United States Patent

[11] 3,597,082

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[21] Appl. No. **617,118**
[22] Filed **Feb. 20, 1967**
[45] Patented **Aug. 3, 1971**
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[54] **UNCOPYABLE PHOTOCHROMIC PAPER**
5 Claims, 1 Drawing Fig.

[52] U.S. Cl. 355/133, 283/17
[51] Int. Cl. G03g
[50] Field of Search 355/17, 133; 283/17

[56] **References Cited**
UNITED STATES PATENTS
2,740,324 4/1928 Cahill 355/40

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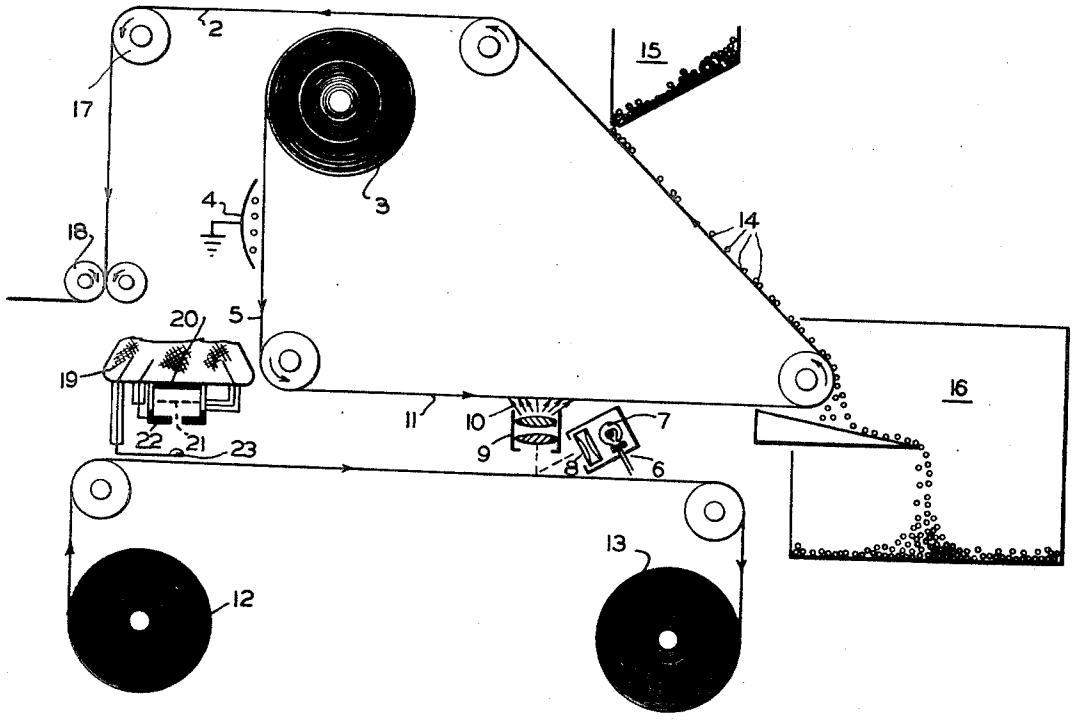
ABSTRACT: A photochromic paper having visible data thereon which, in response to radiation impinging on its surface, temporarily changes color to substantially match the color of the data thereby preventing copying therefrom.



