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COPY-PAPER

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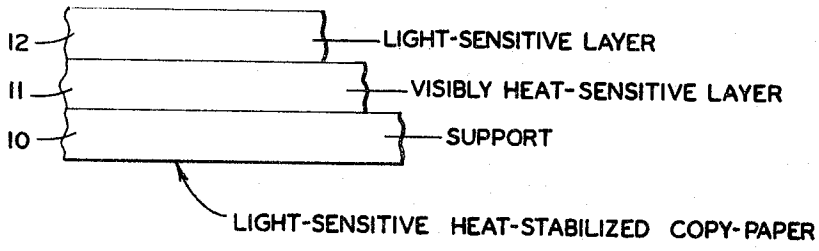

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COPY-PAPER

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This invention relates to the formation of permanent visible reproductions of light-images, and has particular reference to sensitive sheet material or copy-paper adapted thereto.

In one aspect, the present invention makes possible the formation of permanent stable reproductions of light-images while avoiding any necessity for chemical stabilization or fixing, or other treatment with aqueous solutions, vapors, or other external chemical agencies. The invention also makes possible the intensificaton of indistinctly visible reproductions of light-images obtained by more conventional methods and which may involve initial chemical or other image-development. Thus, the invention permits the effective utilization of light-sensitive mechanisms which of themselves do not directly provide visible copies, or copies of adequate intensity or of an effective degree of stability. The invention also provides means for directly producing visible reproductions of low intensity light-images on heat-sensitive copy-papers, and hence makes possible such procedures as the making of full-scale or enlarged reproductions of original graphic subject-matter from reduced photographic negative copies, or microfilm copies, of such subject-matter. The invention furthermore permits the copying of all visible subject-matter, including the making of portraits or the like as well as the copying of colored ink drawings, signatures, paintings, etc., on heat-sensitive copy-paper.

The invention will now be described in terms of illustrative but non-limitative specific embodiments.

Example 1

A transparent, visibly heat-sensitive copy-paper is first prepared by coating a transparent polyester film backing ("Mylar" film) with a mixture of ferric stearate and t-butyl catechol in a solution of ethyl cellulose binder, and removing the solvent by evaporation at room temperature. The resulting sheet has a faint buff color, changing rapidly to blue-black when heated, e.g. to about 100° C. It is suitable for making reproductions of typewritten correspondence or other graphic originals by methods disclosed in Miller et al. U.S. Patents Nos. 2,663,654–7, which also describes various additional typical heat-sensitive copy-sheet structures and formulations having utility in the present invention.

Over the heat-sensitive layer is next applied a thin coating of a solution of equal parts by weight of silver nitrate and polyvinylpyrrolidine binder in a solvent mixture of two parts of water and nine parts of methyl alcohol. The solution is preferably prepared, coated and dried under dark-room conditions or at least under subdued light.

The resulting sheet is contact printed by exposure of the coated surface for six minutes to ultraviolet radiation from a "BH–6" lamp at a distance of six inches and through a photographic negative held in contact with the sensitized surface. Close inspection of the thus exposed sheet shows a very faint brownish image corresponding to the transparent areas of the photographic negative.

The sheet is then briefly irradiated with high intensity light rich in infra-red rays. Apparatus for carrying out this step of the process is described in the Miller et al. patents hereinbefore referred to; and see also Miller U.S. Patents Nos. 2,740,895–6. A dense blue-black image on a buff background is formed, corresponding to the initial

faint brownish image, and fully visible through the transparent film backing. The copy as thus viewed is stable on long aging even though the back surface gradually darkens to a uniform gray-brown appearance or is otherwise altered.

Example 2

A heat-sensitive copy-sheet consisting of a thin heat-transparentizable opaque water-resistant coating of hydrogenated fatty oil wax particles and cellulosic binder on a thin transparent paper support previously coated with a thin layer of titanium dioxide pigment, an infra-red-transmitting blue lake pigment, and polymeric binder, all as more fully described in Clark et al. U.S. Patent No. 2,710,263, is supplied on the uncoated surface of the support with a very thin layer of silver halide-gelatin photographic emulsion, applied and dried under darkroom conditions. The sheet is briefly exposed to an enlarged light-image projected from a microfilm transparency, producing a latent image, and a corresponding visible image is developed by treatment of the silver halide layer with a conventional photographic developer solution. A faint black image is obtained, the darker areas corresponding to the light-struck areas. The dried sheet is then exposed to brief intense irradiation as in Example 1, resulting in the selective transparentizing of those portions of the waxy coating overlying the developed visible image. A high contrast reproduction of the original light image is thus obtained, having deep blue image areas against a white background as viewed from the wax-coated side. Further exposure to light of the unstabilized silver halide layer causes a general darkening of said layer, but without impairing the legibility of the image as viewed from the heat-sensitive side. This darkening may be avoided by fixing and washing if desired.

