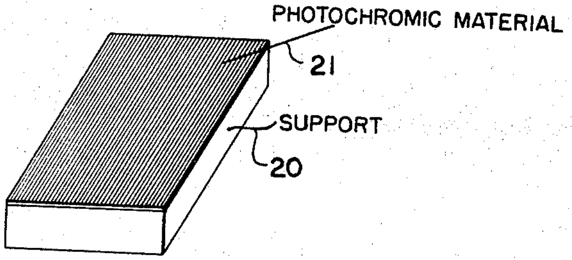
Sept. 12, 1967 P. L. FORIS **3,341,330**

METHOD OF FORMING THERMALLY STABLE PHOTOCHROMIC IMAGES AND PRODUCT

Filed Jan. 16, 1964

4 Sheets-Sheet 1

FIG. 1



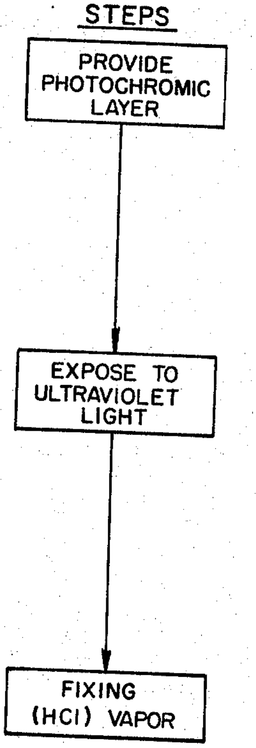


FIG. 2

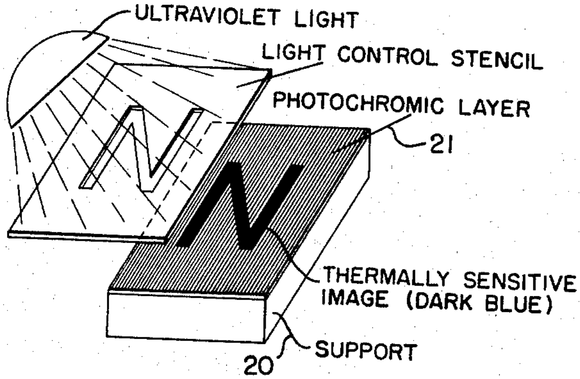


FIG. 3

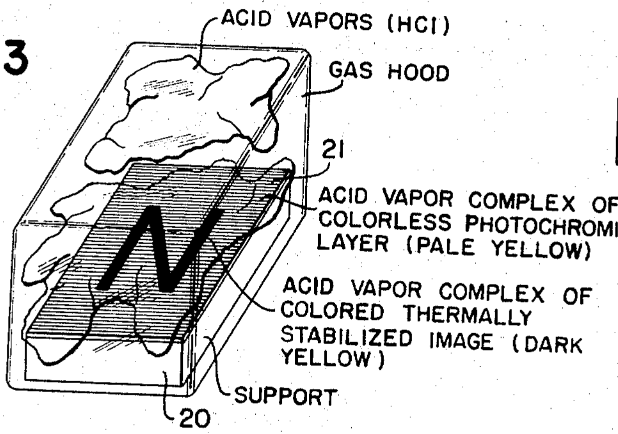


FIG. 4

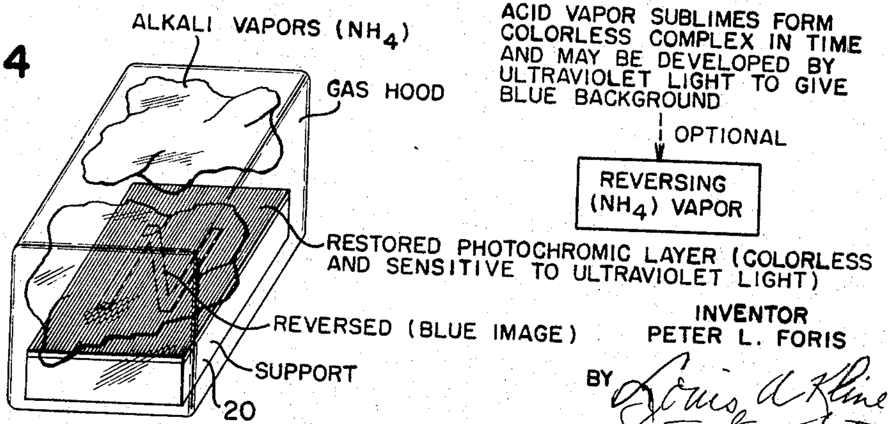


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FIG. 5

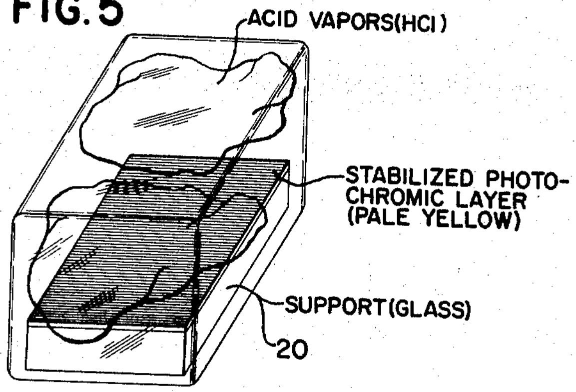


FIG. 6

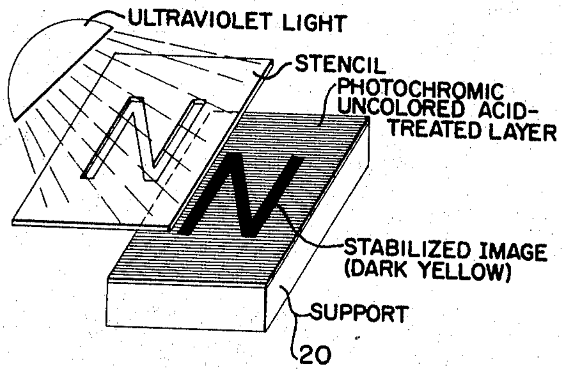
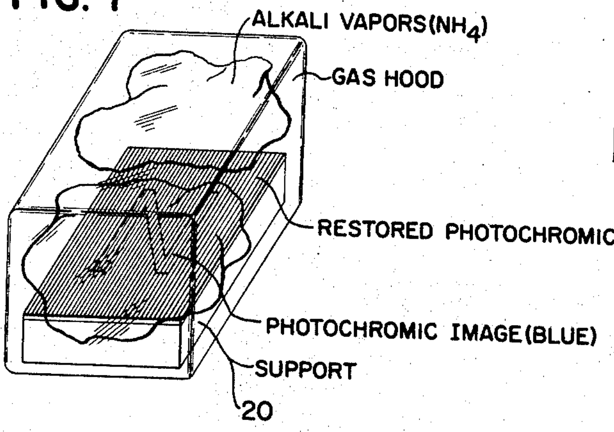