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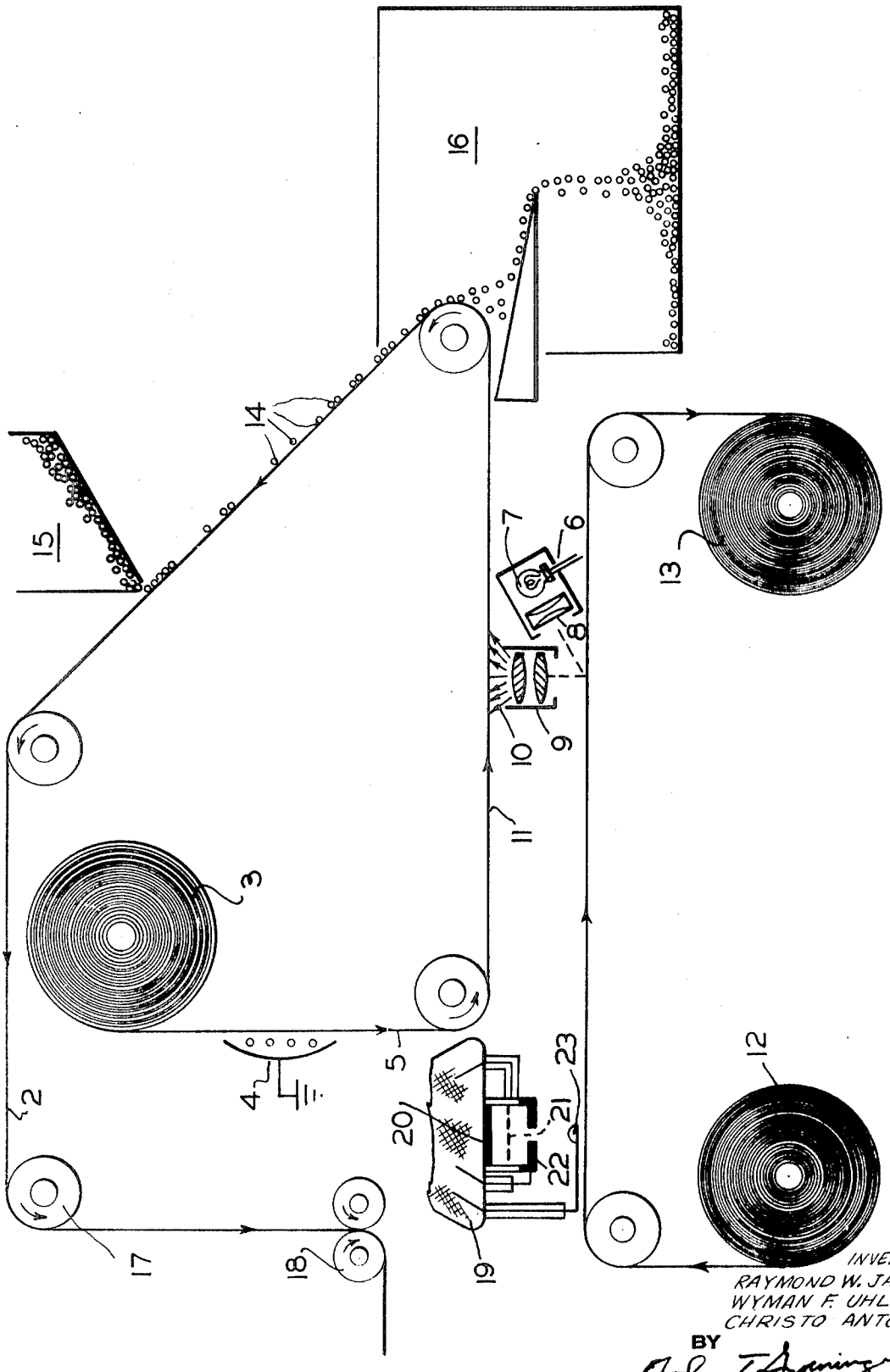

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UNCOPYABLE PHOTOCHROMIC PAPER

BACKGROUND OF THE INVENTION

This invention relates to uncopyable paper and more particularly, to a specially treated paper which when exposed to radiation will inhibit copying therefrom.

A problem in industry today is the copying of copyrighted materials by the use of xerographic techniques and other conventional copying processes. While this problem has been discussed extensively among publishers, nothing has been proposed to date which would overcome this problem.

SUMMARY OF PRESENT INVENTION

In accordance with the present invention a sheet of paper is impregnated or coated with a photochromic material. An image is then placed on the paper by any conventional technique such as writing, printing, etc. Upon exposure of this sheet to radiation, the photochromic material changes to a color which substantially matches the color of the image on the piece of paper. As a result, a copying machine is not capable of distinguishing between the image and nonimage area on the paper and a blank copy sheet is produced. After exposure, the photochromic material reverses to its original color, leaving the image on the original clearly visible to the eyes.

DRAWING

The sole Figure is a diagram of illustrating one example of the use of the present invention.

DETAILED DESCRIPTION

The photochromic material may be incorporated in a paper during the paper manufacturing operation. It may be mixed directly with the pulp prior to paper formation, and/or applied at a size press of the paper machine. The latter is preferred as the photochromic material deposited at the size press will be positioned on the paper surface and thereby made fully responsive to activating radiation. The photochrome may also be mixed with a compatible binder and coated on a sheet by any conventional technique as, for example, reverse roll coating, brush coating, wire-wound bar coating, spraying, etc.

Any conventional imaging material may be employed to image he photochromic sheet, e.g. pencil, ink etc., the only requirement being that the color of the imaging material be adjusted to match the color of the selected photochrome when it changes color in response to exposure to radiation.

