May 21, 1963 E. BERMAN 3,090,687

PHOTO-CHEMICAL PRINTING

Filed Nov. 6, 1957 6 Sheets-Sheet 1

FIG. 1

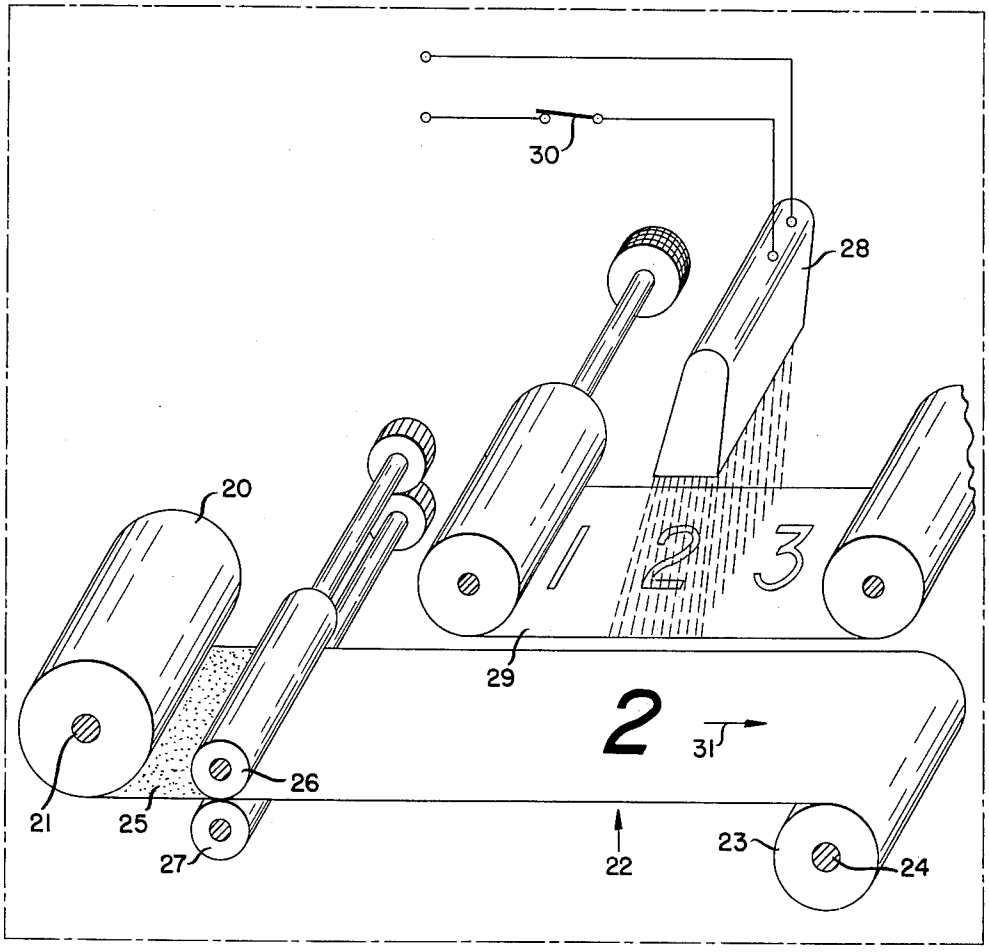

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PHOTO-CHEMICAL PRINTING

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FIG. 2

