Oct. 14, 1958 F. A. HAMM 2,856,284

PHOTOMAGNETIC PRINTING PROCESS

Filed Jan. 7, 1955

Fig. 1



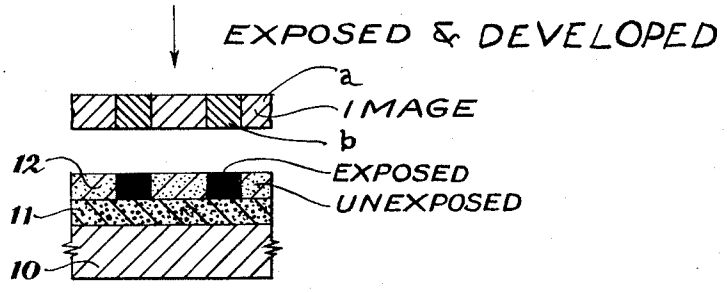
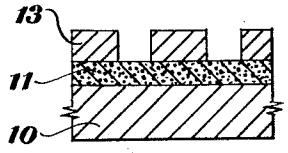


Fig. 2



Fig. 3



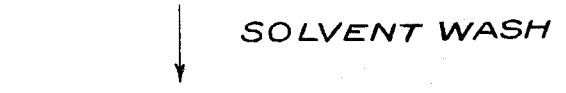


Fig. 4



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2,856,284

PHOTOMAGNETIC PRINTING PROCESS

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Application January 7, 1955, Serial No. 480,488

6 Claims. (Cl. 96—35)

This invention relates to the preparation of photographic resist materials and to methods of forming images therefrom.

The use of bichromated glue for preparing resists in the photoengraving industry is well known, and such materials have been used for many years. It is also well known that a pigment can be incorporated in the sensitized glue and a pigmented image thereby obtained. In the preparation of an image in this way, the coating of pigmented colloid must necessarily be quite thin so that exposure to light will harden the colloid throughout its entire thickness and the hardened portions will then adhere to the support upon washing with water. The unexposed portions will dissolve away and this process will yield a positive from a negative.

The process of my invention yields a negative image from a negative, that is, a reversal image is obtained. The material of my invention can be applied easily to most supports and can be processed in a simple manner. Its speed range is ideal for practical purposes, and it can be handled and coated in safe light. Other advantages of my process and material will be evident from the following description of my invention.

The present invention makes use of the superior light-sensitive properties of photographic gelatino-silver-halide emulsions and polymeric materials which have properties superior to the mentioned bichromated materials.

Accordingly, one object of my invention is to provide superior light-sensitive materials for making photographic resists which can be used as printing plates. Another object is to provide photographic resist materials which can be used for long periods of time without degradation of the printing surface. Still another object of my invention is to provide photographic resists which give a number of copies from the same printing surface, each of the copies being characterized by superior resolution and sharpness. Other objects will become apparent from a consideration of the following description and examples.

In practicing my invention a ferromagnetic iron oxide, such as gamma ferric oxide (Fe_2O_3) or ferroso-ferric oxide (Fe_3O_4), is uniformly dispersed in an aqueous gelatin solution or a solution in an organic solvent of a polymeric material and the mixture is coated uniformly on a surface. A photographic gelatino-silver-halide emulsion is then coated over this layer containing the ferro-magnetic iron oxide. The photographic emulsion is then exposed in the usual manner and processed to a relief image. The relief image is then magnetized or sensed, developed with finely divided iron (ferromagnetic) and copies obtained by contact transfer printing, for example. Although a relief or resist image is formed in the silver-halide emulsion layer, it is the magnetic property of the iron oxides which is the important aspect in the production of copies from the master. The quality of the master is not impaired by light, heat, moisture, or pressure. The magnetism is not readily inadvertently erased.

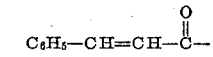
While neither the gelatin undercoat nor the polymeric layer are materially affected by the exposure, it has been

found that better resolution can be obtained between the exposed and unexposed areas with the polymeric materials as hereinafter defined.

