Oct. 13, 1964 M. HEPHER ETAL 3,152,898

PHOTOGRAPHIC MATERIAL FOR SPIRIT DUPLICATING

Filed July 28, 1960

Fig. 1

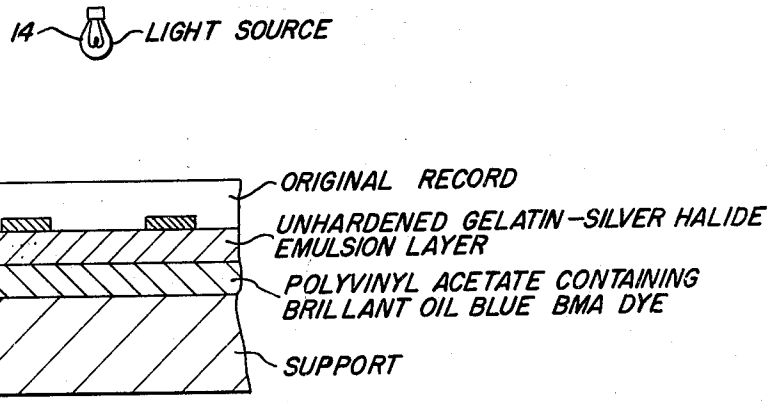


Fig. 2

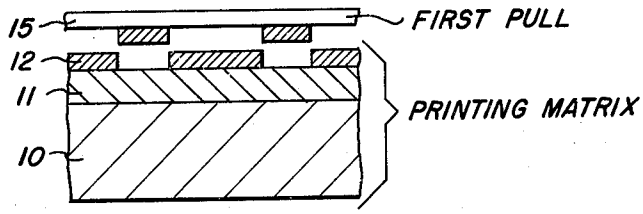
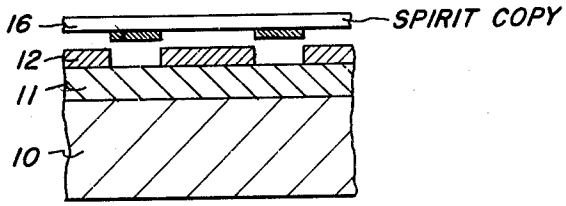


Fig. 3



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PHOTOGRAPHIC MATERIAL FOR SPIRIT DUPLICATING

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This invention pertains to a photographic element designed for preparing the printing matrix for spirit duplicating processes.

Spirit duplicating processes are well known and widely used. They provide one of the most inexpensive methods of making up to 100 copies from a document. Spirit duplicating machines are comparatively cheap and quite common. However, there is no commercial process that offers a method for making a master by simple photographic means.

In the conventional spirit duplicating system the image is formed in reverse on a master by transfer from a carbon-type sheet coated with a composition containing a high proportion of a spirit soluble dye such as Crystal Violet, Victoria Blue, and the like. The preparation of a master is normally carried out by typing or hand drawing. Then the image is transferred from the master to the copy sheets, the surfaces of which have been wetted with an alcohol or alcohol-water mixture.

Known photographic processes for making printing matrices or spirit duplicating processes involve complicated and lengthy wet processing. Photographic methods have been devised for making masters for solvent dye transfer. However, these masters are capable of giving only a few copies.

It is therefore an object of this invention to provide a photographic element designed for preparing the printing matrix for spirit duplicating by means of a simple photographic process. Other objects will become apparent from the following specification and claims.

We have found that these and other objects can be achieved by using the photographic element of our invention to make printing matrices for spirit duplicating processes.

In its simplest form our photographic element consists of a sheet of paper similar to that used for normal photographic sensitizing that is coated with a layer of water-insoluble alcohol-soluble dye in a suitable water-insoluble binder over which is coated a thin layer of unhardened silver halide emulsion with an incorporated tanning developing agent.