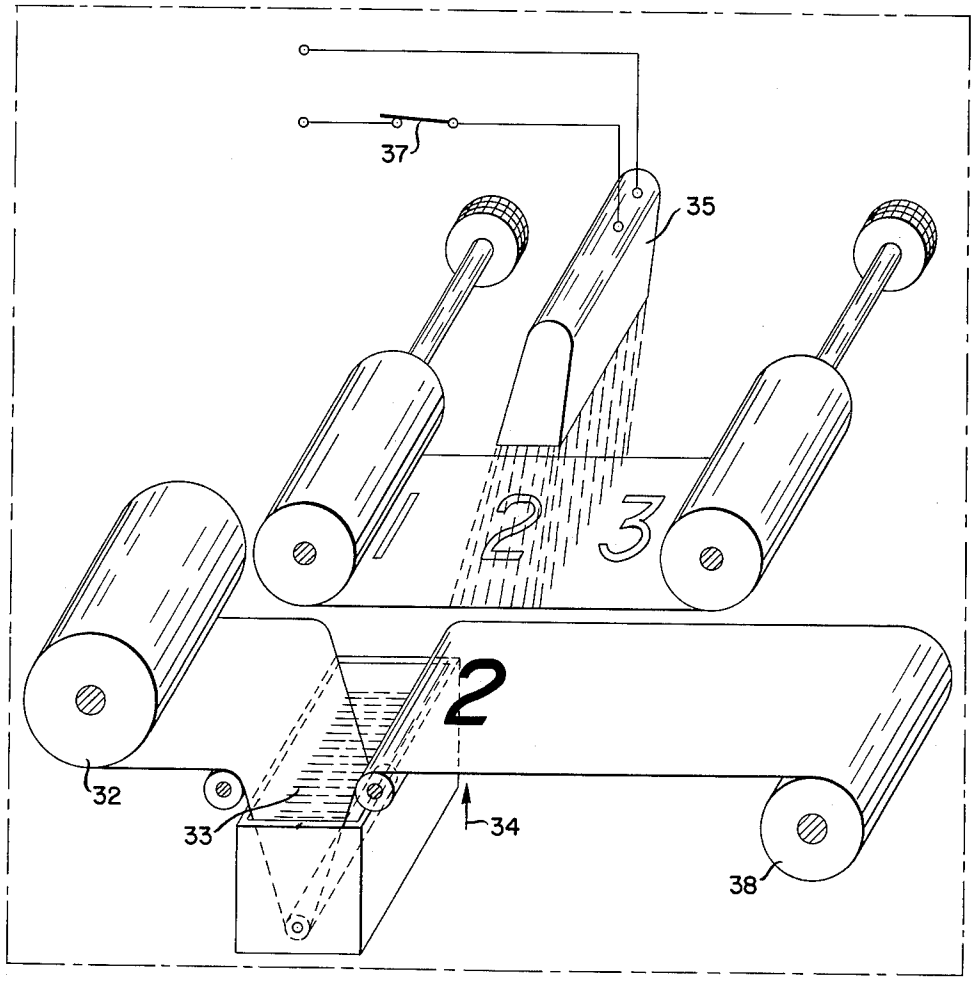

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FIG. 3

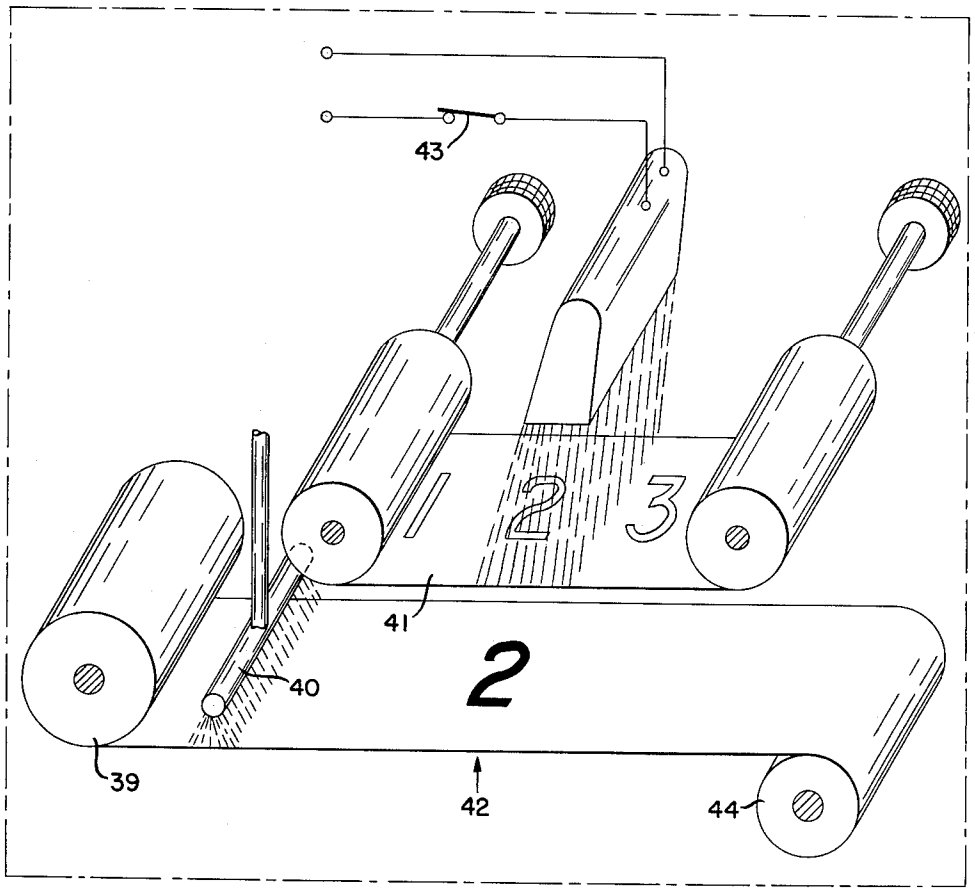

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FIG. 4

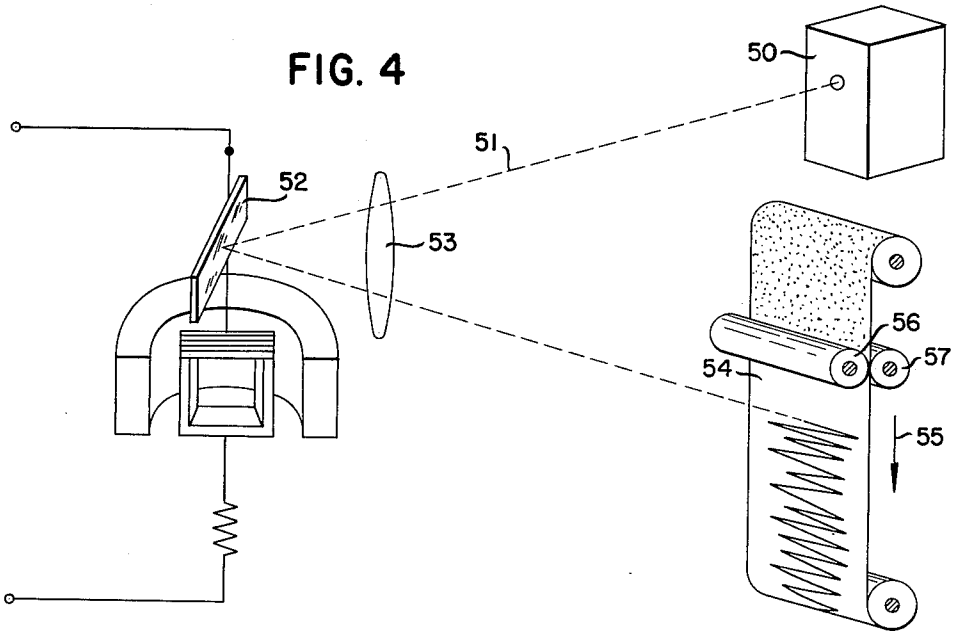

FIG. 5

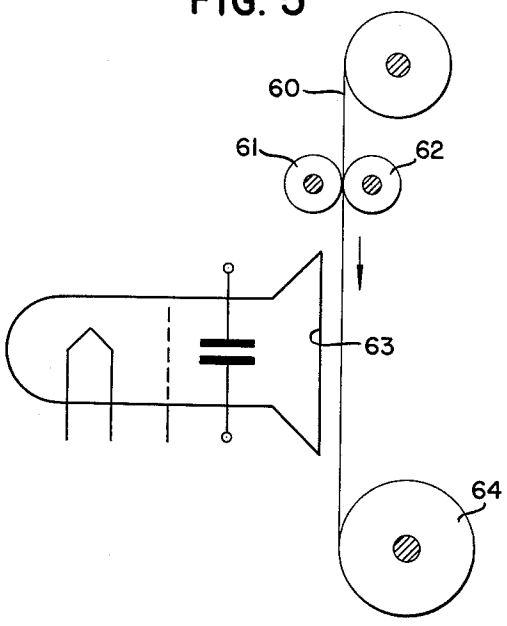