The photochromic material utilized in the practice of the invention may include any of the well-known photochromic materials, inorganic and organic, which are photochromic in the solid state and may be selected, e.g., from the list of hundreds of photochrome materials which are photochromic in the solid state disclosed in the article entitled "Phototropism" in the Reviews of Pure and Applied Chemistry, Volume II, No. 1 (1961). Photochromes which in their stable form are colorless or light in color are preferred and include phosphotungstic acid, silicotungstic acid, benzyldihydraphenol hydrazine, copper chloride, spiropyrans, bilophenes and triarylmethaneleucocyanides.

The amount of photochromic material will vary depending upon a particular photochromic compound employed and the particular desired properties. Generally, the amount of photochromic material must be greater than 1 pound per 24 inch by 36 inch, 500 sheet ream of paper. Below 1 pound there would be insufficient density upon development. If the photochromic material is incorporated in a coating, here should be at least 1 part of photochrome to 10 parts of binder.

The upper limit on the amount of photochrome is governed by the practicality of the feel of the paper which is designed to be used for normal writing purposes. Generally, the amount of photochrome and binder should be kept below 50 pounds per ream of paper.

The exciting radiation required to cause he color change and the velocity of the color change will depend upon the particular photochrome employed. Generally, the exciting radiation which causes the phototropic change in photochromic solids lies in the ultraviolet region or in the lower range of the visible spectrum and has a wavelength less than 5000 A. The color reverts back when the photochromic sheet is placed in the dark.

The general nature of the invention having been set forth, the following examples are now presented as illustrations but not limitations of the methods and means of carrying out the invention.

EXAMPLE I

To 100 parts of 10 per cent polyvinyl butyral solution in ethyl alcohol was added 10 parts of phosphotungstic acid. This formulation was coated on a sheet of paper in a range of 10 pounds (dry solids basis) per ream (24 inch by 36 inch, 500 sheets) applied with a No. 18 Meyer rod to the paper, giving a coating of about 0.2 mils. The resulting product had bond-type quality and the color of the paper was unchanged. A penciled drawing was made on the sheet to provide a visible gray image.

The paper was exposed to light flash from a strobotron which was placed closely adjacent the surface of the sheet. The coating turned a dense gray substantially matching the gray color of the image previously recorded on the paper. In his condition, the paper was passed through conventional electrofax and xerographic equipment. Copies produced were uniformly gray over their entire surface and no image could be detected.

EXAMPLE II

Five parts of silcotungstic acid, 5 parts of phosphotungstic acid, and 10 parts glycerine were added to 100 parts of an aqueous acetate acrylic copolymer emulsion. Water was added to bring the composition up to a workable viscosity for a coating. The coating was flooded onto a sheet of paper and the excess was doctored off the surface. The sheet was then dried. The sheet had a pale yellow shade. An ink drawing was made on the sheet.

The paper was exposed to a light flash from a strobotron which was placed closely adjacent the surface of the sheet. The coating turned a dense gray (more dense than that in Example I) substantially matching the color of the inked drawing on the paper. In this condition the sheet was passed through an electrofax machine and copies produced were uniformly gray over their entire surface.

EXAMPLE III

Five parts by weight of beta-tetrachlor-ketonaphthalene was dissolved in 95 parts by weight of methyl ethyl ketone. The coating was flooded onto a sheet of paper and excess doctored off the surface. The sheet was then dried. The coating was colorless. Information in the form of typed letters blue-violet in color was applied to the sheet.

The paper was exposed to ultraviolet light for about 5 minutes from a source consisting of two 15 watt black fluorescent tubes spaced about 6 inches from the surface of the sheet. Upon exposure, the coating changed from colorless to violet in color thus effectively masking the typed image. In this condition the sheet was passed through an electrofax machine and copies produced were u5iformly gray over their entire surface.

It is to be understood that the present invention can be incorporated into any conventional copying process, such as xerography, electrophotography, diffusion transfer, verifax, etc. The particular source of radiation and the duration of the radiation will depend upon the particular photochrome used.

In order to illustrate one example of the use of the present invention in conventional electrophotography, reference is now made to FIG. 1, which is a schematic diagram of ap-

paratus capable of being employed in the present invention. Reference is made to U.S. Pat. No. 3,121,006, U.S. Pat. No. 3,052,539, and U.S. Pat. No. 3,052,540 for a detailed description of Electrophotographic apparatus and paper and by his reference incorporated herein.