The silver halide emulsion layer of the material is exposed to a positive image by contact printing or by projection printing. Then the incorporated tanning developing agent in the exposed silver halide emulsion layer is activated by immersing the material in an alkaline solution. In those areas where the silver halide has been exposed, the gelatin is tanned or hardened as a silver image is developed, while the gelatin in the areas of the emulsion that were not exposed remain unhardened. The unhardened areas of the gelatin silver halide emulsion are then stripped off by squeegeeing this layer of the element into contact with a plain sheet of paper and after 20 or 30 seconds stripping off the paper with the unhardened emulsion, thus exposing in these areas the resin dye layer of the printing matrix. The gelatin stencil image on the matrix is then dried, then the matrix is placed on the cylinder of a spirit duplicator and positive images transferred to receiving or copy paper by the usual method.

Alternatively, the strongly colored dye used in the resin layer of the photographic element described above for

making a printing matrix can be replaced by a dye intermediate or color-forming compound that does not absorb light in the region of sensitivity of the silver halide in the photographic emulsion layer. This element can be exposed as described above or more advantageously by reflex printing in which the image side of the original document to be copied is held in firm contact with the light-sensitive silver halide emulsion layer of the photographic element while the light-sensitive emulsion layer is exposed by passing the exposing light through the support of the photographic element. The printing matrix is then prepared by developer activation, stripping and drying as described above. The dye intermediate or color-forming component is then transferred to the receiving sheet and converted into the strongly colored dye by reacting the dye intermediate with a suitable coupler or reagent either in the transfer solvent or in the receiving sheet.

Any suitable support may be used for making the photographic element of our invention. If the element is to be used for projection or contact exposure, the support may be paper, a plastic such as cellulose acetate, cellulose nitrate, polyethylene terephthalate, polystyrene, polycarbonate, etc., glass, metal, etc. However, if the element is to be used for reflex exposure, the support used must not be opaque to the exposing light but must transmit this light sufficiently well to facilitate exposure of the light-sensitive silver halide emulsion layer by this method. For this purpose any of the supports listed excepting metal are suitable. Plain paper or paper of the kind usually used in the production of commercial photographic papers which usually bear a gelatinous subbing layer are used advantageously.

The resin dye layer coated over the support should advantageously possess the following characteristics.

A. It should facilitate clean and complete transfer of the exposed emulsion that is coated over it after processing but at the same time tenaciously hold the exposed areas of gelatin.

B. It should act as a carrier for the dye or dye-forming component without hampering its extraction during spirit duplicating.

C. It should be preferably alcohol soluble but substantially insoluble in water or alkali.

D. It should be inert toward the light-sensitive silver halide emulsion layer that is coated over it and be free from hardening agents. A polyvinyl acetate which has not been hydrolyzed or sufficiently hydrolyzed to make it water soluble is a preferred resin for making our photographic elements. Other resins which can be used include zein, alcohol-soluble nylon plastic, polyvinyl butal, polyvinyl formal, polyethylacrylate, polymethylmethacrylate, etc.

Small quantities of other substances can be added to the resin layer to modify the stripping properties of the layer. For example, polyvinyl phthalate can be used advantageously for this purpose. Alternatively, a thin layer of an alkali-swellable or alkali-soluble colloid such as polyvinyl phthalate may be coated between the resin layer and the light-sensitive silver halide emulsion layer.

The photographic elements of our invention that are designed for contact or projection printing contain dye in the resin layer. This dye should advantageously fulfill the following conditions.

A. It should be readily soluble in alcohol but substantially insoluble in water.

B. It should be inert towards the emulsion layer that is coated over the resin layer.

C. It should have a high tinctorial power to give the required number of copies.

The carbinol bases of certain dyes or the lactones of triphenylmethane dyes can be used with success. Dyes which we have found particularly advantageous for use in making such resin layers are Brilliant Oil Blue BMA identified as Colour Index No. 61555, Solvent Blue 16 of the Colour Index, The Society of Dyers and Colourists, Bradford, England, 2nd Edition, Part 1, volume 2, page No. 2877; the carbinol base of Victoria Blue; Grasol Blue R; Celanthrene Sky Blue B; 6-(2',4'-dinitro-6'-N-ethylsulfonamide - benzeneazo) - N - β,γ - dihydroxypropyl-2-methyltetrahydroquinoline; and other dyes of J. B. Dickey et al. U.S. Patent 2,391,886, granted January 1, 1946, etc. These dyes are available commercially.

