

- [54] **PHOTOSENSITIVE SHEETS COMPRISING ORGANIC DYES AND SENSITIZERS**
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- [51] Int. Cl. **G03c 1/76; G03c 3/00; G03c 1/72**
- [58] Field of Search **96/89, 48 QP, 67**

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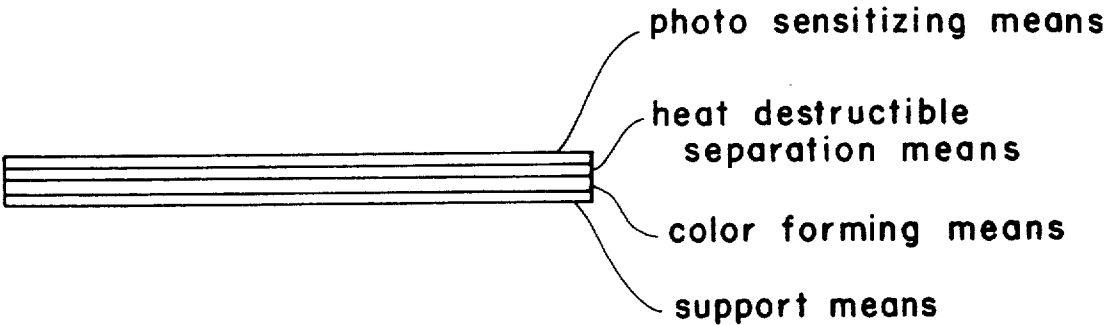
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[57] **ABSTRACT**

A copy sheet light stable under ordinary room temperature conditions includes a low cost substrate coated with a color forming means which is rendered photosensitive by a heat activatable sensitizing material included in the coating. A heat activatable desensitizer may also be present. The sensitizer is preferably encapsulated in a heat rupturable means which is destroyed upon heating the copy sheet to a predetermined threshold temperature. A copy system utilizing the copy sheet need include only a means for superimposing the original to be copied and the copy sheet and a heat and light source.

9 Claims, 5 Drawing Figures



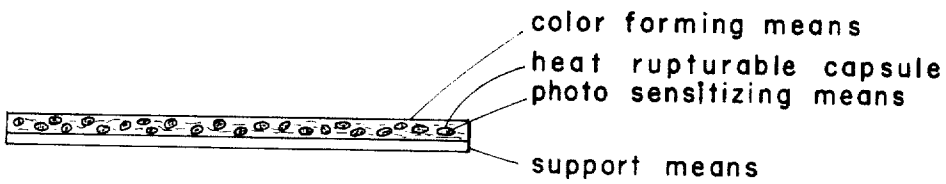
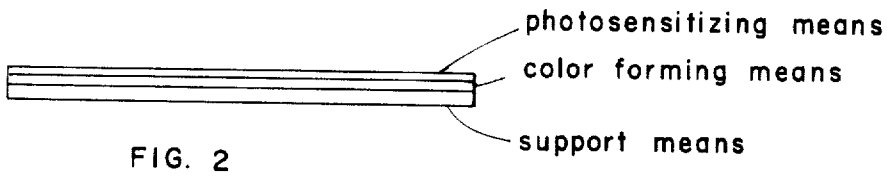
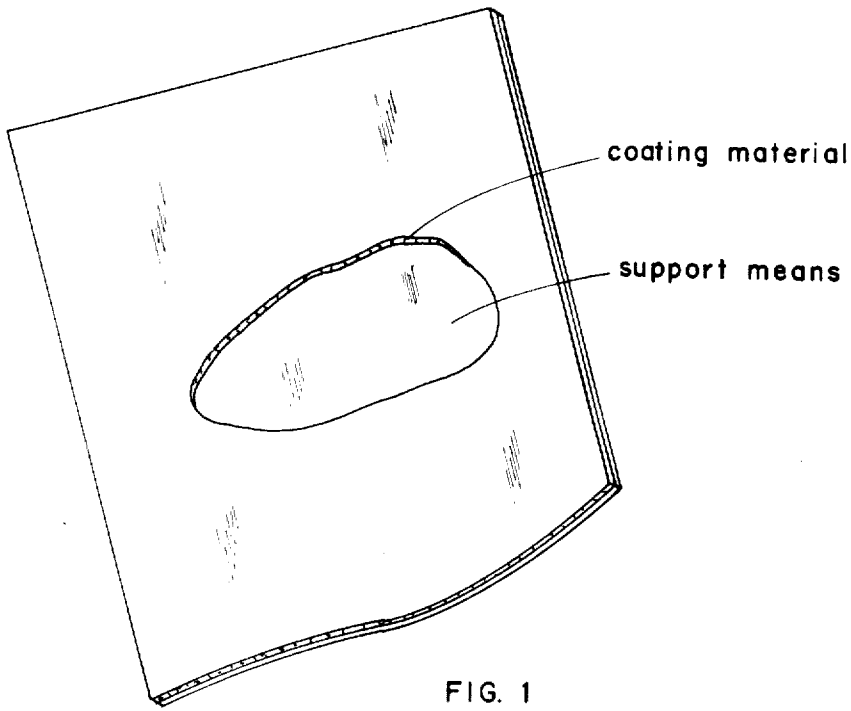