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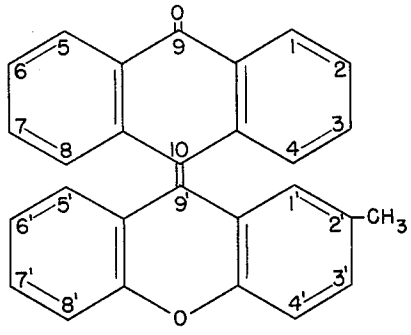
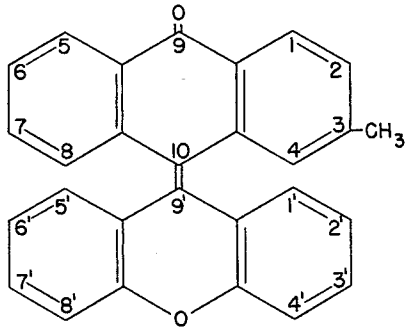
FIG. 6



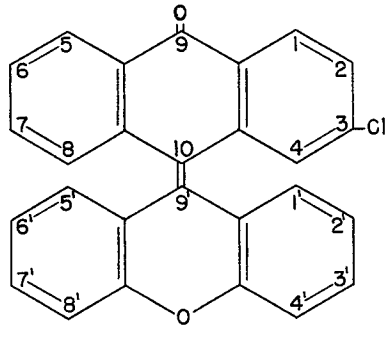
10-(9'-2'-METHYLXANTHYLIDENE)-ANTHRONE

FIG. 7



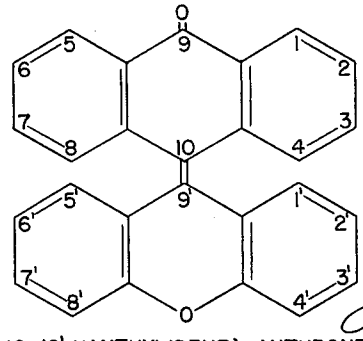