Among the polymeric materials having this property are those obtained from monoethylenically-unsaturated compounds. Among the most useful of these synthetic polymers are those which contain a cinnamoyl group either in the form of an ester, or some other functional grouping, such as a chalcone. Such synthetic resins have been previously described in a number of domestic and foreign patents, for example:

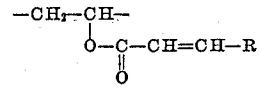
Allen et al., U. S. 2,566,302, issued September 4, 1951;
Minsk et al., U. S. 2,610,120, issued September 9, 1952;
Minsk et al., U. S. 2,670,285, issued February 23, 1954;
Minsk et al., U. S. 2,670,286, issued February 23, 1954;
Minsk et al., U. S. 2,670,287, issued February 23, 1954;
Minsk et al., U. S. 2,690,966, issued October 5, 1954;
Smith et al., U. S. 2,691,584, issued October 12, 1954; and
Yates, Ger. 807,894, ausgegeben July 9, 1951.

The polymeric materials which have been found to be most useful in practicing my invention comprise those resins which contain the cinnamoyl group, which can be represented by the following formula:

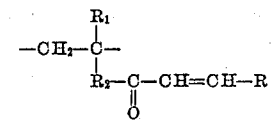


Particularly useful polymeric materials or resins comprise those obtained by esterifying polymers containing reactive hydroxyl groups with a cinnamoyl halide, such as cinnamoyl chloride. An example of such a resin is one obtained by esterifying polyvinyl alcohol with cinnamoyl chloride in accordance with the process described in the copending application of L. M. Minsk, U. S. Serial No. 207,052, filed January 20, 1951 (now U. S. Patent 2,725,-372, issued November 29, 1955). Other resins which can be used in my invention are described in the copending applications of L. M. Minsk and W. P. Van Deusen, Serial Nos. 462,124 and 462,125, both filed October 13, 1954. Still another resin which can be employed in my invention is described in the copending application of L. M. Minsk, W. P. Van Deusen and E. M. Robertson, U. S. Serial No. 308,283, filed September 6, 1952 (now U. S. Patent 2,751,296, issued June 19, 1956).

The resins described in the above prior art include polymers having recurring structural units having the formula:



wherein R represents a monocyclic aryl group of the benzene series, such as phenyl, m-nitrophenyl, o-chlorophenyl, etc. groups. Other polymers having recurring structural units having the formula:



wherein R has the values given above, R_1 is a hydrogen atom or a lower alkyl group (e. g., methyl, ethyl, propyl, butyl, etc.), and R_2 is a monocyclic arylene group (e. g., phenylene, methylphenylene, etc.) can be employed (U. S. 2,566,302).

In the accompanying drawing, the various figures show in enlarged cross-sectional view the structure of a representative sensitive element of my invention at various stages in the process of producing printing plates having selected areas covered by resist images.

Slightly different processing conditions are necessary

when a photographic element containing the gelatin undercoat and when a photographic element containing the polymeric undercoat are employed. While each of these undercoating layers contains the ferromagnetic iron oxide, an additional processing step is used in the treatment of the photographic element containing the polymeric undercoat. This a result of the reversal process wherein an etch-bleach bath is employed and is described in detail below.

The relief image thus formed is magnetized or sensed using a recording head so that the relief image is now also a magnetic image. This magnetization can be accomplished in known manner, at various A. C. frequencies and speeds of motion of the magnetic matrix. However, the condition of 200 cycles/second, 8 volts, 30 milliamperes, and a speed of about 2–3 inches per second has proved to be very satisfactory. Contact recording (sensing) is desirable. Other methods of magnetizing the relief record can be employed equally well. Such methods of magnetization are matters of common knowledge.