FIG. 7



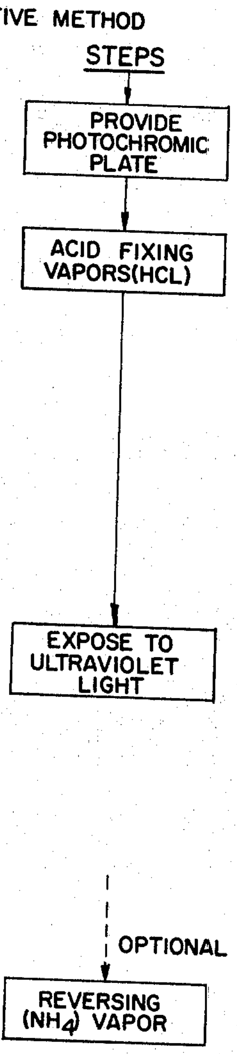


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FIG. 8

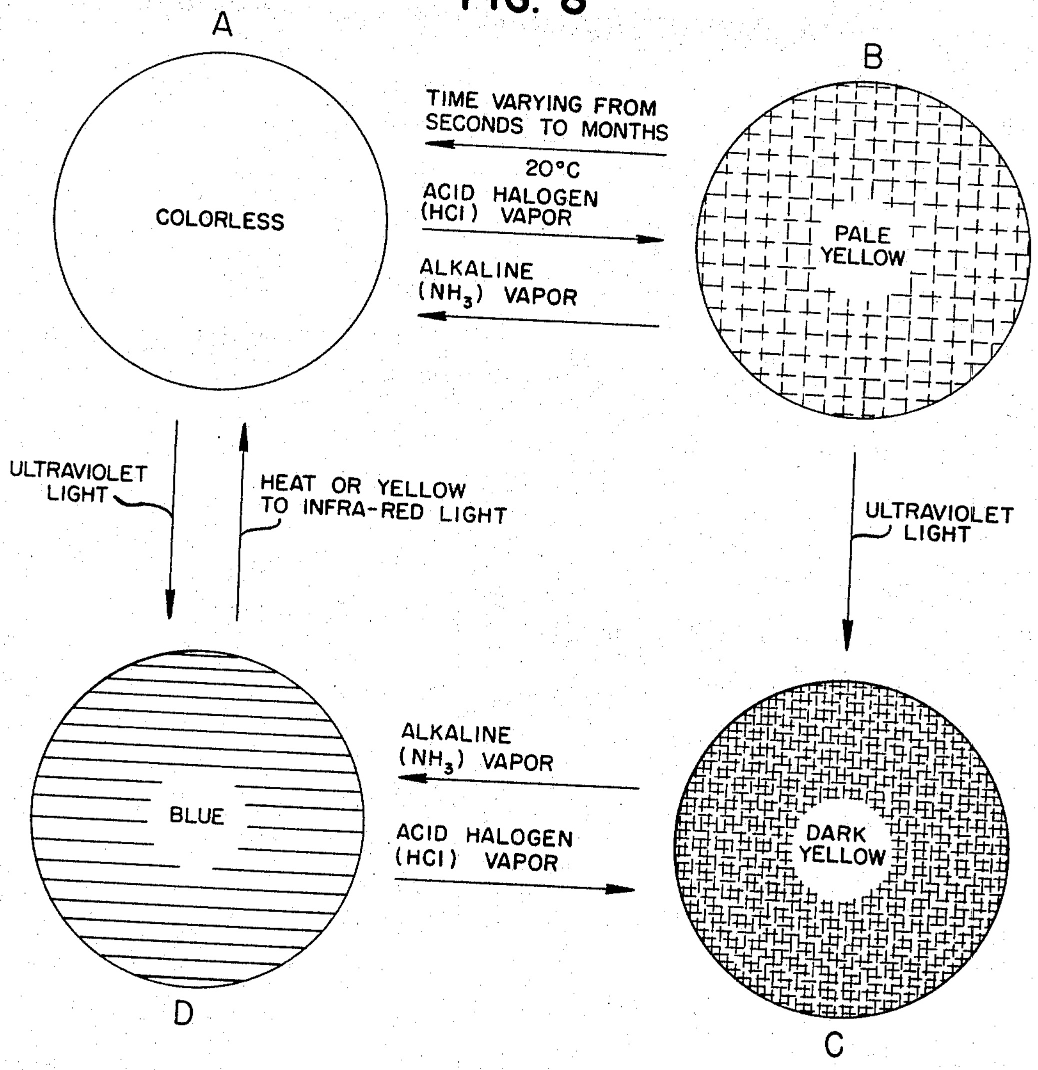

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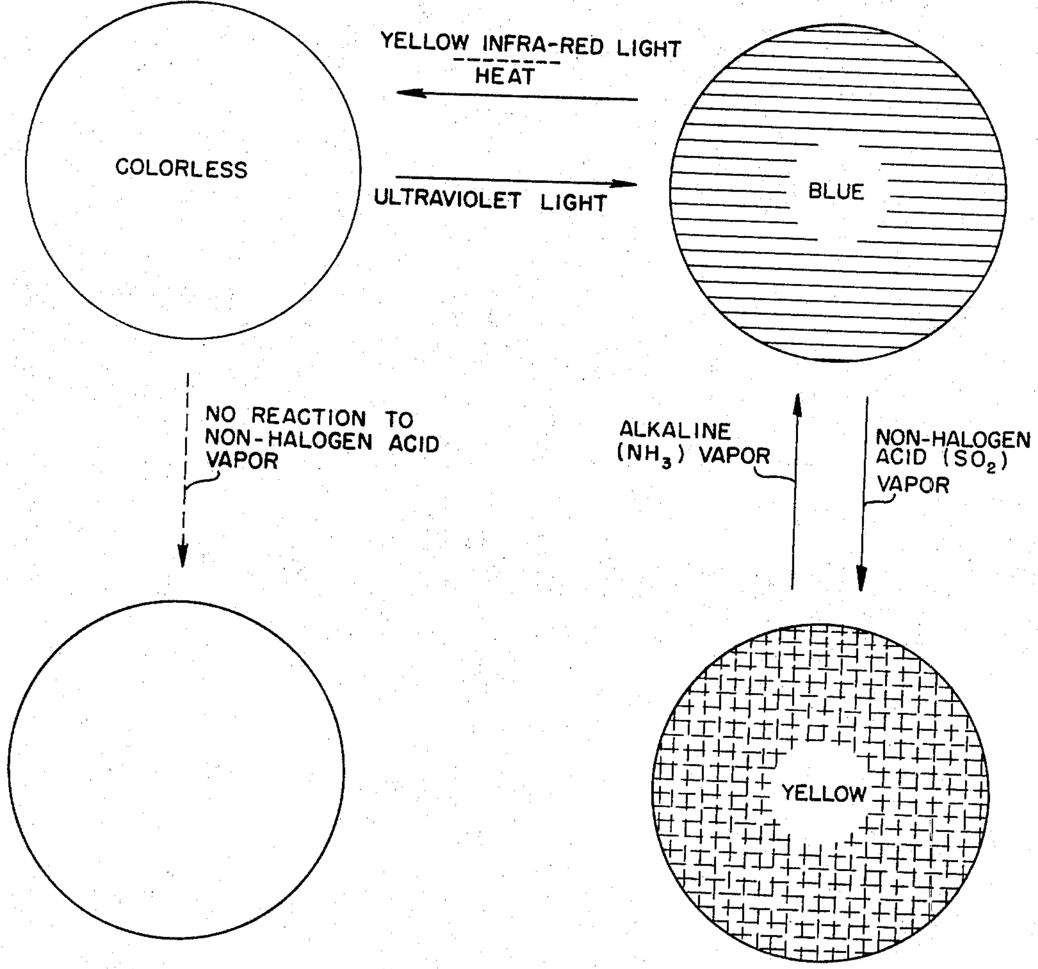
FIG. 9