The photographic elements of our invention that are designed for reflex printing contain a colorless dye-forming material. The one or two component systems used should advantageously have the following characteristics.

A. The spectral absorption of the color-forming component used beneath the emulsion that is in the resin layer must be low in the actinic region (green).

B. At least one component has to be freely soluble in alcohol but completely insoluble in water.

C. The component present in the sub-layer or resin layer should be stable at the pH of the emulsion.

D. Color formation during the spirit transfer should be instantaneous and a high density image should be produced.

E. The dye produced should be stable to light and atmosphere.

One example of a colorless material useful for making this type of photographic element is bis(para-dimethylaminophenyl)methane which is incorporated in the resin layer. This material is oxidized during the transfer operation to produce a deep blue dye. The transfer solvent used for this purpose contains cupric chloride and phosphotungstic acid in methyl alcohol in order to facilitate oxidation of the colorless dye former and produce the dye.

Other classes of organic dyestuff derivatives that can be used for the present process are the leuco bases and the lactones of triphenylmethane dyes. For example, Leuco Malachite Green and Malachite Green lactone. The leuco compound is oxidized during the transfer operation to the carbinol base of Malachite Green which in the presence of an acid changes to the dye proper. The lactone on the other hand gives a corresponding dye in the presence of an acid or other acetic inorganic compound.

The use of lactones and lower alkyl ethers of triphenylmethane dyes in the field of manifolding and conventional spirit duplicating is described in the following British patents, 712,216 assigned to National Cash Register Company, 798,180 assigned to Caribonum Limited, and 800,733 also assigned to Caribonum Limited.

The dyes produced from triphenylmethane lactones by adsorption onto attapulgite, for example, are not completely stable at atmospheric conditions. For this reason up to 50 percent of an oxidizable dye-forming material such as benzoyl leuco methylene blue should be added to the dye-forming layer. In such a system the lactone takes part in the adsorption reaction immediately upon making contact with the acidic substance and turns to a dark blue. The benzoyl leuco methylene base when in contact with the acidic substances oxidizes after the passage of some time and turns to a dark blue color reinforcing the color formed from the lactone which is apt to fade after being exposed to light and air.

In addition to the above-described compounds, colorless xanthene derivatives such as those mentioned in British Patent 712,216 are alcohol soluble compounds which give readily a red dye when contacted with inorganic clays. The derivative is xanthene 9, orthobenzoic acid, 3,6-diethylamino-9-para-nitroanilino lactam.

Examples of thin light-sensitive substantially unhardened organic colloid silver halide emulsion layer coated over the resin dye layer useful for our photographic elements as described in U.S. Patent 2,592,368, issued April 8, 1952, in the name of E. C. Yackel and U.S. Patent 2,596,756, issued May 13, 1952, in the name of H. C. Yutzy et al. These emulsion layers preferably contain an incorporated developing agent of the gelatin-tanning or hardening type; however, emulsions are also used that do not contain incorporated developing agent.

After exposure the photographic element with the emulsion layer containing incorporated developing agent is developed by immersion in a development activator such as those described in Yutzy et al., U.S. Patents 2,716,059 and 2,739,890. If the emulsion of the element does not contain incorporated developing agent, the exposed element is developed in a solution containing developing agent and activator. Following development, the wet photographic element is squeegeed into contact with a receiving sheet which may be a piece of ordinary paper, a translucent copy paper, or a paper containing thiourea and sodium formaldehyde bisulfite as described in U.S. Patent 2,865,745; then the receiving sheet is separated from the photographic element so as to remove the unexposed and unhardened gelatin from the photographic element and lays bare the spirit soluble resin layer containing the dye or dye-forming compound. Alternatively, it is possible to produce a good master by rinsing the exposed and developed matrix in water at 110° F. This method is not as convenient as the stripping method, however, since it takes longer for the photographic element to dry sufficiently before it can be used on the spirit duplicating process to produce the multiple copies.