FIG. 3a

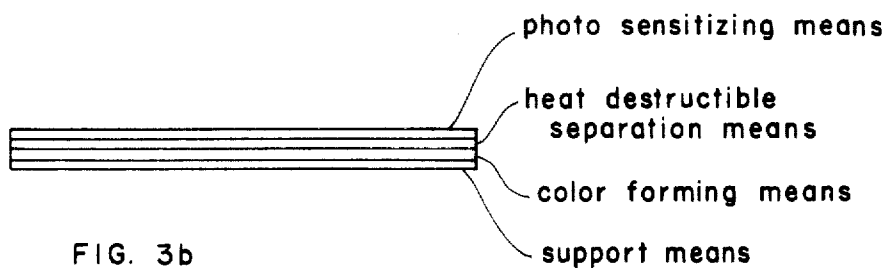


FIG. 3b

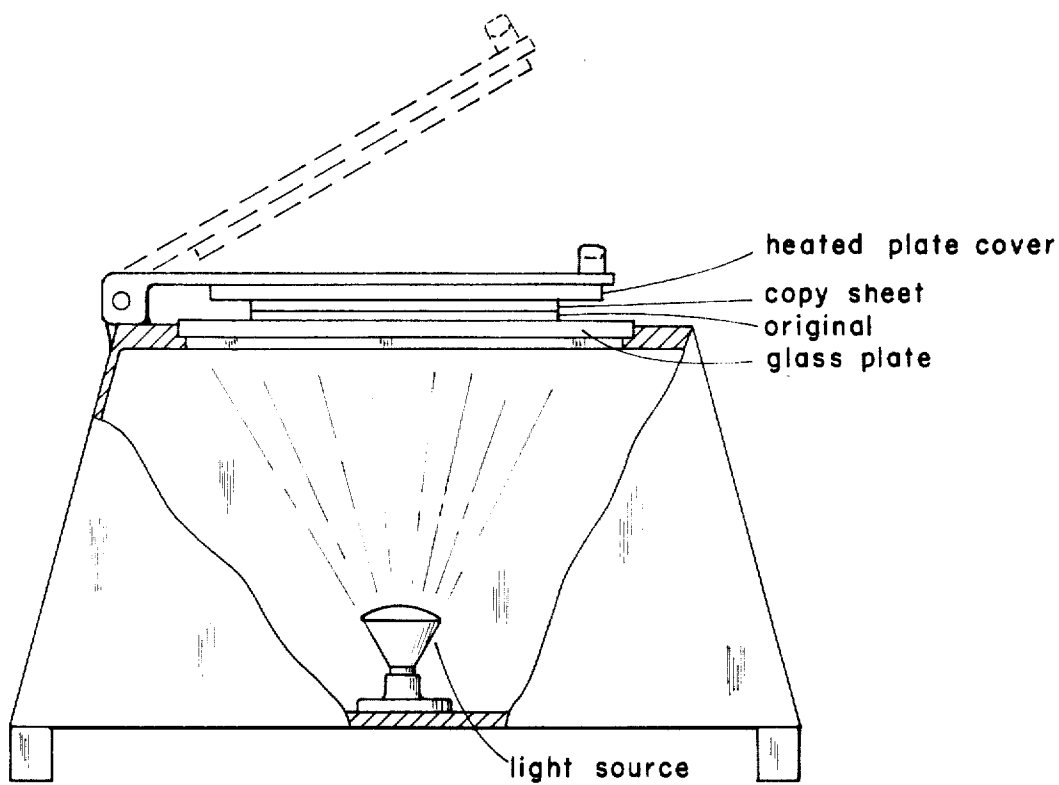


FIG. 4

PHOTOSENSITIVE SHEETS COMPRISING ORGANIC DYES AND SENSITIZERS

BACKGROUND OF THE INVENTION

This invention relates to copy sheets for copying or reproducing an image from an original and to methods for manufacturing the same. In particular, this invention is directed to copy sheets incorporating compositions which become photosensitive upon effective sensitization by heat activatable sensitizing compositions.

Present day industrial, business office, communications home and other activities often evidence a need for efficient and inexpensive copying methods and means. As a result many different copying techniques, particularly in the office copying field, have been suggested. However, no single approach has been fully satisfactory from all aspects.