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United States Patent Office

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METHOD OF FORMING THERMALLY STABLE PHOTOCHROMIC IMAGES AND PRODUCT

Peter L. Foris, Dayton, Ohio, assignor to The National Cash Register Company, Dayton, Ohio, a corporation of Maryland

Filed Jan. 16, 1964, Ser. No. 338,136

17 Claims. (Cl. 96—48)

This invention relates to a method of creating thermally-stable photochromic images in layers and to means for converting such images into states having various persistences.

The images in contemplation are created in or on a layer of material having sensitivity to ultraviolet light, the sensitivity of such layer being contributed by the presence of molecules of at least one photochromic compound.

Photochromic compounds are those that undergo, what is believed to be, an internal molecular rearrangement, from a normal condition, when subjected to ultraviolet radiation, and in which rearranged-condition each molecule radiation, and in which rearranged-condition each molecule has a light-absorption characteristic different than it had in the normal condition. The molecules in the layer are affected by radiation individually, and each molecule acts in an independent way to contribute to the overall visual concert-effect in a given area that is provided with a sufficient profusion of such molecules. Of course, in any given area there must be enough of the photochromic material supplied so that the total effect on the human eye, or other photo-sensing means, is as though there is a continuous layer of material to be sensed, the eye not being able to discern the individual contribution of any one of the molecules alone. Before this invention, of means for stabilizing images made photochromically, such images could not be retarded from reverting to the normal state, because of the effect of ambient temperature, except by lowering the temperature of storage, and the images would be lost. By this invention such images are not lost at room temperature or at higher or lower temperatures because of this reversion tendency.

The ultra-violet-light-rearranged-condition of the photochromic material will, for the purposes of this disclosure, be termed the "colored" state and the normal condition will, in some instances, be termed the "colorless" state, because most of the compounds evidence to the normal human eye, while in the "colored" state, in daylight or artificial light, a distinctive color within the visible spectrum and, on the other hand, in the "colorless" state evidence a colorless, a white, or a light-colored hue. In an aggregation of such molecules which are used in association with each other in making the sensitized layer, some molecules may be in one state or another dependent on the light and heat energy to which they may have been subjected, that is to say—the "colored" state or the "colorless" state, but all of the molecules, if the "colored" state, will in the absence of ultraviolet light revert to the "colorless" or equilibrium state in time, at a rate which increases with the ambient temperature. The reversion to the "colorless" state, therefore, causes a gradual fading of a "colored" image with time. On the other hand, the "colored" state is assumed substantially instantaneously if a powerful source of ultraviolet light is applied to the photochromic compounds while the molecules are not bound in crystalline arrangement. This "instantaneous" change, of course itself is effected molecule-by-molecule but in a short enough time that the rate of change is not apprehended by the human mind. The compounds differ among themselves as to the rate of reversion at a given temperature, the reversion to normal of the "colored" state of the molecules of some compounds being so fast at room temperature as to render them of no utility as a persistent color-contributor, whereas the molecules of other compounds remain in the "colored" state for hours, days, months, or years, depending on their molecular structure, in spite of the ever-present urging of them to the normal "colorless" state by ambient heat. In some compounds that should color in ultraviolet light according to the behavior of analogous compounds, there is no evidence that they do, but if a layer containing such compounds is fixed to a complex chemical form according to this invention, before being subjected to ultraviolet light, such layer is useful for making permanent records with the tool of ultraviolet light. The different colors exhibited by the compounds of different kinds, together with the difference in their rate of molecular reversion due to ambient temperature, give a great opportunity for those who practice the invention to select among the known compounds, of which there are many, in order to fit the condition of end use of the contemplated photochromic layer. The invention provides for the use of materials that never before could be used successfully for recording data. The behavior of a layer will, to the eye, be a composite of the behavior of the individual component molecules of whatever kind of photochromic material is used, whether of the same kind of molecules or of different kinds of molecules interspersed together.

The condensation of Fischer's Base with salicylaldehyde yields a benzo-indolinospiro pyran compound which in unsubstituted form is not useful for record keeping with ultraviolet recording means, presumably because of ambient temperature conditions, but by the practice of this invention can be made useful for such purpose. The derivatives of such compounds which have proved very useful for recording of something less than permanently durable records now are more useful in that respect because of the formation of a thermally-stable complex of the compounds according to this invention.