Referring to Figure 1, conventional apparatus is shown and will be briefly described. Paper 2 coated with a photoconductive composition, as well known in the art, is unrolled from a roll 3 and led past a charging device 4. Here, one side 5 of the paper 2 is given an overall electrostatic charge. The paper 2, carrying the charge, is then exposed to light images projected on it by projector 6.

The projector 6 may be of conventional-type comprising an enclosed light source 7, condensing lens 8, projection lens 9, and an aperture 10 in the form of a narrow elongated slit. The material to be copied is on paper 11 and the sheet is passed through the projector by being unwound from a reel 12 and wound on a takeup reel 13. The speed of the takeup reel is controlled by conventional variable speed drive means (not shown).

As the paper 11 is exposed to the light images being continuously projected upon it by the projector 6, electrostatic latent images are formed on the paper web 2. The electrostatic latent images are then developed by cascading a composition 14 comprising an electroscopic developer, which may comprise a fusible resin and carrier particles, fed from a reservoir 15 across the exposed side of the paper 2 as it is led in an inclined path. Particles of the powder adhere either to the charged portions of the image or to the edges of the charged portions. The excess of powder and carrier particles may be collected in a receptacle 16 and recycled through the reservoir 15. The carrier particles may comprise tiny glass beads.

The paper carrying the developed images is then led over a heating device which may comprise a heated drum 17, to fuse and fix the powder making the images permanent. The paper is then passed through drive rollers 18 which may be driven by a variable speed motor (not shown) to control the speed of the paper. The speed of the drive rollers 18 and of the film takeup reel must be synchronized so that the speed of the paper and the speed of the film 11 through the projector are the same.

The entire apparatus may be enclosed to keep out external light or only that part encompassing charging unit, exposure unit and developing unit may be enclosed.

In accordance with the present invention, the copying machine above described may be made inoperative by employing specially treated paper, made, e.g., as above described in Examples I and II, in place of conventional bond paper 11. In this instance, an additional light source 19 is required which will impinge on the paper prior to the paper reaching projector 6. Light source 19 is a conventional strobotron which is a gas filled tetrode used to produce a short duration flash of light and comprises a cathode 20, control grid 21, screen grid 22 and anode 23. The strobotron may be of the type shown and described in on page 124 of the Encyclopedic Dictionary of Electronics & Nuclear Engineering by Sarbacher (Prentice Hall 1959). It is to be understood that if the photochrome selected is responsive to radiation provided at exposure station 6, and if it changes color rapidly prior to formation of a latent image on web 2, then the additional light source 19 can be eliminated.

In using specially treated paper in place of paper 11 in the above-described copying machine, the paper is exposed to the strobotron 19 and held in this position until the photochromic material on the sheet changes to a color substantially matching the color of the image material on the sheet. When the sheet arrives at projector 6, the entire sheet is of a single color thereby inhibiting the projection of a light image on the paper 2. By placing sheet 11 in the dark, the image on sheet 11 will appear again after a predetermined period of time dependent on the particular photochrome employed.

The expression "photochromic material" as employed herein means those materials which undergo a color transformation in the visible region when the material is exposed to an exciting radiation but revert to their original color (or to a transparent or white state) in the dark.

As will be apparent to those skilled in the art, alterations and substitutions are possible in the practice of this invention without departing from the spirit or scope thereof.

What we claim is:

1. A support including a photochromic layer, visible data on said photochromic layer having a color substantially matching the color of the excited form of said photochromic layer.

2. A support as defined by claim 1, wherein said photochromic layer comprises a sheet of paper, photochromic material incorporated into said sheet of paper.

3. A support as defined by claim 2, wherein there is at least 1 pound of photochromic material per 3,000 square feet of paper.

4. A support as defined by claim 1, wherein said photochromic layer comprises a photochromic coating on said support, said coating comprising a compatible resin binder and from about 10 percent to 90 percent by weight of a photochromic material.

5. A support as defined by claim 1, wherein said photochromic layer includes photochromes selected from the group consisting of phosphotungstic acid, silicotungstic acid, benzyldthydraphenol hydrazine, copper chloride, spiropyrans, bilophenes and triarylmethaneleucocyanides.

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,597,082 Dated August 3, 1971

Inventor(s) Raymond W. James, et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 66, "u5iformly" should read -- uniformly --; line 70, cancel "verifax".

Signed and sealed this 31st day of October 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334.