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COPYING MATERIAL AND PROCESS FOR THE PREPARATION OF AUXILIARY COPIES FOR MULTICOLOR PRINTING

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ABSTRACT OF THE DISCLOSURE

This invention relates to a copying material for use in the preparation of auxiliary copies for multicolor printing comprising a biaxially stretched and thermo-set polyester film as a support and a light-sensitive copying layer thereon, the latter containing at least one compound selected from the group consisting of a p-benzoquinone diazide and a p-benzoquinone imino diazide, at least one acid- and alkali-resistant dyestuff which is soluble in organic solvents, and at least one film-forming, substantially colorless, alkali-soluble resin.

The present invention relates to a copying material and to a process for the preparation of auxiliary copies for multicolor printing.

"Auxiliary copies" in the sense of the present invention are all monochrome transparent copies of color separations or multi-colored originals, which are used by the printer in known manner for registering, mounting and judging reproducible silver film copies or color separations in color process work. Such copies are mainly color proofing foils, registration guides, and films for the final control of a mounting.

Austrian Pat. No. 266,591 discloses a process for the preparation of auxiliary copies for multicolor printing. The light-sensitive copying material used for this process consists of a colorless, transparent and dimensionally stable plastic film, preferably a biaxially stretched and thermo-set polyester film, as the support, and a copying layer which consists of at least one p-benzoquinone diazide or p-benzoquinone imino diazide and at least one acid-resistant and alkali-resistant dyestuff. This copying material is image-wise exposed, e.g. under a screened color separation or a positive or negative transparency of the originial in black and white, and the latent image thus produced is developed by means of a weakly acid to weakly alkaline aqueous solution. During development, the unexposed areas of the reproduction layer are dissolved away, whereas the exposed areas remain unchanged.

Although by this process auxiliary copies of very good quality are obtained with regard to the reproduction of color shades and optical density, there is a certain danger that the quality of the copies may be impaired by careless treatment of the copying material. For example, the unexposed copying layers and the finished copies are sensitive to mechanical damage by rubbing or scratching. Further, the quality of the copy may be impaired by an improper performance of the developing process, e.g. by rubbing too long or too vigorously with the developer liquid. Moreover, traces of adhesive or the like cannot be removed from the copies after use, because the layers are soluble in most organic solvents suitable for this purpose. In addition thereto, when reproduction material of this type is subjected to a minute examination, differences in the thickness of the copying layer become apparent, which of course have some effect upon the optical density reproduced in the copy.

Further, it is known that certain resins, e.g. phenol-formaldehyde condensates, may be added to light-sensitive copying layers containing the diazo compounds described above when they are supported on metal supports. Offset printing forms prepared with such copying materials are distinguished by a better and more permanent differentiation between ink-receptive and ink-repellent areas of the surface and thus yield longer printing runs.

The present invention provides a copying material and a process for the preparation of auxiliary copies for multicolor printing which, as compared with the known material mentioned above, yields more uniform and less sensitive copies.

The invention is based on a copying material for the preparation of auxiliary copies for multicolor printing, in particular of color proofing foils, registration guides and films for final mounting control, which consists of a biaxially stretched and thermo-set polyester film as the support and a light-sensitive reproduction material applied thereto which contains at least one p-benzoquinone diazide and/or p-benzoquinone iminodiazide and at least one acid- and alkali-resistant dyestuff which is soluble in organic solvents. By the present invention, a copying material of this type is provided which contains, in addition, at least one film-forming, practically colorless, alkali-soluble resin in the reproduction layer.

For processing, the material is exposed under a silver film color separation or a positive or negative transparency of the original in black and white, and the resulting latent image is then developed with a weakly alkaline aqueous solution.

The light-sensitive copying material according to the invention has the advantage over the known, otherwise identical material containing no film-forming, colorless, alkali-soluble resins, in that it is considerably more resistant to the developer liquids used during the copying process and to organic solvents, such as are used for removing traces of adhesive and for cleaning. Furthermore, the layers according to the invention are much more homogeneous and less senstive to mechanical damage by rubbing, scratching, and the like. The image areas of the developed copy have an improved adhesion to the polyester support and are insensitive to acid and alkaline solutions.