The "fixing" of a photochromic layer, as provided by this invention, halts the thermal reversion tendencies of the "colored" state of an image therein to the "colorless" state by the formation of a chemical complex of some kind, the exact nature of which is not fully understood but which, if the compound is a benzo-indolinospiro pyran, imparts a yellow color to the layer, such color being pale in any portion not subjected to ultraviolet light and of a deep yellow color where struck by ultraviolet light to form the image. However, this complex, while forming with the molecules in "uncolored" state does not render the "uncolored" molecules fixed against being changed to the deep yellow "colored" complexed state by subsequent ultraviolet light. Therefore, to make permanent records, the photochromic layer may be treated with acid vapors before or after being subjected to ultraviolet light.

A photochromic layer, if treated with the acid vapor before or after image formation, may be reversed to the uncomplexed state with alkaline vapors. In this respect the invention provides far superior recording systems to that possible with any photochromic layers heretofore known. The photochromic art before this invention provided a rather evanescent recording medium, not having the permanence required for durable records.

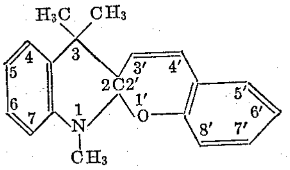
The photochromic layer of this invention may be an amorphous solid layer of the molecules laid down on a plate, sheet, or other support web, by evaporation of a concentrated liquid solution of the photochromic compound, preferably applied thinly thereto, or it may be a solid solution film of photochromic molecules in a polymeric film-former material. It is within the scope of the invention to lay down on the same support web two or more different layers of material, distinguished or not by their photochromic compound content or differing by the state of the photochromic material be it amorphous in solid state or in solution. It is also within the concept of the invention to have different areas of the same record material support sheet sensitized with different photochromic compounds to give a distinctive color to the areas according to the compound used, thus one area may have data recorded in one distinctive color associated with the photochromic molecules employed therein, which is in contrast to that of an adjoining area which employs other types of photochromic molecules. Or the different areas may be distinguished by a difference in the thermal persistence characteristics of different photochromic compounds used.

The recording of data may be made onto the novel record material by a beam or a cone of ultraviolet light of proper intensity and wave length, selectively applied directionally or by controlled intensity to the sheet. It will be apparent that light-control means such as shutters and stencils may be used to give selective operation of recording light, or other manner of light control may be used—such as filters, variations of period of the light-application, or the use of two or more sources of light acting together.

The fixing of a photochromic layer with an acid vapor can be carried out by placing the record material, in part or in whole, within a gas-confining compartment, such as a chemical hood, and the same apparatus may be used with the vapors used for the reversion of the layer or images as will be described. The layer also may be selectively fixed or reverted by applying the vapors locally to an area desired to be modified to the exclusion of the remainder of the layer, in any pattern or mode desired, such selection choice extending to a sheet of support material coated with a layer on either side whereof one side is treated differentially to the other to obtain a combination of images visually observable in thickness.

The objects of the invention may be stated as being to provide means for making thermally-stabilized photochromic layers, or images in such layers, in the form of chemical complexes; to provide means for reversing such fixed layers or images to their former uncomplexed state; and in general to provide a means for making permanent records with photochromic materials that because of temperature conditions could not before be used.

The best known photochromic compounds now generally in use in making record material for room temperature environmental use are the before-mentioned benzo-indolinospiropyrans, having a normal structure



in which substitutions may be made as follows:

6′-nitro-5′,7′-dichloro
6′-nitro-7′,8′-dichloro
5′,6′,8′-trichloro-7′-nitro
7′-nitro-8′-carbomethoxy
6′-nitro-7′-chloro
5′,6′-dinitro, 8′-methoxy
6′-nitro, 8′-fluoro
6′-nitro, 8′-iodo
6′-nitro, 8′-bromo
5′-nitro, 6′,8′-dichloro
6′-bromo, 8′-nitro
6′-iodo, 8′-nitro
6′-chloro, 8′-nitro

to give room-temperature-operable photochromic materials even though not thermally-fixed. These materials and thousands of others are disclosed in United States Patent No. 3,100,778, which issued Aug. 13, 1963 on the application of Elliot Berman. The naphtho-pyran analog and the 1-phenyl derivative also may be mentioned, as well as those in which the 3-carbon atom has been replaced with O or S.

The molecules of these compounds must have molecular freedom to change configuration, and in such free state are easily converted to the "colored" form by ultraviolet light while in solution, be it a liquid solution or a solid solution, or in an amorphous solid state adherent to a support surface or included within a polymeric film support. In crystalline form these compounds are difficultly converted to the "colored" state and difficultly revert to the "colorless" state so as to render them useless for record-making on a commercial scale. Moreover, a liquid solution of photochromic material which has had the photochromic molecules converted to the colored state and allowed to dry into a crystalline state, while the photochromic molecules are still in the colored state, is fixed in such a converted state for all practical short-term purposes of record keeping, except for fading, but cannot be reversed successfully to active condition. With the use of the best of such compounds as heretofore known, images can be formed and exist in layers made thereof for some hours or days, without thermally reverting to the "colorless" form, but such is not permanent enough for records that must be preserved. The number of possible photochromic compounds available for use, is so great that a comprehensive listing of them would be impossible, but reference has been made to the United States Letters Patent which has disclosed photochromic compounds of the benzo-indolinospiro pyran class, and to analogous compounds, that are operative in connection with acid-vapor fixing and alkaline-vapor reversion, as claimed.