Any suitable solvent may be used in the spirit duplicating process which will dissolve the dye or dye-forming compound and preferably be capable of dissolving the resin layer. Methyl alcohol or the mixtures of methyl alcohol and other organic solvents such as acetone, toluene, etc., can be used to advantage in making multiple copies of our photographically produced printing matrix on a spirit duplicating machine. Other materials may be added to the spirit solvent for specific purposes. For example, phosphotungstic acid, citric acid, and oxidizing agents such as cupric chloride, etc.

Any paper such as that used for receiving sheets on spirit duplicating process can be used for receiving the dye image from our printing matrix. Plain paper may be used to advantage as a receiving material excepting in those cases where special conditions are required. For example, when the lactones of triphenylmethane dyes are used as a colorless dye former in the resin layer, the corresponding dye is formed in the presence of an acid or acidic inorganic compound. This may be present in the spirit duplicating solvent or may be present on the surface of the receiving sheet. For example, the receiving sheet may contain inorganic compounds such as attapulgite, kaolin, bentonite, etc.

The following examples will illustrates typical embodiments of our invention but are not to be considered as limiting our invention.

Example I

A sheet of baryta paper was coated with a 3 percent solution of polyvinyl acetate in methyl alcohol containing 1 percent of Brilliant Oil Blue BMA and then dried. Then a 1 percent solution of polyvinyl phthalate in 1 percent ammonia solution was applied to the above coating, dried and a thin coating was applied over the polyvinyl phthalate layer consisting of a substantially unhardened gelatin silver chloride emulsion containing 3,4-dihydroxyl diphenyl as a developing agent and prepared as described in Yutzy et al., U.S. Patent 2,596,756, Example 1.

After being dried, the above photographic element was exposed for 15 seconds to a positive transparency,

and activated for 30 seconds at 83° F. in an aqueous activator solution having the composition:

	Percent
Sodium carbonate	4
Urea	10
Potassium bromide	0.1

Following treatment in the activator, the developed light-sensitive emulsion layer of the photographic element was squeegeed into contact with a receiving sheet. After 10 to 20 seconds, the sheets were separated when all of the unhardened emulsion transferred to the copy paper, leaving on the dyed matrix a negative stencil of hardened emulsion.

The matrix obtained after drying was contacted with a sheet of receiving paper which had been previously wetted with methyl alcohol. Twenty copies were obtained from this matrix.

Example II

A sheet of baryta paper was coated with a mixture of 90 cc. of 3 percent polyvinyl acetate in methyl alcohol, 10 cc. of 3 percent polvinyl phthalate in 70/30 methyl alcohol/acetone and 1 g. of Brilliant Oil Blue BMA dye. Over this was coated a thin layer of the gelatin silver chloride emulsion of Example I. After drying, it was exposed and processed as in Example I. Similarly twenty copies were obtained from this printing matrix by a spirit duplicating process.

Example III

A sheet of baryta paper was coated with a mixture of 5 g. of polyvinyl acetate, 2 g. of Michler's Hydrol and 100 cc. of methyl alcohol. After drying, this layer was coated with a gelatin silver chloride emulsion layer prepared as in Example I. After drying, this layer was exposed, processed and dried as in Example I. The dried matrix was then used to prepare copies by a spirit duplicating process in which the solvent had the following composition:

Acetone	cc.. 5
Toluene	cc.. 2.5
Phosphotungstic acid	g.. 1
Citric acid	g.. 1

Methyl alcohol to make 100 cc.

Formation of the blue-colored reproduction of the original was instantaneous but the maximum density developed on drying.

The accompanying drawings FIGS. 1, 2, and 3 will serve to further describe the process for making printing matrices from our photographic element and using them to produce spirit copies.

In FIG. 1, our photographic element comprising support 10 over which is coated layer 11 containing polyvinyl acetate and Brilliant Oil Blue BMA dye over which is coated layer 12 consisting of a substantially unhardened gelatin silver chloride emulsion layer that is being exposed to the image in the original record 13 by light from light source 14.