The procedure just described permits the taking of photographs for the reproduction of printed or other graphic originals with minimum exposure to light, but requires the additional step of chemical development of the latent image. Similar sheets may be used in the procedure described in connection with Example 1, but with increased exposure to directly provide a temporarily useful intermediate reproduction of the type obtained with photographic "print-out" papers.

Example 3

A visibly heat-sensitive copy-paper of the type described in connection with Example 1 is coated with a thin layer of an iron ammonium citrate-potasssium ferricyanide solution as employed in making blueprint paper. Mixing, coating, and drying are carried out under darkroom conditions. Exposure of the dried treated surface to a light-image causes darkening of the surface in the light-struck areas. The resulting print may if desired be stabilized by washing with water or preferably with a dilute solution of potassium dichromate, and dried, and then irradiated with infra-red to develop a corresponding permanent image in the visibly heat-sensitive layer. Alternatively, the intermediate print may be irradiated without being stabilized, in which case the entire light-sensitive layer eventually darkens while the heat-sensitive layer retains the stabilized image.

Example 4

The light-sensitive blueprinting composition of Example 3 is similarly applied to a transparent supporting web which carries on the reverse surface a heat-transparentizable opaque coating of a mixture of fusible wax particles and non-fusing binder as described in connection with Example 2. The intermediate image produced on exposure of the light-sensitive layer to a light-image is reproduced in the heat-sensitive layer, by exposure to radiation high in

infra-red, in the form of transparent image areas in a white opaque background. The blue color of the intermediate image is visible through these transparent areas, producing a blue-and-white stable print.

Example 5

A transparent supporting web is provided on one major surface with an infra-red-absorptive visibly heat-sensitive layer prepared by incorporating titanium dioxide pigment in a ferric stearate-gallic acid-ethyl cellulose heat-sensitive composition. A white or light buff opaque coating is thus obtained which is convertible to a dense blue-black by contact with a heated article or by momentary exposure to appropriate high intensity illumination. The supporting web is provided on the opposing major surface with a slightly acidic light-sensitive layer containing a diazonium salt and a coupling agent, as used in the preparation of diazotype printing plates and the like, producing a faint yellow color.

The diazo-coated surface is first exposed to a light-image by exposure through a photographic negative transparency, and is treated with ammonia to develop an intense colored image on a white or slightly yellowish background. The resulting print is also a negative; i.e. the sensitive layer develops the intense color only in those areas not exposed to light.

The sheet is then exposed from the same surface to high intensity flash irradiation such as is produced by a 500 watt-second discharge between terminal electrodes in a 10-inch quartz tube filled with xenon under reduced pressure, the flash having a duration of about 1000 microseconds with peak intensity at about 100 microseconds. Darkening of the heat-sensitive layer occurs in areas corresponding to the background areas of the previous negative print, thus producing a positive print having blue-black image areas on a white or light buff background.

Any diazotype light-sensitive layer may be used which produces image areas capable of absorbing the radiations applied. In the specific example, the image areas are converted to an intense yellow. The background areas remain a faint yellow or are bleached to an off-white.

The intensity of the flash irradiation is sufficient to cause blistering or other degradation of a photographic transparency. The procedure described permits the production of a positive print from a negative original on a heat-sensitive copy-paper without danger of damage to the original through overheating during exposure.

Example 6

Thin transparent paper (map overlay tracing paper) is first coated with a smooth uniform layer of a fluid dispersion of 125 parts by weight of ferric stearate and 35 parts of alcohol-insoluble precipitate of hexamethylenetetramine and pyrogallic acid in a solution of 30 parts of polyvinyl butyral in sufficient alcohol to provide a coatable mixture. The coating is dried at room temperature, leaving a residual dried layer of approximately 0.7 lb. per sq. yd. A second coating of a suspension of about 12 parts of zinc oxide pigment in a solution of about 7½ parts of ethyl cellulose in acetone is next applied and dried, producing a thin visibly opaque coating. The sheet is stored for several hours under dark conditions and is then coated over the zinc oxide layer with a thin layer of silver nitrate solution, e.g. by lightly rubbing with a cotton swab moistened with the solution, the operation being performed under subdued light. After drying, the coated sheet is first exposed to a light-image, causing darkening of the light-struck silver-coated areas. It is then momentarily intensely irradiated with infra-red on the imaged surface, producing a corresponding but much more distinct image in the heat-sensitive layer which is visible through the transparent paper support layer. Further exposure to light causes uniform darkening of the silvered surface without affecting the visible image in the heat-sensitive layer.