With the foregoing newly found principles in mind, the invention will be described with reference to the drawings in which:

FIG. 1 shows a support **20** with the layer **21** comprising the photochromic compound made either in an amorphous thin layer form or in a solution state (solid-solution form or liquid-solution form) or made as a thin solid film of polymer material with the photochromic material in substantially an amorphous form distributed therein. From a convenience point of view, and to prevent rapid sublimation of the material, a solution of the photochromic material in a thin polymer film solution-former is to be preferred;

FIG. 2 shows the application of ultraviolet light to the layer **21** under the control of an aperture-type of stencil which is to be taken as typical of light-image control means, the image of the letter N in dark blue colored form being represented in solid black on layer **21**;

FIG. 3 shows the plate **20** bearing the image **21** being subjected to the acid-vapors of HCl within an enclosure, whereby the image N is fixed as a dark yellow complex with a pale yellow background shaded horizontally;

FIG. 4 shows the layer with the fixed photochromic image during its treatment with ammonia vapor to reverse it to unfixed condition;

FIGS. 5, 6 and 7 refer to an alternative method, especially useful for photochromic compounds not ordinarily operable at room temperature, wherein as shown in FIG. 5, the prepared photochromic layer is treated first with acid vapor, before any image is impressed thereon, to fix the whole layer to a pale yellow complex of the "colorless" form of the photochromic material, to prepare it for the reception of images by ultraviolet light; FIG. 6 shows the fixed "colored" record condition of FIG. 5 after being subjected to ultraviolet light; and FIG. 7 shows the photochromic "colored" image reversed by having been subjected to ammonia vapor;

FIG. 8 is a flow-diagram of the changes of state in a photochromic layer image, according to the teachings of the invention using a halogen acid; and

FIG. 9 is a flow-diagram of the changes of state in a photochromic layer image, according to the teachings of the invention using non-halogen acid vapors.

It will be understood that the data to be recorded may be in terms of the "colored" portion of the layer or, on the other hand, in terms of the "colorless" portion of the layer, the image being that portion affected by ultraviolet light.

Inasmuch as the acid-complex of the part of a layer not subjected to ultraviolet light will lose its acid vapor in a short time, by sublimation, the deep yellow of the image is retained and it may be visually enhanced by flooding all of the layer with ultraviolet light, to color the background to give an enhanced visibility to the deep yellow of the image by color-contrast.

To form an amorphous layer of photochromic material by deposition from a liquid solution, the material is dissolved in a readily evaporable liquid applied in a thin film to a clean substrate surface, such as the surface of a sheet of glass. Purity of these compounds tends towards unwanted crystallization of such layers, if compounds are used singly. A mixture of closely related photochromic compounds will prevent the crystallizing tendency through steric hindrance. An impure photochromic compound is more apt to yield an amorphous film than a pure one. Substituents may be added to the compounds in various ways to achieve the best results, as more fully set forth in an application for United States Letters Patent, filed of even date by this applicant, wherein the forming of etching-fluid-resist images in photochromic compounds and amorphous films was disclosed and claimed.

Images, then, formed by the ultraviolet light in amorphous layers of photochromic material tend to fade and disappear in time through thermal decay phenomena through heat energy obtained from the environment. The invention is directed to means for fixing such images against such fading and disappearance, and to provide means for re-establishing the material by a reversing step so as to be responsive to further recording, or to be more available for an optimal step of coloring the background to improve observation.

(A) PREPARATION OF A SOLID

Amorphous layer on a support sheet

Glass is a most suitable substrate for preparing films or layers according to the invention, being smooth, rigid, transparent in its ordinary form, and highly resistant to the materials employed. However, any equivalent support of metal, fiber, mineral, ceramic, polymer, and the like, may be used, as desired.

First, a 10 percent, by weight, solution of a typical benzo-indolinospiropyran which may exist in amorphous or solution form either in the "colorless" or "colored" form at room temperature is prepared with benzene, a highly useful one being the 6'NO_2-8'OCH_3 derivative having the full formula 1,3,3-trimethylindolino-6'-nitro-8'-methoxybenzopyrylospiran. Second, an amount of the solution is applied to a 4" x 4" glass plate of 1/16 inch in thickness, which is spun at 500 r.p.m. at room temperature to remove the excess solution and to dry out the photochromic material to a film of amorphous characteristics, which condition will persist for several days after which crystallization may start.