It is surprising that, by adding the above-identified resins in accordance with the invention, on the one hand the adhesion of the exposed areas of the layer to the polyester film is improved while, on the other hand, the development of the reproduction material, i.e. the removal of the unexposed areas of the layer from the film surface, is not impeded. From the known addition of such resins to light-sensitive layers on metal supports for the preparation of offset printing plates—where they served the purpose of increasing the printing run—no suggestion could be found for the solution of the problem of the present application, i.e. to improve the uniformity of copying layers and the adhesion of the developed image parts thereof to polyester films, which latter differ substantially in their surface characteristics from metal supports. This is the more so as the layers according to the invention contain a substantial amount of dyestuff in addition to the diazo compound causing developability.

In the copying material according to the invention, diazo compound and dyestuff are preferably contained in a proportion by weight of about 5:1 to 1:2. The quantity of resin added may vary within wide limits. Normally, it ranges from about 0.1 to 20 parts by weight, preferably from about 1 to 6 parts by weight per 10 parts by weight of diazo compound.

Film-forming, practically colorless, alkali-soluble resins which are very suitable are, e.g.: epoxy resins, phenol/

aldehyde condensates, such as novolaks, alkali-soluble polystyrene copolymers, such as copolymers of polystyrene and maleic acid, alkali-soluble polyvinyl chloride copolymers, homopolymers and copolymers of vinyl acetate, and polyvinyl acetals.

The light-sensitive p-benzoquinone diazides and p-benzoquinone iminodiazides contained in the copying material according to the invention are known. Suitable members of this group of compounds are described in U.S. Pat. Nos. 2,759,817, 2,754,209, 3,050,387, 3,175,906, and 3,180,732.

The organic solvent-soluble or -dispersable, alkali- and acid-resistant dyestuffs contained in the copying material according to the invention must not change their color shades under the influence of dilute alkaline or acid solutions. For the preparation of color proofing foils, they should, as far as possible, correspond to the desired standard colors for the color-proofing process, viz yellow, magenta and cyan blue. Frequently, a black is also required for the color proofing process. Dyestuffs which correspond in their color shades to those of the German industrial standard color scale 16.508 are preferred, e.g. Fat Yellow 5 G (C.I. Suppl. 572), Fat Yellow 3 G (C.I. 2822), Celliton Yellow 3 G (C.I. 3401), Fat Red G (C.I. 2834), Fat Red HRR (see the next paragraph but one), Fat Red 5 B (C.I. 2851), Fat Black HB (C.I. 2899), Zapon Fast Black RE (C.I. Suppl. 121), Zapon Fast Black B (C.I. Suppl. 121), Zapon Fast Blue HFL (C.I. 2880), Zapon Fast Blue FLE (C.I. Suppl. 593), Zapon Fast Red BB (C.I. 2864), Zapon Fast Red BE (C.I. 2845), Zapon Fast Fire Red B (C.I. Suppl. 593), Zapon Fast Red GE (C.I. Suppl. 584), Zapon Fast Yellow B (C.I. 2827), Zapon Fast Yellow GR (C.I. 2823), and mixtures of these.

The numbers prefixed by the letters "C.I." after the names of the dyestuffs denote the relevant page numbers in the Color Index, Part I, second edition, 1956. The numbers prefixed by "C.I. Suppl." after the dyestuff names denote the page numbers in the Color Index, Part I, second edition, Supplement 1963.

Fat Red HRR is an azo dyestuff of the empirical formula $C_{22}H_{16}N_4O$, prepared by the coupling of 1 mole of p-aminoazobenzene with 1 mole of β-naphthol.

For the preparation of color proofing foils according to other than German standards, or of registration guides, and for the final control of mountings, it is of course possible to use dyestuffs which differ from the above mentioned standard colors. Dyestuffs of low ultraviolet absorption, but good visual contrast, e.g. blue dyestuffs, are particularly suitable for the preparation of registration guides.