Example 7

In this example the zinc oxide-ethyl cellulose layer of Example 6 is applied directly to the thin paper backing. After a suitable aging period under dark conditions, silver nitrate solution is swabbed over the coating and the sheet is dried, again in absence of light. The resulting sheet darkens on exposure to light. Prior to such exposure it is provided on the uncoated surface with a thin layer of a heat-sensitive composition of equal molar proportions of silver behenate, behenic acid, and protocatechuic acid, together with resinous binder material. The sheet is first exposed on the first-coated side to a light-image, producing a visible but slight darkening at the light-struck areas. It is then briefly exposed on the same surface to high intensity infra-red rediation. The darkened image areas differentially absorb the radiation and the resulting heat-pattern causes a corresponding visible change in the heat-sensitive layer. During irradiation, the heat-sensitive surface is preferably insulated from contact with heat-absorptive surfaces. Viewed from the heat-sensitive surface, the copy is a black-on-white mirror image of the original white-on-black light-image.

Zinc oxide is a preferred example of a particulate light-sensitive electron donor material. Other examples include photochromic complex compounds such as

$$(Co(C_2H_4N_2H_4)_3)_2(S_2O_8)_3$$

and photoluminescent pigment materials such as silver-activated zinc sulfide. Such materials are known to provide free electrons under the action of ultra-violet light or equivalent actinic radiation. Likewise, silver nitrate is a preferred example of electron acceptor material which undergoes a visible change in contact with the thus irradiated zinc oxide; gold chloride and chloroplatinic acid act similarly under the same conditions. The color change occurring in the silver nitrate-zinc oxide layer on exposure to a light-image is sufficient to provide a degree of contrast adequate for many purposes, but the image is not permanent under subsequent illumination. On the other hand, the image obtained in the heat-sensitive layer is stable to light and provides an image of improved contrast.

Example 8

Thin transparent paper is first provided with a heat-sensitive layer as described in connection with Example 1, and is then further coated with a thin continuous layer of four parts of strongly photoconductive zinc oxide in one part of the resinous copolymer of equal parts of styrene and isobutylene. The volatile ketone vehicle is removed and the sheet stored under dark conditions.

For use, the sheet is placed against a grounded flat metal surface with the coated surface uppermost and is electrostatically charged from a conductor adjacent thereto at a potential of about 2,000 volts. The sheet is then exposed to a light-image, permitting dissipation of the electrostatic charge at the light-struck areas. The resulting image pattern is made visible by development with colored electrostatically charged powder. The powder adheres to the charged areas but not to the discharged areas, producing a copy of the original light-image. The copy-sheet is then suitably isolated from heat-conductive surfaces and the imaged area is briefly intensely irradiated. The radiation is preferentially absorbed at the powdered areas and the resulting heat-pattern produces a corresponding visible image pattern in the heat-sensitive layer which is seen as a mirror image through the transparent paper carrier web.

Where a fusible color powder is used in developing the electrostatic image, or a fusible binder is used in the photosensitive layer, the powder is found to be permanently bonded to the surface of the sheet. Such action is not required, however, the powder may as effectively be completely removed, as by brushing, once the image has been made permanent in the heat-sensitive layer.

Various other light-sensitive materials may be sub-

stituted for the exemplary materials hereinbefore suggested. They may, for example, be self-developing, as with the blueprint paper composition of Example 3 or the silver nitrate of Example 1 or the zinc oxide-silver nitrate combinations of Example 6 or 7; or they may require chemical development of a latent image as with the silver halide layer of Example 2 or the diazotype coating of Example 5; or physical development may be indicated, as in the case of Example 8. Various other heat-sensitive layers may likewise replace the chemically reactive color-producing layers of Examples 1, 3, or 5–8, or the physically transparentizable layers of Examples 2 and 4. Furthermore the copy-forming heat-pattern may be produced in the light-image areas, or as Example 5, in the heat-sensitive layer itself. Various other combinations and modifications will occur on consideration of the disclosures hereof. In all cases, there is formed at the light-sensitive layer a pattern of image and background areas which differ in visible appearance and in ability to absorb light, thus permitting the subsequent development of a corresponding heat-pattern by momentary intense irradiation, and resulting in the production of a corresponding visible print pattern in the heat-sensitive layer. Although the radiation may be primarily absorbed and the heating effect produced either in the darkened areas of the light-sensitive layer or in the unmasked areas of the heat-sensitive layer, it will be seen that in all cases the visibly different image and background areas of the converted light-sensitive layer will be significantly dissimilar in their ability to absorb the radiation employed in producing the heat-pattern with which the final print is developed.

