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REPROGRAPHIC PROCESS

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ABSTRACT OF THE DISCLOSURE

Reprographic materials including a coating of light-sensitive diazonium salt are exposed imagewise to light to create a corresponding image of photo-decomposition products which exhibit a substantially greater adhesiveness for finely divided powder or dust than the original diazonium salt. The material thus exposed is contacted with a finely divided powder which adheres to the photo-decomposition products, thereby rendering visibly distinct the light exposed image areas.

This invention relates to a new reprographic process. More specifically, it relates to a new reprographic process based on utilization of photo-chemical reaction followed by toner development.

The term, "reprographic process," used herein is intended to generically mean any reproduction methods using various principles including previously known photography.

In obtaining a reproduction from an original, for example, hand-written documents, printed matters or the like, various reprographic methods have been known which include diazo process, silver diffusion transfer process, electro-photographic process, thermographic process, etc. However, these known methods are disadvantageous because of their necessity for use of copying sheets bearing thereon an expensive agent. In addition, the image resulted by the known methods occasionally suffer from coloration or fading. Some of the known processes should necessarily be operated in a photographic darkroom or by use of an agent which may be severely corrosive or have disagreeable odor. These disadvantages as experienced in the prior art can be overcome by a process of the present invention.

In accordance with the present invention, there is provided a reprographic process which comprises exposing a photo-sensitive sheet through an image-bearing original to light, thereby to form a latent image corresponding to said original and then developing the resulted latent image, as such or after its having been thermally treated, with a toner thereby to obtain a reproduction of the original. The photo-sensitive sheet comprises a support and a coating thereon of a photo-sensitive layer comprising a normally non-dustable, thermally non-transferable substance which can be converted through photo-chemical reaction alone or together with subsequent thermal treatment to a dustable mass.

It is accordingly the principal object of the present invention to provide a new reprographic process based on utilization of photo-chemical reaction followed by toner development. A further object of the invention is to provide a process for preparing permanent copies of good contrast from an original. Yet another object of the invention is a process for economically preparing multiple copies of an original. Still another object of the invention is a method of preparing a master sheet useful in the further preparation of multiple copies in duplicating processes. A further object of the invention is a light-sensitive sheet useful in a novel reprographic process. Other objects, features and advantages comprehended by the present invention will be apparent from the descriptions and claims which follow.

As outlined above, a reprographic process according to the present invention comprises:

(1) Subjecting a normally non-dustable, thermally non-transferable photo-sensitive substance, which can be converted through photo-chemical reaction alone or together with thermal treatment to a dustable mass, to exposure to light through an image-bearing original, thereby to form the corresponding latent image; and

(2) Developing with a toner the latent image as it is or after it has been thermally treated.

The term, "non-dustable," used herein means that the material has little or no dust-adhering property. It should be noted that the term, "non-developable with a toner," has the same meaning as "non-dustable," when the former term is used in connection with an image.

The term, "thermally non-transferable," used herein means that a material distributed on a support fails to show an appreciable transfer onto a receptor even when the supported material together with the receptor is brought into increased temperature for a few seconds.

Previously known copying processes using formation of dust-adhering or dust-developable images include the process using the selective distillation of oil (cf. Japanese Patent Publication No. 17,166/1962), which is the so-called "Imagic Process," and the process using the supercooling phenomenon (cf. Japan Printer, vol. 47, No. 4, page 12 (1964)). However, these prior processes in which a latent image corresponding to said original is formed by infrared irradiation have such a disadvantage that a portion described with an ink of difficulty IR-absorbing nature is so insensitive that it is not reproduced on a copying sheet. Contrarily, a reprographic process of the present invention which is based on utilization of photo-chemical reaction of the above-defined photo-sensitive material permits the reproduction of originals having a poorly IR-absorbing pattern. Electro-photographic process is well known as a method using toner development. However, this prior process is not satisfactory when an original to be reproduced is a photography of continuous tone or includes a black portion of the large area, because the process provides only a copy with inferior image quality due to so-called "edge effect." In contrast to this, a reprographic process according to the present invention is capable of reproducing even a continuous tone original or a large black zone to give a sharp and clear image.