The most widely accepted copying methods are those based on electrostatic techniques, particularly xerography. Nevertheless, the complexity and sensitivity of these procedures are well known. Presently available electrostatic equipment requires a relatively large initial investment in hardware and, in addition, individual copies are comparatively expensive. Furthermore, even with relative care, equipment of this type is easily damaged thus making maintenance costly and resulting in unproductive down time.

Photographic copying techniques utilizing light sensitive material which is developed subsequent to exposure to light generally result in wet copies and require the production of a negative. Also, individual copy costs with such processes are relatively high. More significantly, however, copy sheets utilized in processes of this type must be stored in darkened areas in a manner similar to photographic film, a requirement resulting in inconvenience and inefficiency in an ordinary office.

Other techniques employ heat sensitive copy sheets, in contrast to light sensitive copy sheets, to develop an image. These thermographic methods, while utilizing copy sheets that need not be stored in darkened areas and producing copies of relatively lesser expense, experience major disadvantages in the areas of image resolution. Since heat is readily diffused, blurring of the image with lack of sharp, well defined copy occurs. Due to the nature of the copy sheet material that must be used, fading, tearing and cracking of the copy sheets after long storage is also a problem.

The prior art has also suggested various combinations of photography and thermography including techniques identified as "thermophotography" and "photo-thermography." With the former, a heat sensitive copy sheet is exposed to differential heating as in conventional thermography; however, a latent image is produced which is subsequently developed by exposure to light. Although this procedure may render the copies more stable, the basic difficulties of poor resolution and inability to copy colored originals, inherent in thermographic procedures, is not obvious. In the reverse technique, photothermography, a copy sheet is first exposed to light, as in a conventional photographic procedure, and then developed by heat in contrast to more conventional chemical developing procedures. In this procedure, the original copy sheet used is still light sensitive thus still requiring troublesome storage in a darkened area.

The foregoing discussion, illustrative of the more commonly known procedures for copying and exem-

plary of the disadvantages associated therewith, demonstrates the need for improved copying techniques and means which overcome the drawbacks connected with those presently known.

SUMMARY OF THE INVENTION

The copying system and method of the present invention overcomes the disadvantages inherent in prior art techniques by providing inexpensive, ordinarily light stable copy sheets which are rendered sensitive to light upon heating above a predetermined threshold temperature. Upon sensitization, the copy sheets are capable of producing color images having good resolution by the use of relatively simple equipment which is comparatively easy to maintain.

The copy sheets and copying methods and means of the present invention provide reproductions having the high definition of detail usually resulting from photographic techniques, wherein light sensitive materials are the color image forming means, without the dark room storage and chemical development difficulties inherent in prior art uses of such techniques. At the same time, the present invention provides the advantages of prior art thermographic techniques since the copy sheets are stable under ambient light and temperature conditions and dry processing is possible. Moreover, good resolution of copies without fading and cracking of copies is achieved along with the ability to copy colored originals.

The copy sheets of this invention incorporate a color forming means which is rendered light sensitive by a sensitizing material. The sensitizing material becomes effectively active subsequent to the application of heat to the copy sheet at a predetermined threshold temperature. Subsequent to production of the desired image upon the copy sheet, the color forming means may be rendered desensitized by a desensitizing agent also included thereon. At ordinary storageroom conditions of light and temperature the unused copy sheets of this invention remain stable for extended periods of time. Subsequent to sensitization and exposure to light to provide an image, the color forming means may be desensitized to provide a stable copy having long storage life. Thus, it is an object of this invention to provide copy sheets which are light stable at ordinary ambient conditions, become photosensitive upon heating above a selected threshold temperature and produce a color image from an original.

A further object of this invention is the provision of a copying method and means utilizing light and heat while producing dry copies, exhibiting good resolution and stable storage life, from colored originals by using copy sheets stable to light and temperature under normal ambient conditions.

The copy sheets of this invention may have color forming means including a mixture of color forming compositions selected to produce multicolor copies which would reproduce originals of substantially any color. The color forming means compositions and sensitizing material compositions may be applied to a desired substrate and may be kept separated by heat destructable means. The copy sheets of this invention are readily usable in simplified apparatus involving little more than a light source, a glass plate and a heated plate to enclose the original and copy sheet.

A further object of this invention is the provision of a method for manufacturing photothermographic copy

sheets. An additional object is the provision of a copying technique utilizing simplified apparatus which is inexpensive and relatively maintenance free. Still other objects will be apparent from the following description.

BRIEF DESCRIPTION OF THE DRAWINGS

Several embodiments are illustrated in schematic form in the accompanying drawings as an aid to better understanding of the invention.