3-METHYL-10-(9'-XANTHYLIDENE)-ANTHRONE

FIG. 8



3-CHLORO-10-(9'-XANTHYLIDENE)-ANTHRONE

FIG. 9



10-(9'-XANTHYLIDENE)-ANTHRONE

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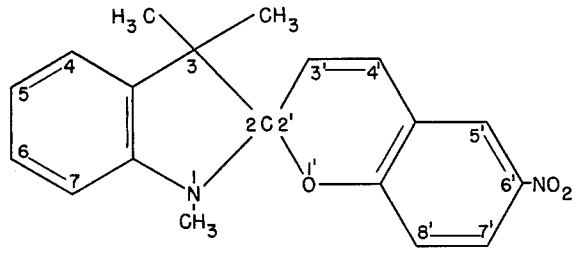
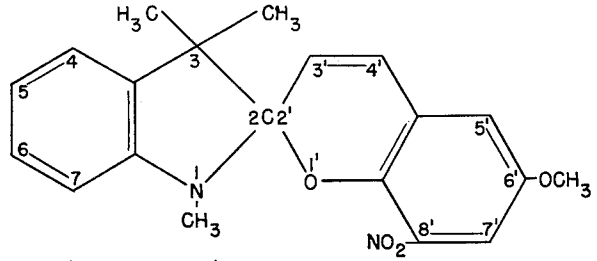
FIG.10