A typical light-and-heat-sensitive copy-sheet as hereinabove described is illustrated in the accompanying drawing, showing a copy-sheet comprising a supporting web **10**, a visibly heat-sensitive coating **11**, and a light-sensitive coating **12**. Various combinations of these components are contemplated; thus the two sensitive coatings may be on opposite sides of an extremely thin support web, as indicated in Examples 2 and 7, or preferably on the same side as in the remaining examples, and their coating outermost. Where the heat-sensitive coating is between the light-sensitive coating and the support, the latter will normally be transparent; this structure is generally preferred, since the printed heat-sensitive coating is thus protected by the transparent support, and the latter, particularly where a thin paper is employed, provides an effective marking surface which will accept subsequent pencil or other markings. The support web may be omitted, its function then being provided by the film-forming binder components of either or both of the sensitive layers. On the other hand, additional layers, e.g. transparent protective surface coatings, may be added if desired. In some instances such layers assist in providing intense print-images in the heat sensitive layer by helping to prevent loss of heat from the composite sheet during irradiation of the intermediate image. Alternatively, separate temporary heat barriers may be provided for this purpose where desired.

The image-intensifying action of the copy-sheets of this invention makes possible the effective use of ordinarily less desirable light-sensitive compositions. Thus, light-sensitive coatings which by themselves yield images of low visible intensity, or which are unstable when exposed to light or other conditions of use, or which require prolonged or complicated treatment to stabilize, may be employed in these constructions with formation of fully effective permanent reproductions of light-images.

I claim:

1. A duplicating sheet comprising a support, a light-insensitive visibly heat-sensitive thermographic coating, and a visibly light-sensitive coating including a water-soluble salt, said light-sensitive coating being capable of forming visibly distinct infra-red-absorptive images in the light-struck areas, said thermographic coating being capable of undergoing permanent visible change only in said light-struck areas by the heating effect obtained when the sheet so imaged is briefly exposed to high intensity infra-red.

2. The duplicating sheet of claim **1** wherein the water-soluble salt is a silver salt.

3. The duplicating sheet of claim **1** wherein the water-soluble salt is a ferric salt.

4. The duplicating sheet of claim **2** wherein the light-sensitive coating includes zinc oxide.

5. The duplicating sheet of claim **2** wherein the light-sensitive coating includes polyvinyl pyrrolidone.

6. A unitary copy-sheet adapted for making a permanent thermographic reproduction of a light-image, comprising a thin paper-like support, a heat-sensitive coating capable of remaining substantially unchanged in appearance on prolonged light-exposure and of undergoing permanent visible change on being briefly heated to a conversion temperature within the approximate range of 60 to 150° C., and a light-sensitive coating consisting essentially of zinc oxide and water-soluble silver salt.

7. A unitary copy-sheet adapted for making a permanent record of a light-image directed thereon and comprising a thin flexible support web having distributed thereover a light-resistant visibly heat-sensitive first mixture of reactant components which mixture on being briefly heated to a conversion temperature within the approximate range of 60 to 150° C. undergoes an irreversible chemical reaction with formation of a visibly distinct reaction product and, coextensive therewith, a light-sensitive second mixture of reactant components different from said first mixture and including a water-soluble ferric salt and a ferricyanide, and which on exposure to light undergoes an irreversible chemical reaction with formation of a visibly distinct infra-red-absorptive reaction product.

8. A unitary copy-sheet adapted for making a permanent visible record of a light image and comprising a transparent support member and, distributed over one major surface of said support, an obscuring transparentizable layer of particulate material fusible to permit permanent visibility of said support through said layer on being briefly heated to fusion temperature, and, coextensively distributed over the opposite surface of said support, a light-sensitive mixture of reactant components including a water-soluble ferric salt and a ferricyanide and which on exposure to light undergoes an irreversible chemical reaction with formation of a visibly distinct infra-red absorptive product.

9. A duplicating sheet for making a permanent thermographic reproduction of a light-image by a process involving exposing the sheet to said light-image so as to form an infra-red-absorptive image in the light-struck areas, and briefly exposing to intense infra-red radiation to cause heating at said image areas and formation of an intensified permanent image, said sheet comprising a support, a heat-sensitive coating capable of remaining substantially unchanged in appearance on prolonged light exposure and of undergoing permanent visible change on being briefly heated, and over said heat-sensitive coating a light-sensitive coating comprising a water-soluble silver salt and a reactant therefor, said light-sensitive coating being of such character that, upon exposure to a light image and without photographic development, it will produce an infrared absorptive deposit in the light-struck areas.

10. A duplicating sheet as described in claim **9** in which the water-soluble silver salt consists essentially of silver nitrate.

11. The method of making a permanent stable reproduction of a graphic original on a unitary copy-sheet having a light-resistant visibly heat-sensitive layer and a coextensive light-sensitive layer, said light-sensitive layer being increased in radiation-absorbency on exposure to light and including a water-soluble salt, said method comprising exposing said light-sensitive layer to a light-image

of said original to produce a visibly distinct differentially radiation-absorptive pattern having increased radiation absorbency at the light-struck areas, and briefly irradiating said pattern with high intensity radiation which is preferentially absorbable in said areas of increased radiation absorbency, whereby to cause localized heating and a visible change in the heat-sensitive layer at the location of the said light-struck areas.

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