FIG. 2 shows how the exposed photographic element of FIG. 1, which has been developed, is converted into a printing matrix by stripping off the unexposed, undeveloped gelatin areas of layer 12 with receiving layer 15 which was squeegeed in contact with layer 12 and then stripped off.

FIG. 3 shows how a Brilliant Oil Blue BMA dye image has been transferred from the exposed areas of resin dye layer 11 to the receiving sheet 16 by a spirit duplicating process to produce the spirit copy.

The photographic element of our invention is valuable for use in preparing multiple copies of printed documents. It provides a simple and rapid process by which an original document may be copied by contact printing, projection printing or reflex printing and by which this photographic exposure may be converted into a printing matrix for producing multiple spirit copies using commonly available spirit duplicating equipment. Our photographic element makes it possible to eliminate the involved and complicated wet processing that is required by prior art materials available for producing spirit duplicating matrices. Our photographic elements are not only adapted to make the spirit duplicating matrices rapidly and simply but are adapted to be used in lighted office areas on equipment that is generally readily available.

The invention has been described in detail with particular reference to preferred embodiments thereof but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A photographic element designed for preparing a printing matrix for spirit duplicating processes, comprising:
   (I) a support,
   (II) a water-insoluble, alkali-insoluble layer coated over said support, said layer comprising:
      (*a*) a water-insoluble, alkali-insoluble organic resin binder selected from the class consisting of a polyvinyl acetate, zein, an alcohol-soluble nylon plastic, polyvinyl butal, polyvinyl formal, polyethylacrylate, and polymethylmethacrylate, and
      (*b*) a water-insoluble, organic solvent-soluble member selected from the class consisting of 6-(2',4' - dinitro - 6'-N-ethylsulfonamidebenzeneazo) - N-β,γ-dihydroxypropyl-2-methyltetrahydroquinoline, Brilliant Oil Blue BMA, Solvent Blue 16, Grasol Blue R, Celanthrene Sky Blue B, the Carbinol base of Victoria Blue, Michler's hydrol, a lactone of a triphenylmethane dye, a leuco base of a triphenylmethane dye, a lower alkyl ether of a triphenylmethane dye, and xanthene 9, orthobenzoic acid, 3,6-diethylamino-9-p-nitroanilino lactam, and coated over said layer,
   (III) a thin light-sensitive substantially unhardened organic colloid silver halide emulsion layer.

2. A photographic element of claim 1 in which the water-insoluble, organic solvent-soluble member in the water-insoluble, alkali-insoluble layer is alcohol-soluble.

3. A photographic element of claim 1 in which the thin, light-sensitive substantially unhardened organic colloid silver halide emulsion layer is an unhardened gelatino silver halide emulsion and contains 3,4-dihydroxydiphenyl as an incorporated gelatin hardening developing agent.

4. A photographic element of claim 1 in which the water-insoluble, alkali-insoluble layer contains polyvinyl phthalate.

5. A photographic element of claim 1 containing between the water-insoluble, alkali-insoluble layer and the thin light-sensitive substantially unhardened organic colloid silver halide emulsion layer, a thin water-insoluble layer consisting of polyvinyl phthalate.

6. A photographic reproduction process utilizing a photographic element designed for preparing a printing matrix for spirit duplication processes, comprising:
   (I) a support,
   (II) a water-insoluble, alkali-insoluble layer coated over said support, said layer comprising:
      (*a*) a water-insoluble, alkali-insoluble organic resin blender selected from the class consisting of a polyvinyl acetate, zein, an alcohol-soluble nylon plastic, polyvinyl butal, polyvinyl formal, polyethylacrylate, and polymethylmethacrylate, and
      (*b*) a water-insoluble, organic solvent-soluble member selected from the class consisting of 6-(2',4' - dinitro - 6'-N-ethylsulfonamidebenzeneazo) - N - β,γ-dihydroxypropyl-2-methyltetra-

hydroquinoline, Brilliant Oil Blue BMA, Solvent Blue 16, Grasol Blue R, Celanthrene Sky Blue B, the Carbinol base of Victoria Blue, Michler's hydrol, a lactone of a triphenylmethane dye, a leuco base of a triphenylmethane dye, a lower alkyl ether of a triphenylmethane dye, and xanthene 9, orthobenzoic acid, 3,6-diethylamino-9-p-nitroanilino lactam, and coated over said water-insoluble layer,