Suitable photo-sensitive substances used in this invention are those which are normally non-dustable, or thermally non-transferable, but which, when brought into photo-chemical reaction, convert to such a state as having dust-adhering property as it is or after its having been thermally treated. The simplest illustration of these materials is light-sensitive diazonium compounds which undergo such a photo-chemical reaction. For example, useful materials are the double salts of 2-methyl-4-N-diethylamino-benzene diazonium chloride, p-N-ethyl-N-B-hydroxyethylamino-benzene diazonium chloride, N-dimethylamino-benzene diazonium chloride, N-diethylaminobenzene diazonium chloride, 4-N-benzoylamino-2, 5-diethoxybenzene diazonium chloride, N-ethyl-N-benzylamino-benzene diazonium chloride and 4-morpholino-benzene diazonium chloride with zinc chloride. 4-N-diethylamino-2-ethoxy-benzene diazonium borofluoride and 1-diazo-2-naphthol-4-sulfonic acid also are usable. All the diazo compounds mentioned above are normally non-dustable and further they are thermally non-transferable in such a degree that they do not show appreciable trans-

fer onto a receptor when these compounds carried on a tracing paper (40 g./m.^{2}) as a support and superposed with a receptor are subjected to thermal gradient from the back side of the support contact for one second with a hot roll having a surface temperature of 180° C. These compounds, after photochemical reaction, are thermally transferable under the above-specified condition. The specified compounds can be used singly. More than two of these compounds may be used in admixture to have increased sensitivity.

In carrying out the reprographic process of the present invention, the above-specified photo-sensitive substance may be used in a layer on a suitable support. In order to prepare such a reprographic element as referred to above, the following general procedures may be used: The photo-sensitive substance, with or without a small amount of a binder, is prepared as a solution or dispersion which is then applied onto the surface of a support. Suitable supports include papers, and metallic or plastic sheets. Suitable binders are film-forming high molecular materials having a poor heat-softening property, e.g. gelatin, polyvinyl alcohol, carboxymethyl cellulose, vinyl chloride-vinylidene chloride copolymer, vinylidene chloride-acrylonitrile copolymer, ethyl cellulose, cellulose triacetate, etc. Alternatively, if a support having a somewhat rough surface is used, a photo-sensitive substance can be rubbed onto said surface to produce a useful reprographic element. Further, alternatively, the photo-sensitive substance may be either incorporated into a paper-making material or top-coated over the surface of papers, in order to have a reprographic copying paper comprising an internal layer of the photo-sensitive substance.

Formation of a latent image on the thus prepared reprographic element is realized by exposing the said element through an image-bearing original to light. This is most conveniently carried out by means of a printer used in a conventional diazo copying processor. The use of such a printer is particularly advantageous because the printer provides both light exposure and heat at the same time when a reprographic element contacts the warmed glass drum of the printer. For the purpose of reproduction from microfilm as an original, exposure to light by using an appropriate optical system, e.g. an enlarger in which Oslam Model UV–500 lamp is used as a light source, is satisfactory. When the reprographic element is exposed to light, the photo-sensitive substance is brought into imagewise photo-chemical reaction by which the corresponding latent image having a dust adhering property is formed.

However, there are some instances where the concerned photo-sensitive components exposed to light give only such images which are thermally transferable and non-dustable. In those instances, the reprographic element having been exposed to light is heated to a suitable temperature whereby an image portion resulting from photochemical change is then converted to a latent image having dust-adhering property. As will be clear to those skilled in the art, the term "thermal treatment," used in the specification and claims, should be understood to include direct application of heat, as well as thermal transfer onto an appropriate receptor.

In the present invention, the latent image formed on the reprographic element is developed with a toner thereby to provide a reproduction. For this purpose, various methods can be used. Where only a single reproduction is necessary or where an offset master or spirit printing master is to be obtained, the latent image formed on the reprographic element can be directly developed with an appropriate developing toner. In another embodiment which shows the particular advantage of the present invention, the resulting latent image which is thermally transferable is transferred to one or more receptor sheets on which the transferred image is developed with a toner. This embodiment allows the preparation of a number of copies. The typical procedures include placing the latent image-bearing element onto a suitable receptor sheet in the face-to-face relation and then passing the resulted composite over a hot roll kept at 50–300° C. or passing the composite together with an infrared-absorbing sheet, e.g. black paper, through a thermographic copying using an infrared lamp. By this thermal transfer technique, it is possible to reproduce a latent image on several receptor sheets. Each of the transferred images may be developed with toner dust. The technique gives very clear copies with good resolution, possibly due to the fact that image transfer is conducted in a vapor phase, Any papers are suitable as receptor sheets, and this makes a cost per single copy very low. Plastic films or sheets and metallic plates also can be used as receptor sheets, and accordingly, a reprographic process using the thermal transfer techniques is usable for preparation of templates or print wiring boards.