If longer persistence in the amorphous state is required, half of the photochromic material is replaced by the 7-phenyl-6'NO_2-8'OCH_3 derivative.

These films are dark blue in the "colored" form, are substantially without hue in the "colorless" form and are subject to direct contact reaction with the acid and alkaline vapors.

(B) PREPARATION OF A SOLID

Solution layer on a support sheet

In this preparation a glass slide, or its equivalent, is coated with a composition consisting of one part of a 10 percent, by weight, solution of polyphenyl phenol-formaldehyde in benzene, and one part of 10 percent benzene solution of the selected photochromic dye, and spun to dryness. This solid solution layer will respond to ultraviolet light by turning blue, and in the thin-film condition will be available for complexing with the acid vapors and for reversal by treatment with alkaline vapors. It is suggested that, for showing the versatility of the compounds, the 5Cl-6'NO_2 derivative of the mentioned parent benzo-indolinospiropyran be used, but such is in no way to be deemed to limit the selection.

(C) PREPARATION OF A COMPOSITE

Layer system on a support sheet

In this preparation two or more films or layers are formed on an inert plate in any arrangement, such as in superposition on the same side or on different sides of the plate, or in overlapping relation on the same side.

For instance, an initial layer of the 5Cl-6'NO_2 derivative of the parent benzo-indolinopyrospiran may be laid down on a plate, an image created thereon by ultraviolet light, and a complex formed with HCl vapor, after which the background pale yellow complex is removed with toluene, leaving the toluene-resistant image in dark yellow. Over this image is placed a second amorphous layer of the 6'NO_2-8'OCH_3 derivative, from benzene solution, and a selected image is created with ultraviolet light over the first image. The treatment of the plate again with HCl vapor results in the two superimposed, but not necessarily alined images in deep yellow. Treatment of the whole plate with ammonia vapor yields a purple image on the bottom and a blue image over-laying it, as the "colored" states of the two images are of different hue.

Example I.—In this example, the preferred one, a sheet is prepared according to preparation instructions (A) and subjected to a cone of ultraviolet radiation, from a source producing radiation strong at 3000 A., through a stencil as in FIG. 2 to produce the letter N in dark blue on a colorless background. The ultraviolet-light-exposed sheet then is placed under a hood with HCl vapor, at atmospheric-pressure and room-temperature, for a few seconds, by which time the layer has turned yellow with the image N appearing as a darker yellow hue. On removal from the HCl vapor the paler yellow portions of the layer will, within a few minutes, resume the "colorless" state due to sublimation of the vapor, leaving the N image in thermally-stabilized form of deep yellow hue. The background will still be sensitive to ultraviolet light.

Example II.—The steps of Example I are followed with the further step of flooding the finished plate with ultraviolet light to produce a blue-colored background for the deep yellow N.

Example III.—A sheet prepared according to the instructions (B) is first subjected to HBr vapor for a few seconds at atmospheric pressure and room temperature to turn the film to the pale yellow complex. Next, the complexed layer is subjected to a selectively directed beam of ultraviolet light to trace an image which appears in dark yellow against a pale yellow background.

Example IV.—Example III is followed with the added steps of:

(1) subjecting the layer to alkaline vapor (NH_3) to reverse the complex,

(2) making a new trace of different pattern with an ultraviolet light beam, and

(3) re-fixing the layer by again subjecting the layer to the HBr vapor,

thus fixing as images both traces even though made at different times.

Example V.—Any of the foregoing Examples I to IV is reversed to normal as to part of its area only by subjecting only such part of it to NH_3 vapor, the other parts being physically masked.

Example VI.—In this example photochromic layers are laid down on either face of a sheet made of material opaque to ultraviolet light but which is transparent to visible light of the longer wave lengths. Images are made with ultraviolet light on each layer of different subject matter and one or both sides are fixed by halogen acid vapors. Then at will, whatever area is to appear in normal "colored" state is treated with the reversing alkaline vapor. The sheet is viewed from one side or the other by incident light or through the sheet by transmitted light to obtain a composite effect.

Example VII.—In this example a plate is prepared according to instructions (A), an image is formed thereon by projecting ultraviolet light to it in the desired pattern. The plate then is treated with SO_2 vapor which combines with the colored image to form a stable yellow complex but which leaves the background unconverted in the original colorless form, as SO_2, though an acid vapor is not an acid of the halogen group. This background is still sensitive to ultraviolet light for more recording and fixing.

The stable SO_2-yellow images may be reversed with alkaline vapors as was the case with the other examples.

In this example of the invention, a recording made on the "colorless" state of the layer may be "fixed" only after the recording, whereas if the "fixing" is with a halogen type of acid vapor it may be carried out before the application of ultraviolet light.

It will now be understood and appreciated that the steps of the invention may be employed in a great variety of combinations using the fixing and reversing steps when needed, and that combinations of photochromic compounds and means for forming images to complement or supplement one another, are provided.