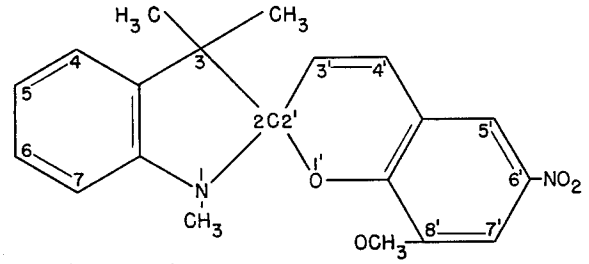
1,3,3-TRIMETHYLINDOLINO-6'-NITROBENZOPYRYLOSPIRAN

FIG.11



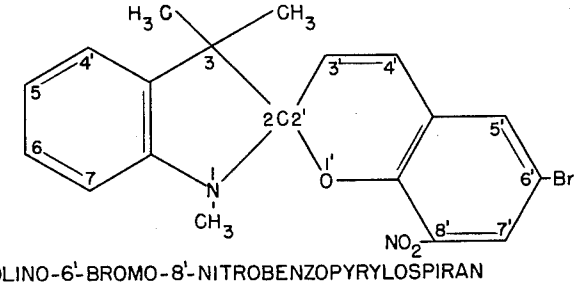
1,3,3-TRIMETHYLINDOLINO-6'-METHOXY-8'-NITROBENZOPYRYLOSPIRAN

FIG.12



1,3,3-TRIMETHYLINDOLINO-6'-NITRO-8'-METHOXYBENZOPYRYLOSPIRAN

FIG.13



1,3,3-TRIMETHYLINDOLINO-6'-BROMO-8'-NITROBENZOPYRYLOSPIRAN

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United States Patent Office 3,090,687 Patented May 21, 1963

3,090,687

PHOTO-CHEMICAL PRINTING

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Filed Nov. 6, 1957, Ser. No. 694,802
2 Claims. (Cl. 96—48)

This invention relates to a photo-chemical printing method and means and more particularly pertains to record material which is wet with a liquid solution of a chemical compound or compounds, while being printed, said compounds being substantially colorless and inert to light when in solid form, but which, when in solution in a liquid become responsive to light of predetermined wave lengths and change in light-absorbing characteristics when such light is projected onto the record material. The solvent is a volatile liquid vehicle. After the color forms, that is to say, after the light absorption characteristics of the compound or compounds have changed through the application of light to the record material at the printing station, in selected patterns, the solvent is allowed to evaporate to render the compound or compounds inert as to light subsequently applied to both the colored and uncolored form.

The term "printing" is used in the broad sense of making visible marks, and includes all means for controlling the application of light to the record material.

Several modes of wetting the record material with the solution before it arrives at the printing station are contemplated; one is to have the light-responsive compound or compounds in particulate solid form coated on the record material and applying the volatile solvent to the coating on that part of the web nearing the printing station, said solvent evaporating after the color has formed. Another proposed method of printing would be to provide the record material which is coated with the particulate light-sensitive compound with microscopic pressure-rupturable capsules containing the volatile liquid solvent, which capsules are crushed just before the record material reaches the printing station, freeing the solvent which dissolves the compound or compounds.

Still another method for preparing the record material by wetting is to apply a liquid solution of the compound, or compounds, to the record material just before it reaches the printing station, the solvent, of course, being volatile. The solvent, or solvents, containing the dissolved color-forming compound may be applied by porous rubber type with only the desired pattern wetting the record material.

The printing method and means which will be described fully in the specification to follow will be referred to as photo-chromic printing, and its chief characteristic as distinguished from ordinary photography methods is that the novel record material, before being wet as described, is as inert to light. The print is made instantaneously by light, as far as human perception is involved, and is fixed by evaporation of the solvent.

