a corona discharge and then exposed under a positive or negative transparency to a light source such as a 60-watt tungsten lamp. After this exposure, a dry electrostatically attractable resinous toner colored with a pigment such as carbon black is applied to the sheet. For best results this is done in reduced light area, preferably under red light. The toner thus applied adheres to the parts of the coating which have not been exposed to the light and a positive image appears. The imaged sheet is heated for a short period at 100–130° C. to fuse the resin of the toner and fix the image.

N,N,N'N', tetra (4-chlorobenzyl)-p-phenylenediamine (M.P. 141.5°–143° C.) and N,N,N'N' tetra (2-chlorobenzyl)-p-phenylenediamine (M.P. 142°–145° C.) have been similarily prepared and applied. The electrophotographic plates based thereon performed equally as well.

Example II

A coating solution is made up as follows:
3 grams polyvinyl butyral (Butvar B–76);
1 gram N,N' disecondary butyl, N,N' dibenzyl;
p-Phenylene diamine;
10 cc. chloroform.

It is preferably applied to a suitable base sheet in amounts of 2 to 4 pounds per ream (dry basis). A latent image can be developed on this coating by exposure to ultra-violet light without the use of a sensitizer in the coating.

Example III

Another suitable coating composition is:
3 grams polystyrene (S-666, Dow Chemical);
1 gram N,N' diisopropyl, N,N' dibenzyl p-phenylene diamine;
10 cc. toluene.

The following table gives the ratio of ingredients that can be used in preparing a coating solution according to this invention.

Ingredients:	Parts by weight
Resin	1
TSPD compound	0.5 to 0.1
Solvent	4 to 10

If aluminum, plastic foil, or a suitable grade of paper is used as a carrier for the coating, the images can be used as master copies for any sort of lithographic duplicating process, provided the non-imaged areas are treated to make them ink repellent and water receptive. In this process, for example, a sheet of paper which has been prepared to have a hydrophilic surface, e.g., a surface coating composed of titanium dioxide, carboxymethyl-hydroxyethyl cellulose or similar water soluble cellulose derivative, and melamine formaldehyde resin (see U.S. Patents 2,778,735 and 2,778,301) is coated with a solution consisting of 1 g. of the TSPD compound of Example I, 2.5 g. of B–76 resin, 50 mg. of Rhodamine B, and 50 ml. of chloroform. The sheet is dried, then charged and imaged in the above manner and fused at 140–160° C. The surface of the sheet is washed with methanol, ethanol, isopropanol, or mixtures of same, thereby exposing again the hydrophilic surface in all areas but the hydrophobic imaged areas. The sheet thus formed may be used in any type of hydrophilic-hydrophobic lithographic duplicating process.

The TSPD compounds are unusual in that they are white while still having good electrophotoconductive properties. Many other photoconductive compounds are colored because of chromophoric groups.

Having described this invention, what is sought to be protected by Letters Patent is succinctly set forth in the following claims.

What is claimed is:

1. An electrophotographic plate comprising a photoconductive insulating layer on a relatively more conductive support, the photoconductive layer containing a N,N,N'N' tetra-substituted-p-phenylenediamine containing at least one benzyl group each in the N, and N' position with the remaining two substituent groups being selected from the group consisting of benzyl radicals and alkyl radicals.

2. The electrophotographic plate of claim 1 wherein said photoconductive insulating layer also contains a dye sensitizer.

3. The electrophotographic plate of claim 1 wherein said photoconductive insulating layer essentially consists of a clear resinous binder and said photoconductive compound.

4. The electrophotographic plate of claim 1 wherein said photoconductive compound is N,N,N'N' tetrabenzyl-p-phenylenediamine.

5. The electrophotographic plate of claim 1 wherein said phenylenediamine is N,N' dialkyl, N,N' dibenzyl p-phenylene diamine, the alkyl groups of which contain in the range of 3 to 4 carbon atoms and are branched.

6. A process for preparing a copy which comprises electrostatically charging the electrophotographic plate of claim 1, exposing said plate to light pattern thereby relieving the electrostatic charge thereon in the background areas and leaving a latent image, toning the imaged areas with a tribo-electric powder and thereafter fusing said tribo-electric powder to fix said image.

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