The magnetic latent image thus obtained is then "developed" to a magnetic visual image using finely divided iron (ferromagnetic). A suspension of this free iron (sometimes referred to as a magnetic ink) in carbon tetrachloride or other vehicle can be flooded over the relief image, or the master image can be immersed in the suspension. In both cases, the magnetic lines of force in the magnetized relief image attract the soft iron (ferromagnetic) particles and hold them firmly in contact with the relief image. Regions in the master which are void of the ferromagnetic iron oxide matrix are free of developing iron. Also, the amount of iron attracted to regions in the relief image will be somewhat dependent on the thickness of the image at any given region.

Copies can best be made by contact transfer. One method comprises using a moist, pressure-sensitive adhesive transfer material, such as dye transfer paper. The dye transfer paper is slightly moistened on the gelatin side and this side is placed in contact with the developed master. Gentle pressure results in transfer of the iron from the surface of the master matrix to the gelatin surface of the dye transfer paper. There is thus obtained an image on the transfer paper which consists of free iron embedded in gelatin. The record thus obtained can be preserved by spraying with a solution of an organic solvent containing dissolved resin, such as polymethyl methacrylate, polymethyl acrylate, etc.

Alternatively, transfer of the image from the resist material to a desired surface can be accomplished by placing the master image in contact with dry dye transfer paper with the gelatin coating thereof in contact with the developed master. When dry heat is applied to the rear surface of the dye transfer paper, transfer of the iron from the master surface occurs. A heat-sealing iron can also be used.

Copies can also be obtained from the relief image before it has been "developed" with the metallic iron by placing a thin sheet of paper, such as onion skin paper, in close contact with the magnetically sensed but "undeveloped" master. The magnetic reluctance of this thin copy paper is sufficiently low so that some magnetic lines of force pass through the paper and attract the finely divided free iron which has been placed on the rear surface of the thin paper. Thus, copies are made by flooding the air side of the sheet of paper, in contact with the relief image, with a suspension of the free iron. An unlimited number of copies can be made in this way, and the images thus obtained can be made permanent by coating with a resinous solution as described above.

In general, transfer by means of paper having a gelatin coating or some other colloid coating thereon is preferred to the method using thin paper as described above, since the former method generally gives improved resolution. It is to be noted that in the method of my invention magnetic sensing is required only once. When the copy image becomes too weak, the master can be developed with free iron as before. Six acceptable copies can be prepared using the dye transfer paper techniques described above.

The following example will serve to illustrate further the manner of practicing my invention.

EXAMPLE

A lacquer containing 7.5 percent of polyvinyl cinnamate (U. S. 2,690,966) was ball-milled with gamma ferric oxide for a period of about 48 hours. The resulting mixture contained about 20 percent by weight of gamma ferric oxide. The resulting mixture which was in the form of a viscous solution or suspension was placed on a magnesium plate and whirled at a speed of approximately 50–80 R. P. M., or if desired, by machine-coating methods, and the coating dried at room temperature or elevated temperature in subdued light. After drying the coating was about 15 microns thick. A photographic gelatino-silver-halide emulsion was then coated over the polyvinyl cinnamate layer. A photographic negative was then positioned in contact with the photographic emulsion and exposure was made in a reciprocity sensitometer with a light flux of 1300 candle power at 2 meters. The photographic silver halide emulsion layer was then developed in Kodak's Developer D–19 for four minutes and the developed emulsion was fixed in a 30 percent sodium thiosulfate solution in the usual manner. After washing, the exposed emulsion was allowed to dry in the usual manner.

The developed and fixed emulsion was then immersed about 45 seconds in an etch-bleach bath of the following composition:

Part A

Cupric nitrate	grams	200
Potassium bromide	do	10
Glacial acetic acid	cc	160

Water to make 1 liter.

Part B

3% hydrogen peroxide solution. Equal parts by volume of A and B above were mixed immediately before use.

After the silver image was completely bleached by the above solution, the outer surface of the element was rinsed with water and the resulting relief image was allowed to dry.