The constituents of the reproduction layers are dissolved in an organic solvent or a mixture of organic solvents, applied without further pretreatment to the surface of a supporting film, and dried. Suitable organic solvents are, e.g.: glycol ethers, such as ethyleneglycol monomethyl ether and ethyleneglycol monoethyl ether; esters, such as butyl acetate and amyl acetate; ethers, such as dioxane; ketones, such as methyl ethyl ketone and cyclo hexanone; and also dimethyl formamide.

Colorless, clearly transparent, biaxially stretched and thermoset polyester films are used as supports. Because of their easy accessibility, commercial polyethylene terephthalate films are preferred. It is noteworthy that no previous treatment of the film surface is required to cause good adhesion of the layer.

For the preparation of color proofing foils, the copying materials are exposed under a photographic negative or positive to ultraviolet light. It is preferred to use, as originals, screened negative silver film color separations which have been prepared from a colored original in a copying camera. In each case, the color separation used corresponds to the dye in the coating of the light-sensitive plastic film according to the present invention, i.e. a yellow plastic film is exposed under the yellow silver film separation, a red plastic film under the red silver film separation, and so on. After exposure, the copying layer is removed from the parts not struck by light by means of an aqueous, weakly alkaline solution, normally a 0.5 to 5 percent by weight solution, i.e. the layer is developed. A reverse image (negative) of the original used, viz of the silver film color separation, is thus obtained.

Suitable alkaline substances are, e.g., alkali metal silicates, alkali metal phosphates, alkali metal carbonates and/or organic bases, such as ethanolamines, alkyl amines and alkylene diamines. The developed films are dried, and colored images are thus obtained which, when the cyan, magenta, yellow, and, in some cases, black color separation copies are placed over one another in precise register, either correspond exactly to the colored original or, alternatively, render possible a rapid correction of the silver films by one of the conventional after-treatments.

The copying material according to the invention can be stored for months, can be prepared rapidly and easily, and results in a saving in labor when used. The color proofing process by means of color proofing foils obviates the expensive and time-consuming machine proofing hitherto necessary in multicolor offset and frequently also in gravure and relief printing. In addition, an impression is very quickly gained in the printing plant of the color shade to be expected when printing at a later stage, and this can be corrected immediately without, as was hitherto frequently necessary, having to stop a printing run already in progress, which involves losses in material, time and energy.

Light-sensitive copying materials according to the invention containing a blue dyestuff in the light-sensitve layer are also very suitable as registration guides. As is known, for the reproduction of colored originals in offset, gravure and relief printing, the usual procedure is first to expose an original, provided with register crosses, in a copying camera through a screen and color filter onto silver film three to four times in succession. For example, for one exposure a blue filter is used, for the second a green filter, and for the third a red filter, and, in most cases, a fourth exposure without a color filter is also made. After development of the films, the silver film color separations are obtained. Each of these color separations serves as original for the exposure of one light-sensitive printing plate.

After development of the exposed printing plates, printing forms are obtained which correspond to the four silver film color separations and from which printing can be effected, e.g. in a color printing machine. The exposure of the printing plates must be carried out very carefully in order that, in the machine, the printing plates will make successive contact with the same points of the material which is to be printed.

In order to achieve this, different methods of mounting are employed when exposing the printing plates. The highest accuracy of register of the composite is achieved by preparing a blue foil as a so-called "registration guide." The function of a "registration guide" in color printing is, e.g., that the silver film color separations are successively brought into alignment with the blue foil with the aid of the register crosses on the color separations and the registration guide, or of the image edges. The registration guide may be exposed together with the respective silver film color separation, because it is transparent to the normally used short-wave light. An uncoated, transparent foil also may be placed on the blue foil serving as registration guide and the silver film color separations successively positioned in register therewith, and the registration guide then may be removed from the transparent foil before exposure. The originals so mounted permit exposure of the printing plates in precise register and therefore printing in precise register on the material to be printed in the printing machine.

In this latter method of assembly, a transparent copy produced in accordance with the invention also may be used as a so-called reference copy.