A toner usable for development is prepared by mixing a pigment into a resin as a binder which may melt at a relatively low temperature or may be easily dissolved in an organic solvent vapor, and then pulverizing the resulted mixture to a particle size of 5–100 microns. Generally, a toner usable for an electro-photographic process can be employed as such. By selecting a pigment exhibiting a suitable color according to the purpose, a copy having any desired color can be obtained. Further, use of a pigment stable against heat, light and chemical attack permits the preparation of copies substantially permanently free from discoloration or fading. Further, if a suitable resin is selected, a toner usable for an offset printing master can be obtained, and if a dye soluble in a spirit type solvent is used instead of a part of the pigment, a toner usable for a spirit printing master is obtained.

In carrying out development for a reprographic process of the present invention, the above-indicated toner is used in the manner commonly known in an electrophotographic process, e.g. cascade method, magnet brush method, smoke chamber method, etc. The developed image may be fixed by the known method, e.g. by application of heat or treatment with a solvent.

The process according to the invention may be considered so-called "negative-positive process," as the exposed portion on a photo-sensitive sheet becomes dust-adhering. Accordingly, if a copy reproduced should be a positive image, the original bearing a negative image should be used. A negative image-bearing original can be easily prepared by the known photographic techniques. However, it is also possible to obtain a positive copy from a positive image-bearing original when the following procedures are used: A reprographic element is prepared by using a support having the dark-colored background, and then this is subjected to light exposure through a positive image-bearing original. The portion which has been converted to a dust-adhering state as the result of photo-chemical reaction is treated with a toner containing white pigment such as titanium white or lead white, thereby to obtain a positive image. More simply, the reprographic element may be exposed to light through an original and then heated. Thereafter, the entire surface of the sheet is exposed to light, thereby to obtain a positive image. If a reprographic element having white-colored background is used, the portion which has become dust-adhering after exposure to light is treated with titanium white or other toner to nullify the dust-adhering property completely and then the entire surface of the reprographic element is uniformly exposed to light thereby to convert the shadow portion of the positive image of the original to dust-adhering. Then the element is treated with an ordinary coloring toner thereby to have a developed positive copy.

The present invention is an entirely novel process for copying, which succeeds in overcoming several disadvantages encountered in the prior art. Namely, according to the present invention, a photographic dark room is not necessary and, as it is a dry process, a dry copy may be

rapidly obtained. Further, in case of copying documents, the present process will be one of the most economical copying methods and if a number of copies should be prepared the required expense per single copy is by far low was compared with that of any one of the conventional processes. Further, a definite copy immune from coloration or fading may be prepared according to the process, since the visible image is formed by treatment with a toner containing a stable pigment. A further advantage of this invention is that the process can be used to carry out thermal transfer of an image from a single copy (as master) to several sheets of ordinary paper. Still another advantage is that the present process provides a reproduction having any desired color other than black when a toner having suitable color pigment is selected for development. If color-separated negatives are used in superposed state, a colored copy is also obtainable.

The following examples describe certain ways in which the principle of the invention has been applied, but are not to be construed as limiting its scope.

EXAMPLE 1

Finely powdered 4-N-benzoylamino-2,5-diethoxy-benzene diazonium chloride-zinc chloride double salt is rubbed onto a tracing paper by means of buff rolls at the final stage of the paper-making steps. The thus prepared photo-sensitive reprographic sheet is placed into contact with an original, which is a hand-written transparent paper, in the back-to-face relation. The resulting composite is subjected to light exposure from the side of the original (front copying) by means of a commercially available diazo-copying machine with 800 w. mercury lamp as light source and with a glass drum having a surface temperature of 70° C. The light-exposed portion is now dust-adhering. It is then dusted with a powdered toner and heated to give a fixed image which is negative with respect to the original. Alternatively, the said portion is dusted with titanium white and thereafter, the whole surface of the sheet is exposed to ultraviolet irradiation, thereby to make the remaining portion dust-adhering. The thus treated sheet is treated with a coloring toner to effect development of a contrasting image which is positive with respect to the original.