(III) a thin, light-sensitive substantially unhardened organic colloid silver halide emulsion layer;

said process comprising the steps:

(1) exposing with a light image, the said silver halide emulsion layer of the said element,

(2) developing said light image exposed silver halide emulsion layer with an aqueous alkali organic colloid tanning developer to form an image of silver and hardened organic colloid,

(3) squeegeeing the said developed emulsion layer of said element to a second support to which only the unhardened parts of the said emulsion layer adhere.

(4) separating the said second support with the adhering unhardened emulsion layer leaving a hardened developed emulsion stencil over the said water-insoluble, alkali-insoluble layer of the said element,

(5) drying said element from step 4,

(6) squeegeeing a receiving sheet onto the stencil side of the said element in the presence of an organic solvent that is in contact with said water-insoluble, alkali-insoluble layer and said receiving sheet, provided when the said water-insoluble, organic solvent-soluble member in item II*b* is a dye-forming compound, that another material is also present which with the dye-forming compound produces a dye, and

(7) separating the said receiving sheet with a transferred dye image from the stencil side of said element.

7. A photographic element designed for preparing a printing matrix for spirit duplicating processes comprising a support, a water-insoluble, alkali-insoluble resin layer coated over the support, said layer comprising polyvinyl acetate and Brilliant Oil Blue BMA dye and a thin light-sensitive substantially unhardened gelatin silver halide emulsion layer incorporating 3,4-dihydroxy diphenyl coated over said resin layer.

8. A photographic element designed for preparing a printing matrix for spirit duplicating processes comprising a support, a water-insoluble, alkali-insoluble resin layer coated over the support, said layer comprising polyvinyl acetate, polyvinyl phthalate and Brilliant Oil Blue BMA dye and a thin light-sensitive substantially unhardened gelatin silver halide emulsion layer incorporating 3,4-dihydroxy diphenyl coated over said resin layer.

9. A photographic element designed for preparing a printing matrix for spirit duplicating processes comprising a support, a water-insoluble, alkali-insoluble resin layer coated over the support, said layer comprising polyvinyl acetate and Brilliant Oil Blue BMA dye and a thin light-sensitive substantially unhardened gelatin silver halide emulsion layer incorporating 3,4-dihydroxy diphenyl coated over said resin layer.

10. A photographic element designed for preparing a printing matrix for spirit duplicating processes comprising a support, a water-insoluble, alkali-insoluble resin layer coated over the support, said layer comprising polyvinyl acetate, polyvinylphthalate and the carbinol base of Victoria Blue and a thin light-sensitive substantially unhardened gelatin silver halide emulsion layer incorporating 3,4-dihydroxy diphenyl coated over said resin layer.

11. A photographic element designed for preparing a printing matrix for spirit duplicating processes comprising a support, a water-insoluble, alkali-insoluble resin layer coated over the support, said layer comprising polyvinyl acetate and the carbinol base of Victoria Blue, a thin subbing layer of polyvinyl phthalate coated over said resin layer and a thin light-sensitive substantially unhardened gelatin silver halide emulsion layer incorporating 3,4-dihydroxy diphenyl coated over said resin layer.

12. A photographic element designed for preparing a printing matrix for spirit duplicating processes comprising a support, a water-insoluble, alkali-insoluble resin layer coated over the support, said layer comprising polyvinyl acetate and bis(para-dimethylamino-phenyl)methane and a thin light-sensitive substantially unhardened gelatin silver halide emulsion layer incorporating 3,4-dihydroxy diphenyl coated over said resin layer.

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