The invention is characterized also by the distinguishing use of halogen acid vapors and non-halogen acid vapors, as the occasion of use demands.

The invention therefore is claimed in a manner to embrace various combinations of steps all coming within the inventive concept.

What is claimed is:

1. The method of forming thermally-stable images made on plates sensitized with a photochromic spiro-pyran material, including the steps of forming the desired image on the plates by application thereto of ultraviolet light in selected image representing areas; and thereafter subjecting the plate having the so-formed image to hydrohalic acid vapors.

2. The method of forming thermally-stable images made on plates sensitized with photochromic spiro-pyran material, including the steps of forming the desired image on the plates with ultraviolet light after having subjected the sensitized plates to hydrohalic acid vapors.

3. The method of forming thermally-stable photochromic images, including the steps of:
(a) providing a layer of record material sensitized with a spiro-pyran photochromic compound;
(b) subjecting the layer to hydrohalic acid vapor to form a chemical complex of the acid vapor and the compound; and
(c) creating an image in the layer by directing ultraviolet light thereto in image-representing pattern.

4. The method of claim **3** followed by the step of subjecting the layer to subliming environmental conditions to drive the vapor from the background areas of the layer not subjected to the ultraviolet light thus leaving the background colorless.

5. The method of thermally-stabilizing ultraviolet-light-formed thermally-decayable images formed in layers sensitized with spiro-pyran photochromic material, consisting of the step of subjecting the layers to acid vapors selected from the group consisting of hydrohalic acid vapors and sulfur dioxide vapors.

6. A method of recording consisting of the steps of:
(a) forming a layer of photochromic material of the spiro-pyran type;
(b) recording data on the layer by directing ultraviolet

light thereto to make thermally-decayable images; and
(c) stabilizing the images by subjecting them to acid vapors selected from the group consisting of hydrohalic acid vapors and sulfur dioxide vapors long enough to form acid complexes with the photochromic molecules.

7. A method of recording consisting of the steps of:
(a) forming an image on a layer of photochromic material of the spiro-pyran type by exposure of it to ultraviolet light in the image-representing areas, and keeping such image from thermal decay by cooling said layer;
(b) and later subjecting the record to acid vapors selected from the group consisting of hydrohalic acid vapors and sulfur dioxide vapors before subjecting the layer to higher temperatures apt to cause thermal decay of the image, said image being reversible to its state in which it is subject to thermal decay by application of ammonia vapors.

8. A method of recording consisting of the steps of:
(a) preparing a record by successively recording data on a layer of photochromic material of the spiro-pyran type at different time periods, and
(b) then fixing the layer by subjecting the layer to acid vapors selected from the group consisting of hydrohalic acid vapors and sulfur dioxide vapors.

9. A method of recording, including the steps of preparing a photochemically-sensitive film comprising compounds of benzo-indolinospiropyran structure; forming an image thereon by applying ultraviolet light in selected patterns; and flooding the film with an acid vapor selected from the group consisting of hydrohalic acid vapors and sulfur dioxide vapors until a yellow complex forms involving the acid and the photochromic molecules.

10. The method of claim **9** followed by the step of treating the complex with ammonia vapor to reverse the fixing of the image.

11. A method of recording data including the steps of forming an image in a layer sensitized with photochromic material by means of first forming a complex of the photochromic material of the layer with hydrohalic acid vapors; and forming the image of the data in terms of an acid complex of the photochromic material of the layer with ultraviolet light.

12. A method of recording consisting of the steps of:
(a) forming an amorphous layer of spiro-pyran photochromic material on a support plate;
(b) recording data on the layer by ultraviolet light to make thermally-decayable images; and
(c) stabilizing the images against thermal decay by subjecting them to acid vapors selected from the group consisting of hydrohalic acid vapors and sulfur dioxide vapors long enough to form complexes with the photochromic material.

13. The product of the process of claim **12.**

14. The method of forming thermally-stable images by ultraviolet light including the steps of:
(a) preparing a film including amorphous photochromic material of the spiro-pyran type;
(b) forming a photochromic "colored"-state image on (a) with ultraviolet light; and
(c) fixing the image against thermal decay of the film by exposure to hydrohalic acid vapors.

15. The product of the process of claim **14.**

16. The use of the method of claim **14** to form a thermally-fixed photochromic image followed by the step of treating the image by exposure of the film to ammonia vapor to reverse the image to the unfixed "colored" state.

17. The method of forming thermally-stable images by use of ultraviolet light, including the steps of:
(a) preparing a film of a solution of spiro-pyran photochromic material in a polymeric film-forming material;
(b) forming an image on the film with ultraviolet light; and

(c) fixing the image against thermal decay by applying to the film acid vapors selected from the group consisting of hydrohalic acid vapors and sulfur dioxide vapors.

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NORMAN G. TORCHIN, *Primary Examiner.*

C. E. DAVIS, *Examiner.*