EXAMPLE 2

A powdered mixture of p-N-dimethylaminobenzene diazonium chloride-zinc chloride double salt and 2-methyl-4-N-diethyl-amino-benzene diazonium chloride-zinc chloride double salt (at the weight ratio of 7:7) is rubbed onto a bond paper by means of buff rolls. When using the same printing machine as in Example 1, an appropriate printing time for the mixture is four seconds, whereas that for individual components is about 10 seconds. This indicates that an increase in speed is twice when the mixture of two components is used. The latent image formed may be developed as described in Example 1.

EXAMPLE 3

A solution of p-(N-ethyl-N-benzylamino)-benzene diazonium chloride-zinc chloride double salt in ethyl alcohol is coated on a bond paper and then dried.

The thus prepared photo-sensitive reprographic sheet is brought into close contact with a continuous tone photographic negative and then the composite is subjected to front copying by using a diazo printer. The negative is removed, and the reprographic sheet is treated with a toner and then heated to effect fixation. Thereafter, ultraviolet irradiation is applied to the whole surface of the sheet in order to decompose the photo-sensitive material remaining in the non-image area. A copy having satisfactorily continuous tone is obtained.

EXAMPLE 4

A microfilm negative is printed to the photo-sensitive reprographic sheet of Example 3 by means of an enlarger in which Oslam Model 500 UV-lamp is a light source. The sheet is then heated at 70° C. for 5 seconds and thereafter worked up in the same manner as in Example 3, thereby to obtain a copy having good quality.

EXAMPLE 5

Sand-buffed aluminum plate of 0.15 mm. in thickness is coated with a methanolic solution of 0.6% 4-(N-ethyl-N-B-hydroxyethylamino)-benzene diazonium chloride-zinc chloride double salt and then dried.

The resulted photo-sensitive element is exposed to light in the same manner as in Example 1 and then treated with a toner for offset master printing. After fixation by heating, a visible image is obtained on an aluminum plate. The plate is then washed with water to remove undecomposed photo-sensitive component. The thus prepared plate is usable as an offset printing master having an oleophilic image area and a hydrophilic non-image area.

EXAMPLE 6

Twenty grams of 4-(N-ethyl-N-B-hydroxyethylamino)-benzene diazonium chloride-zinc chloride double salt is mixed with 500 ml. of a 2.0% ethyl acetate solution of vinylidene chloride-acrylonitrile copolymer (obtainable under the trademark Saran F220). The mixture is ground in a ball mill for 24 hours. The resulting dispersion is applied to a polyester film (0.05 mm. thick) and then dried. The resulted photo-sensitive sheet contains the photo-sensitive component in the amount of 0.9 g./m.^{2}.

This sheet is superposed with a conventional photographic negative and then the composite is subject to front copying at the exposure time of 40 seconds by using the same diazo copying machine as used in Example 1. The sheet is now ready for use as a master for thermal transfer. An unprocessed bond paper is placed in contact with the latent image-bearing surface of the sheet. Heat is applied to the composite from its back sides for 0.5 second by means of hot rolls having a surface temperature of 120° C. The photo-decomposition product of the photo-sensitive component is thermally transferred to the receptor paper to form the corresponding latent image which is then developed with a powdered toner and fixed with trichloroethylene vapor. By repeating these procedures, twenty clear copies are obtained.

The above examples have been presented for the purpose of illustration and should not be taken to limit the scope of the present invention. It will be apparent that the described examples are capable of many variations and modifications. All such variations and modifications are to be included within the scope of the present invention as set forth in the appended claims.

What is claimed is:

1. A reprographic method consisting essentially of:

(a) exposing imagewise to light at a temperature within the range of 50–300° C. reprographic material comprising a support bearing a coating thereon of a light-sensitive diazonium salt selected from the group consisting of unilaterally diazotized p-phenylene diamines and 1-diazo-2-naphthol-4-sulfonic acid, which diazonium salt is normally non-adhesive and becomes adhesive upon exposure to light within a temperature range of 50–300° C., thereby creating in said coating an adhesive image corresponding to said imagewise exposure; and

(b) applying a dry, finely divided powder to at least said adhesive image areas of said coating, whereby said powder adheres to said adhesive image areas and defines said image.

2. A reprographic method according to claim 1 wherein said powder comprises an inert pigment and a thermoplastic resin binder therefor intimately mixed therewith, and including the additional step of heating said powdered exposed areas sufficiently to fuse said binder, thereby fixing said image on said surface.