The base web record material may be paper, but other film-like material or other solid surfaces may be used. It will be evident that, if the solvent is applied shortly before printing, the record material is only sensitive to light shortly before and after printing and at other times is inert to light. If evaporation of the solvent is prevented, the record material may be wetted any time before being printed.

Various ways of forming an image are contemplated, one being a mask with the images to be printed cut out in stencil form so that the light may be projected through the stencil cut-outs onto the wet-sensitized record material. Another method is to subject the wet-sensitized record material to the beam of light emitted by an oscillograph type of galvanometer so as to leave a trace on the

paper of the data issuing from the galvanometer. A photographic transparent negative may be used as a light control means. Another way of projecting light onto the paper is to pass the paper in front of a screen of a cathode ray tube where the fluorescent trace of the electron beam will be recorded on the record material as it passes by.

The invention resides not only in the method of printing but in the record material itself, which may be made light-sensitive only just before printing as has been explained in a broad sense, and which will be explained further on in the specification more fully.

With these and other objects in view, the invention will be explained in the specification to follow with reference to the drawings.

Of the drawings:

FIG. 1 represents an apparatus for the utilization of stencils in forming images on the record material, the supply of record material itself having a solid particulate photo-chromic compound, or compounds, thereon in juxtaposition with microscopic pressure-rupturable capsules containing the volatile solvent liquid, which capsules are broken just prior to bringing the paper to the printing statio to release the solvent so the compound, or compounds, will become dissolved and thus light sensitive.

FIG. 2 shows apparatus for projecting light through stencils onto the record material which has been wetted by a bath of the volatile solvent for the photo-chromic compound just before coming to the printing station.

FIG. 3 shows apparatus used in conjunction with the stencil selector for printing on the record material, the record material being sprayed and wetted by the volatile liquid solvent just before coming to the printing station.

FIG. 4 shows a method for making a trace on the record material by means of a moving beam of light controlled by an oscillograph of the D'Arsonval type.

FIG. 5 shows the novel record material being passed in front of the screen of a cathode ray tube after being made sensitive to light.

FIGS. 6, 7, 8 and 9 are xanthylidene-anthrone or derivatives which are of the photo-chromic type useful in the invention when in solution.

FIGS. 10, 11, 12 and 13 are indolino-benzopyrylospiran derivative compounds which are also useful in practicing the invention when in solution.

General Description

The main, but not exclusive, feature of the invention is to provide record material which is sensitized to light just before coming to a printing station where patterns of light are projected thereon, to produce said patterns in color, said record material being desensitized to light after passing the printing station to fix the print of said image.

Starting with FIG. 1, which shows one form of the invention, there is provided a supply roll **20** of record material which is supported on an ordinary support shaft **21** and is transportable past a printing station indicated by the arrow **22**, to be taken up on a take-up roll **23**, journaled on another ordinary support shaft **24**. At least the surface of the record material on which the images are to be formed is supplied with minute particles of one or more of the compounds shown in FIGS. 6 to 13, inclusive, of the drawings. Although such compounds are representative, there are many others of similar type. The normal color of the compounds in FIGS. 6 to 9, inclusive, is a light yellow color, but turns to red when exposed to light having wave lengths less than 4000 angstrom units, and this photo-chromic reaction only occurs when the compounds are in liquid solution. After changing color through the exposure to light and drying of the images, the compound, or compounds, whether colored or not, are no longer sensitive to light of said wave lengths.

Likewise, the compounds of FIGS. 10 to 13, inclusive,

have a similar reaction to light of the wave lengths specified while in solution. These compounds of FIGS. 10 to 13, inclusive, are normally substantially colorless, turn to a deep blue color in solution when exposed to light of the mentioned wave lengths, and when in the colored form and dried by evaporation of the solvent, they appear black to the eye. When said compounds are dry, either in colored or uncolored form, they are inert to light.