When the copies are to be used for the final control of mounting, the following procedure is employed:

From the readily mounted silver film color separations, which in the case of larger sizes normally consist of several so-called "groups" (e.g. image and text matter), copies are prepared on the material according to the invention by exposing the blue reproduction material under a blue silver film color separation, the yellow reproduction material under a yellow silver film color separation, and the red reproduction material under a red silver film color separation, and developing the copies. When the resulting three colored transparencies are superimposed against a light background, it becomes immediately apparent, from the color, if an error was made in the assembly and in which silver film color separation. Prior to the use of the colored films according to the invention, the mounted silver film color separations themselves had to be superimposed for the final control of the assembly. However, since all color separations appear black, it was not possible to distinguish the individual layers of the mounting. Thus, minor faults could not be detected and did not become visible until later, during printing.

The following examples serve to further illustrate the preparation and processing of the reproduction material according to the invention:

EXAMPLE 1

2 g. of 1 - ((4' - methyl-benzene-sulfonyl)-imino)-2-(2'',5'' - dimethyl-phenyl-amino-sulfonyl)-benzoquinone-(1,4)-diazide-(4), prepared according to Example 1 of U.S. Pat. No. 3,175,906, 1.0 g. of Zapon Fast Blue HFL (C.I. 2880), and 0.5 g. of polyvinyl acetate having a specific gravity of 116 are dissolved in a mixture consisting of 50 ml. of tetrahydrofuran, 40 ml. of ethyleneglycol monomethyl ether, and 10 ml. of butyl acetate.

A 0.1 mm. thick, biaxially stretched and thermo-set polyethylene terephthalate film is sensitized with this solution by roller application and then dried. The sensitized film web is cut into suitable sizes which can be stored for many months in the dark. The layer is exceptionally homogeneous.

For the color proofing process, the blue-colored film is exposed for about 3 minutes, at a distance of about 110 cm. for a 60 amp arc lamp, under a screened blue silver film color separation produced by means of a red filter in a copying camera. The coated layer is then removed in the unexposed areas by wiping with a cotton pad soaked in an aqueous solution containing 3 percent by weight of sodium silicate and 3 percent by weight of trisodium phosphate. After rinsing the developed film with water and drying, a negative, storable, blue-colored image of the silver film original with the conventional register crosses is obtained which is insensitive to scratching and corresponds in its color shade to the standard blue according to DIN 16.508. For removing traces of dust or adhesive tape caused by mounting, the copy may be cleaned with conventional cleansing agents based on aliphatic hydrocarbon fractions, e.g. gasoline, or with acid or alkaline solutions, without damaging the layer.

For use as a registration guide, a silver film yellow separation of the original, e.g., prepared in a copying camera with the aid of a blue filter is fastened to this blue-colored image of the colored original in such a manner that the register crosses or the image edges are in accurate register with each other. The assembly is laid upon a light-sensitive printing plate and exposed by means of an arc lamp. After the conventional development and inking up, the printing plate may be used for printing with yellow printing ink in a printing machine. The assembly consisting of the blue registration guide and the yellow separation is taken apart and the procedure is repeated successively with the silver film red separation, the silver film blue separation, and, if four-color printing is intended, also with a diapositive of the multicolored original obtained without using a color filter. Each time the mounting is disassembled, traces of adhesive adhering to the copy may be removed by rubbing lightly with gasoline, without the layer being damaged or dissolved.

A copying material which contains benzoquinone-(1,4)-diazide-(4)-2-(N-β-naphthyl)-sulfonamide, prepared according to Example 2 of U.S. Pat. No. 2,754,209, instead of the abovementioned diazo compound may be used in the same manner.