3. The method according to claim 1 wherein said powder comprises a spirit duplicating dye.

4. The method according to claim 1 wherein said powder comprises an oleophilic ink receptor.

5. A reprographic method consisting essentially of:

(a) exposing imagewise to ultraviolet light at a temperature within the range of 50–300° C. reprographic material consisting essentially of an electrically non-conductive support bearing a coating thereon of a photosensitive diazonium salt, thereby forming in the light-exposed areas of said material diazonium salt photodecomposition products exhibiting substantially greater adhesiveness than said diazonium salt at a temperature within the range of 50–300° C.;

(b) applying to at least the light exposed areas of said material a finely divided powder consisting essentially of a multiplicity of dry solid particles of a pigment composition having a size range of about 5–100 microns, thereby at least lightly adhering said powder to said photo-decomposition products in said light exposed areas;

(c) removing from said material powder not adhered to said photo-decomposition products; and

(d) effecting a substantially direct adherence between said material and said at least lightly adhering powder.

6. A reprographic method consisting essentially of

(a) providing a reprographic material comprising a support bearing a coating of a light-sensitive diazonium salt which is normally dry and non-adhesive at a given temperature between about 50° C. and 300° C. and which, upon exposure to light, forms photo-decomposition products which exhibit a substantially greater adhesiveness than said diazonium salt at said given temperature and create in light-exposed areas of said coating at said given temperature an image of said substantially greater adhesiveness;

(b) exposing said material imagewise to light at a temperature at least as high as said given temperature; and

(c) applying a finely-divided powder to at least the light-exposed areas of said coating, said powder being visibly distinct with respect to the unexposed areas of said coating.

7. A reprographic method according to claim 6 wherein said powder consists essentially of a uniformly composed multiplicity of dry solid particles of a pigment composition having a size range of about 5–100 microns.

8. A reprographic method consisting essentially of

(a) providing a reprographic material comprising a support bearing a coating of light-sensitive diazonium salt which is normally dry and non-adhesive at a given temperature between about 50° C. and 300° C and which, upon exposure to light, forms photo-decomposition products which exhibit a substantially greater adhesiveness than said diazonium salt at said given temperature and create in light-exposed areas of said coating at said given temperature an image of said substantially greater adhesiveness;

(b) exposing said material imagewise to light at a temperature below said given temperature;

(c) heating said exposed material uniformly to at least said given temperature; and

(d) applying a finely-divided powder to at least the light-exposed areas of said coating, said powder being visibly distinct with respect to the unexposed areas of said coating.

9. A reprographic method comprising:

(a) providing a reprographic material comprising a support bearing a coating of a light-sensitive diazonium salt which is normally dry and non-adhesive at a given temperature between about 50° C. and 300° C. and which, upon exposure to light, forms photo-decomposition products which exhibit a substantially greater adhesiveness than said diazonium salt at said given temperature and create in light-exposed areas of said coating at said given temperature an image of said substantially greater adhesiveness;

(b) exposing said material imagewise to light;

(c) contacting the coated face of said material to a receptor surface;

(d) heating said material to at least said given temperature;

(e) separating said receptor surface from said material face, thereby transferring a portion of said coating in said image areas of greater adhesiveness from said material face to said receptor surface; and

(f) applying finely-divided powder to at least the transfer image areas on said receptor surface, said powder being visibly distinct with respect to said receptor surface.

10. A reprographic method comprising:

(a) providing a reprographic material comprising a support bearing a coating of a light-sensitive diazonium salt which is normally dry and non-adhesive at a given temperature between about 50° C. and 300° C. and which, upon exposure to light, forms photo-decomposition products which exhibit a substantially greater adhesiveness than said diazonium salt at said given temperature and create in light-exposed areas of said coating at said given temperature an image of said substantially greater adhesiveness;

(b) exposing said material imagewise to light at a temperature at least as high as said given temperature;

(c) applying a first finely-divided powder to at least the light-exposed areas of said coating, whereby said powder adheres to said material in said areas;

(d) removing non-adhered powder from said material;

(e) exposing uniformly to light and at a temperature at least as high as said given temperature the reprographic material thus partly treated, thereby creating in areas of said coating previously unexposed to light said substantially greater adhesiveness; and

(f) applying a second finely-divided powder to at least said previously unexposed coating areas, said second powder being visibly distinct with respect to said first powder.

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