Again referring to FIG. 1, the particular form of invention provides the surface of the web of supply roll **20**, which is to be exposed to light, with fine particles of the selected one or more of the compounds which are reactive to light, interspersed or having in juxtaposition thereto microscopic pressure-rupturable capsules containing a liquid voltatile solvent for the light-reactive compounds. Subsequent to printing, the volatile solvent quickly evaporates to leave the light-sensitive compound, or compounds, in their colored or uncolored state as a solid in which they are inert to further change by the light. These capsules are denoted by the speckles appearing in region **25** of the record material of FIG. 1. Just before passing the printing station **22**, the record material is subjected to the action of pressure rollers **26** and **27** which crush the capsules to release the solvent liquid which dissolves the particles of the light-sensitive compound, or compounds, so that when the record material comes to the printing station **22**, the compound, or compounds, in solution are sensitive to the light which is directed thereon by lamp **28** through a selectively operable stencil screen **29**, which screen is adjustable to bring the selected character to the printing station. After the exposure to light which may be brought about by the operation of light switch **30**, the record material is passed in the direction of the arrow **31** where, in passage before being taken up on the take-up roll **23**, the compound, or compounds, are dried by reason of the highly evaporable nature of the solvent. Petroleum-obtained solvents which may be used with the compounds of FIGS. 6 to 13, inclusive, and which are of the readily evaporable type, include ligroin, diethylbenzene, xylene, toluene, cyclohexane, petroleum ether and gasoline. Dibutyl ether also is a satisfactory solvent.

The distance between the printing station **22**, and the take-up roll **23** can be adjusted so as to allow ample time for the solvent to evaporate. It will be understood that not only is the printed image inert to light by becoming dry, but the background of the dried record material not exposed to light, by becoming dried, is also inert to light. The microscopic capsules may be made according to the teachings of U.S. Patent No. 2,800,457, which was issued July 23, 1957, on an application of Barrett K. Green and Lowell Schleicher. A sample step-by-step process taken from that patent, modified to the use of diethylbenzene, includes the emulsification of 80 grams of the diethylbenzene in a solution of 20 grams of gum arabic in 160 grams of water. A sol of 20 grams of pigskin gelatin, having an iso-electric point of pH 8, and 160 grams of water is made and mixed with the emulsion. The pH of the mixture of the emulsion and sol is adjusted to 6.5 and mixed with 500 grams of water, and then the pH is adjusted to 4.5. At this point, the gum arabic-gelatin complex, which forms, has deposited around the internal phase droplets of diethylbenzene and is still in liquid form, as the ingredients up to this point are kept at a temperature of 50° centigrade. At this point, while the ingredients are still at 50° centigrade, 3.8 grams of a solution of 37 percent formaldehyde in water is added as a hardening agent, and the temperature is lowered with agitation of the mixture until a temperature of 10° centigrade is reached, to gel the colloid-encased diethylbenzene droplets. After about thirty minutes of agitation at this lowered temperature, the pH is adjusted to 9, with a solution of 20 percent sodium hydroxide in water. The foregoing process produces, by a phenomenon known as coacervation, a profusion of microscopic pressure-rupturable oil-containing capsules suspended in a colloid-poor residual aqueous medium. The suspension of capsules may be coated directly onto the web to be printed and dried, and this coating may be done either before the photo-chromic compound is applied, at the same time, or after.

As has been said, the record material, after having passed through rollers **26** and **27**, the photo-chromic compound thereon is in solution, and consequently is light-sensitive at the printing station **22**. The volatility of the solvent may determine the relative distances of the supply roll and take-up roll from the printing station.