EXAMPLE 2

2 g. of 1-((4'-methyl-benzene-sulfonyl)-imino)-2-(2''-ethylphenylaminosulfonyl) - benzoquinone - (1,4)-diazide-(4), prepared according to U.S. Pat. No. 3,175,906, 1 g. of Fat Yellow 5 G (C.I. Suppl. 572), and 0.5 g. of an epoxy resin having a melting point of 70° C. and an epoxy equivalent weight of 500 (commercial name: Epikote 1001, manufactured by Shell) are dissolved in a mixture consisting of 50 ml. of tetrahydrofuran, 40 ml. of ethyleneglycol monomethylether, and 10 ml. of butyl acetate, and the resulting solution is used for sensitizing a biaxially stretched and thermo-set polyethylene terephthalate film.

For the preparation of a yellow color proofing foil, the exposed copy is developed with an aqueous solution containing 2 percent by weight of sodium silicate and 0.5 percent by weight of polyethylene glycol. Even vigorous rubbing and wiping cannot damage the yellow colored layer.

EXAMPLE 3

1 g. of benzoquinone-1(4)-diazide-(4)-2-sulfonic acid-(N-ethylphenyl)-amide, prepared analogously to Example 1 of U.S. Pat. No. 2,754,209, 1 g. of Zapon Fast Red BB (C.I. 2864), and 0.5 g. of a reaction product of formaldehyde/phenol resin and chloroacetic acid prepared as described in Example 5 of U.S. Pat. No. 3,050,387, are dissolved in a mixture consisting of 50 ml. of ethyleneglycol monomethyl ether, 30 ml. of methyl ethyl ketone, and 20 ml. of butylacetate.

A red color proofing foil is prepared in accordance with the procedure of Example 1.

EXAMPLE 4

2 g. of the diazo compound described in Example 1, 0.5 g. of Fat Black HB (C.I. 2899), and 0.5 g. of a copolymer of 85 percent by weight of vinyl chloride, 14 percent by weight of vinyl acetate, and 1 percent by weight of maleic acid are dissolved in a mixture consisting of 80 ml. of ethyleneglycol monomethylether and 20 ml. of butyl acetate.

A greyish-black color proofing foil is prepared by the procedure described in Example 1.

When the color proofing foils prepared according to Examples 1 to 4 are laid over one another in precise register, a copy of the colored original is formed which permits an estimation of the correct exposure and development of the silver film color separations by the degree of faithfulness of its color shades.

It will be obvious to those skilled in the art that many modifications may be made within the scope of the present invention without departing from the spirit thereof, and the invention includes all such modifications.

What is claimed is:

1. Copying material for use in the preparation of auxiliary copies for multicolor printing comprising a biaxially stretched and thermo-set polyester film as a support and a light-sensitive copying layer thereon, the latter containing at least one compound selected from the group consisting of a p-benzoquinone diazide and a p-benzoquinone imino diazide, at least one acid- and alkali-resistant dyestuff which is soluble in organic solvents, and at least one film-forming, substantially colorless, alkali-soluble resin.

2. Copying material according to claim **1** in which the weight ratio of diazo compound to dyestuff is in the range of about 5:1 to 1:2, and the weight ratio of diazo compound to resin is in the range of about 10:1 to 10:6.

3. Copying material according to claim 1 in which the resin is selected from the group consisting of an epoxy resin, a phenol-aldehyde condensate, a polystyrene-maleic acid copolymer, a vinyl acetate polymer, and a polyvinyl acetal.

4. A process for the preparation of auxiliary copies for multicolor printing which comprises exposing a copying material to light under a pattern and developing the resulting latent image with a weakly alkaline, aqueous solution, the copying material comprising a biaxially stretched and thermo-set polyester film as a support and a light-sensitive copying layer thereon, the latter containing at least one compound selected from the group consisting of a p-benzoquinone diazide and a p-benzoquinone imino diazide, at least one acid- and alkali-resistant dyestuff which is soluble in organic solvents, and at least one film-forming, substantially colorless, alkali-soluble resin.

5. A process according to claim 4 in which the pattern is a color separation.

6. A process according to claim 4 in which the pattern is a black and white image of an original to be printed.

7. A process according to claim 4 in which the resin is selected from the group consisting of an epoxy resin, a phenol-aldehyde condensate, a polystyrene-maleic acid copolymer, a vinyl acetate polymer, and a polyvinyl acetal.

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