The relief image was then swabbed with cotton soaked in chloroform so that the intermediate polyvinyl cinnamate layer immediately beneath the exposed areas of the photographic silver halide emulsion layer were removed. This treatment removed the polyvinyl cinnamate-gamma ferric oxide layer down to the film base but only at regions where silver had been present. The resist image which had thus been formed was allowed to dry and was sensed magnetically by passing the relief image past a magnetic recording head which had been positioned in the chuck of a milling machine. The table speed was 2.5 inches per second and the length of the air gap in the recording head was 196 mils. The gap width was about 0.75 mil. The displacement normal to the motion of the milling machine was indexed to 150 mils. so that an overlap of 46 mils. occurred during each track length. In order to avoid white separation lines in the printed copies, it was found that the length of the magnetic recording head should be made approximately equal to the width of the area to be magnetized. Magnetic erasure is thus avoided.

The resist image which had thus been magnetically sensed was then treated with powdered iron (ferromagnetic) as described above. Carbonyl Iron, type G, sold by the General Aniline and Film Corp. was found to be useful as the "developing" iron. It was found to be about 98 percent pure and to have a weight-average diameter of about 8 microns. It was spherical in form. The developed image was then placed in contact with moistened dye transfer paper and an image of excellent resolution was obtained.

In a manner similar to that described in the above example, gamma ferric oxide was dispersed in an aqueous gelatin solution, and the resulting dispersion coated on a photographic support, such as cellulose acetate. This gelatin layer was then overcoated with a photographic gelatino-silver-halide emulsion layer and the resulting photographic element exposed and developed in exactly the manner described above. After development, the exposed emulsion was fixed and treated with the etch-bleach bath as described above. However, no subsequent treatment with chloroform was required since the etch-bleach bath also removed gelatin in the intermediate layer down to the film base, but only at regions where silver had been present. The resolution of the prints obtained in the gelatin system was not equal to that of the prints obtained when polyvinyl cinnamate was used as the intermediate layer.

Where the photographic element of my invention is used to record a subject external of a camera and the element used to make an original record, copies made from the master illustrated in the accompanying drawing will have correct orientation. Where the original subject is a photographic negative or a paper document and a contact exposure is made on the master sheet, the original must be orientated to produce a left-right reversal on the master sheet. The copies will then have the correct orientation.

Photographic silver halide emulsions which can be employed in my invention comprise the ordinarily employed gelatino-silver-chloride, gelatino-silver-bromide, gelatino-silver-chlorobromide, gelatino-silver-bromiodide, gelatino-silver-chlorobromiodide, etc. emulsions.

The polymeric resins which have been obtained by esterifying a polymer containing reactive hydroxyl groups with a cinnamoyl halide have been found to be particularly useful in my invention. These polymeric materials generally have at least 60 percent of the free hydroxyl groups esterified. Such polymeric materials can advantageously contain from 60–99.4 mol. percent of cinnamate ester groups, the remaining units being alcohol units (e. g., vinyl alcohol units).

Kodak Developer D–19 has the following composition:

Water, about 125° F. (50° C.)	cc	500
Kodak Elon developing agent	grams	2.0
Kodak sodium sulfite, desiccated	do	90.0
Kodak hydroquinone	do	8.0
Kodak sodium carbonate, monohydrated	do	52.5
Kodak potassium bromide	do	5.0

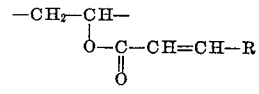
Cold water to make 1.0 liter.

My invention can be further illustrated by reference to the accompanying drawing. Figure 1 shows a support **10** of any suitable material, such as cellulose acetate, polyvinyl acetal, etc., coated with a layer **11** containing a synthetic resin as defined above or gelatin and a ferromagnetic iron oxide, such as gamma ferric oxide. Coated over layer **11** is a photographic gelatino-silver-halide emulsion layer **12**. In Figure 2, the light-sensitive material shown in Figure 1 has been exposed to light under an image having transparent portions *b* and opaque portions *a*, and the light-sensitive material developed in the usual manner. In Figure 3, the developed image obtained from the element shown in Figure 2 has been treated with an etch-bleach bath of the type described above so that the silver image is bleached and etched down to the surface **11**, leaving raised portions **13**. In Figure 4, the element shown in Figure 3 has been treated with a solvent, such as benzene, to remove the exposed portions of layer **11**. This treatment leaves raised portions **13** and **14** which correspond to unexposed portions of the element shown in Figure 2. In the drawing, the process illustrates the use of a colloid in layer **11** which is a synthetic resin. When the colloid used is gelatin, there is no need for the solvent wash illustrated in Figure 4, since the etch-bleach treatment is sufficient to remove not only those portions of layer **12** which have metallic silver therein, but also the area in layer **11** immediately under these deposits of metallic silver. There is thus obtained in the single step a structure which corresponds to that shown in Figure 4.