Referring to FIG. 2, which is another form of the invention, the supply roll **32**, which may be of plain paper, is passed through the bath **33**, consisting of a solution of the photo-chromic compound, or compounds, and a readily volatile solvent, and the paper is wet by the solution passed by the printing station, indicated by the arrow **34**, where it is subjected to light from the lamp **35** upon closing of the switch **36**. The print so made is dried, as in the first example, by evaporation of the solvent on its travel towards the take-up roll **38**. If it be desired to wet only one side of the paper, the record material from the supply roll **39** (FIG. 3) is passed under a spray head **40** which contains a solution of the photo-chromic compound, or compounds, in the selected evaporable solvent, thus sensitizing, by wetting, the one surface of the record material which is to be printed. As before, light is directed through stencil **41** at the printing station **42** to print the image upon the closing of the switch **43**, the drying taking place before the printed material is wound on the take-up roll **44** in the manner described in connection with the first example.

It should be understood that the principles outlined in Examples 1, 2 and 3 are not exhaustive as to the method of wetting record material with a solvent for the photo-chromic compound, or compounds, before being printed, nor is the stencil type of printing control vital to these examples as beams of light may be traced across the wet-sensitized paper at the printing station as shown in Example 4 next to be described.

In FIG. 4, a construction is shown for printing whereby the proper wave lengths of light are projected from a lamp **50** which directs a beam **51**, through a lens system **53**, onto a mirror **52** of an oscillograph of the D'Arsonval type, which light is reflected through lens system **53** onto record material **54** which is moved past a printing station in the direction of the arrow **55**, the wet-sensitization of said record material **54** being caused by the rupture of solvent-containing capsules by pressure rollers **56** and **57** in the manner described in connection with the example of FIG. 1.

In another form of the invention shown in FIG. 5, the record material **60** is passed in the direction of the arrow, after being wet-sensitized through pressure rollers **61** and **62**, across the fluorescent screen **63** of a cathode ray tube, there to be subjected to the trace of the electron beam to cause the image traced thereby to be printed on the record material **60**; thereafter the printed strip may be wound on take-up roll **64** after having dried on its travel from the printing station to the take-up roll.

Neither the particular specified solvents, the methods of wetting, or the means for projecting the light in the desired image onto the wet-sensitized record material, is to be deemed to limit the invention as the invention is directed to the presenting for a limited time at a printing station, a record material web wet-sensitized with a solution of the photo-chromic compound, or compounds, which thereby is in condition for being switched to the colored form upon exposure to the aforementioned wave lengths of light. By the term "light," as used in this specification, it is not intended to limit the electromagnetic radiation to light visible by the human eye, as ultraviolet light and even X-rays are useful to cause the color changes to take place in these compounds. The broad term of the word "light" as specified herein is justified by the definition of light as set forth in the publication, "The International Dictionary of Physics and Electronics,"

published in 1956 by D. Van Nostrand Company, Inc., of Princeton, New Jersey, Toronto, Canada, and London, England.

In addition to the methods described of controlling the light to produce patterns on the record material, as has been said, the color-forming compound on the record material may be wet only in desired areas by application of the solvent, or solvents, containing the color-forming compound, in desired areas by porous type or equivalent.

What is claimed is:

1. Record material including a web coated with solid particles of a chemical compound, which compound when dissolved in a liquid, changes to a distinctive hue upon being exposed to light having wave lengths of less than 4,000 A., said compound being inert to such color change by exposure to light when in the solid form; and said compound particles being in juxtaposition on the web to liquid solvent-containing pressure-rupturable capsules, so that if the capsules are ruptured, the adjacent compound particles will be dissolved and thus will become sensitive to light.

2. A process for printing including the steps of

(*a*) providing a record sheet base member coated with solid particles of a chemical compound interspersed with pressure-rupturable liquid-solvent-containing capsules, the compound assuming a distinctive color hue when irradiated with ultra-violet light while in liquid solution, said solvent being volatile and a solvent for the particles;

(*b*) rupturing the capsules to release the solvent and thereby dissolve the particles; and

(*c*) before the solvent evaporates irradiating the dissolved coating of particles with a pattern of ultra-violet light to depict data in the distinctive color, the evaporation of the solvent leaving the compound fixed in the distinctively colored pattern, where colored, and fixed in the uncolored form where not irradiated with the ultra-violet light.

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