It will be noted that while the colloid used in the intermediate layer (layer **11** in the drawings) can be a light-sensitive resin, the light-sensitive properties of the resin are not employed, since the silver halide emulsion layer is considerably more sensitive than this intermediate layer. In "developing" the magnetic image with ferromagnetic iron, those solvents which have an adverse effect on the colloid present in the layer containing the ferromagnetic iron oxide should not be used, i. e., the ferromagnetic iron can be dispersed in a solvent or vehicle which does not have any substantial dissolving power for the colloid present in this intermediate layer.

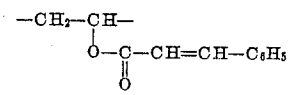
What I claim as my invention and desire secured by Letters Patent of the United States is:

1. A photographic element comprising a support having thereon a layer comprising an ester of polyvinyl alcohol containing at least 60 mol. percent of recurring structural units having the following formula:



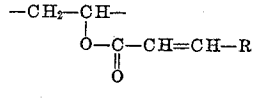
wherein R represents a monocyclic aryl group of the benzene series, and gamma ferric oxide, and superposed on said layer a photographic gelatino-silver-halide emulsion layer.

2. A photographic element comprising a support having a layer comprising a partially esterified, cinnamic acid ester of polyvinyl alcohol consisting of from 60 to 99.4 mol. percent of recurring structural units having the formula:



the remaining recurring units being vinyl alcohol structural units, and gamma ferric oxide, and superposed on said layer a photographic gelatino-silver-halide emulsion layer.

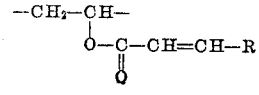
3. A photomagnetic printing process wherein a photographic element comprising a support having thereon a layer comprising an ester of polyvinyl alcohol containing at least 60 mol. percent of recurring structural units having the formula:



wherein R represents a monocyclic aryl group of the benzene series and ferromagnetic iron oxide, and superposed on said layer a photographic silver halide emulsion layer is (1) exposed to an image, (2) the thus exposed photographic element is developed to a relief image, (3) the relief image is sensed magnetically, (4) the magnetized relief image is developed with ferromagnetic iron in finely divided form, and (5) the finely divided ferromagnetic iron is transferred to a receiving sheet having coated thereon a gelatin layer.

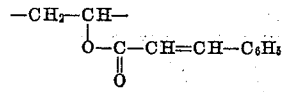
4. A photomagnetic printing process as defined in claim 3 wherein the ferromagnetic iron oxide is gamma ferric oxide.

5. A photomagnetic printing process as defined in claim 4 wherein the ester of polyvinyl alcohol consists of from 60 to 99.4 mol. percent of recurring structural units having the formula:



wherein R represents a member of the class consisting of phenyl, m-nitrophenyl and o-chlorophenyl groups, the remaining recurring units being vinyl alcohol structural units.

6. A photomagnetic printing process as defined in claim 5 wherein the partially esterified, cinnamic acid ester of polyvinyl alcohol consists of from 60 to 99.4 mol. percent of recurring structural units having the formula:



the remaining recurring units being vinyl alcohol structural units.

References Cited in the file of this patent

UNITED STATES PATENTS

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2,635,534	Huebner	Apr. 21, 1953
2,690,966	Minsk et al.	Oct. 5, 1954

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