FIG. 1 is a schematic view of an embodiment of a copy sheet according to this invention;

FIG. 2 is an enlarged cross-sectional view through a portion of another embodiment of a copy sheet according to this invention;

FIGS. 3A and 3B are enlarged cross-sectional views through a portion of further embodiments of a copy sheet of this invention; and

FIG. 4 is a schematic side view, partly in section, showing the basic elements required for a copier system utilizing a copy sheet according to this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to FIG. 1, there is shown in schematic a copy sheet illustrative of this invention. Structurally, the copy sheet basically comprises a support element or substrate carrying a coating material as illustrated. The support element may be formed of any suitable substrate material such as paper, plastic sheets, metal foils, and other adaptable materials for specialized applications. Paper, because of its availability and low cost, is preferred and readily usable since the relatively low temperatures used herein are not harmful thereto.

The coating material includes a sensitizable color forming means and a heat activatable sensitizing means to photosensitize the color forming means. The color forming means includes a color forming composition which is selected so as to be substantially insensitive to light at ambient temperatures below about 35°C and, in particular instances, preferably below even somewhat higher temperatures, for example, 50°C, in the absence of a material which will activate it so as to be sensitive. The sensitizing means includes a composition which is ineffective to sensitize the color forming composition at ambient temperatures and is only activated to perform its sensitizing function at or above a threshold temperature greater than ambient temperatures, preferably a temperature between about 35°C and 175°C. This latter higher limit assures that unduly high temperatures which may possibly have a deleterious effect on the support element are not required.

The essential criteria for a color forming composition which will satisfy the requirements of this invention are light stability under ordinary ambient conditions and capacity for photosensitization, to provide a color change in areas exposed to light, by a sensitizing means which is activated at or above a threshold temperature beyond ambient temperatures. Knowing this, those skilled in the art may select materials which will satisfy these general requirements. For example, numerous organic dyes are known and available which fit within the restrictions defined by this invention.

Preferred dyes for use as the color forming composition in the copy sheets of this invention are the dyes of the Xanthene class. Xanthene dyes which have been found particularly effective include Erythrosin B (C.I. 45,430), Rhodamine B (C.I. 45,170), Rodamine 6G

(C.I. 45,160), Pyronine G (C.I. 45,005), Eosin B (C.I. 45,400), Uranine (C.I. 45,350), Rose Bengal (C.I. 45,435), C.I. Basic Red 11 (C.I. 45,050), Saccharein (C.I. 45,070), Rosamine (C.I. 45,090) and Rhodamine 12GM (C.I. 45,310).

The bridging carbon or aryl groups of the Xanthene dyes may be substituted by a —COR, —COOR, —SCN, —CN or —NO₂ group which will, for the purpose of the systems to be described in more detail hereinafter, decrease the light exposure time over the use of a more conventional Xanthene dye by approximately 50 percent. Examples of materials of this type may be found in U.S. Pat. Nos. 1,880,572 and 1,880,573.

Another class of particularly useful dyes are the Thiazines which show excellent printing characteristics, most of these dyes yielding a printing image with less than 10 seconds light exposure time. However, these dyes are slightly less desirable than the Xanthene dyes listed previously since, after yielding a printed image, Thiazine dyes require more care in stabilization. Specifically, Thiazine dyes tend to fade if exposed to a constant light source rich in ultraviolet light. Thus, they are preferably utilized when the duplicated copy would not be likely to be constantly exposed to such light. Exemplary Thiazine dyes which have been found to be particularly useful are Thionin (C.I. 52,00), Methylene Blue (C.I. 52,015), Methylene Green B (C.I. 52,020) and New Methylene Blue N (C.I. 52,030).

Another group of dyes useful as color forming means in accordance with the instant invention are the Triarylmethane dyes, particularly Malachite Green (C.I. 42,000), Victoria Blue B (C.I. 44,045), Crystal Violet (C.I. 42,555) and Erioglaurine (C.I. 42,090).

The Azine dyes are also useful according to the concepts of this invention, one particularly desirable material in this class being Phenosafranin (C.I. 50,200).

The Azo dyes are also found to be quite useful according to the instant invention although it has been found that dyes of this group bleach out faster and whiter if small quantities of sulfuric acid are included in the sensitizing phase. Exemplary materials within this class which are found to be particularly desirable include Tartrazine (Monoazo — C.I. 19,140) Chromotrope 2R (Monazo — C.I. 16,570), Ponceau 2R (Monazo — C.I. 16,150), Fast Red S (Monazo — C.I. 15,620), Thiazol Yellow G (Monazo — C.I. 19,540), Buffalo Black NBR (Disazo — C.I. 20,470), Sulfocyanin G (Disazo — C.I. 26,410) and Sulfocyanin 5R (Disazo — C.I. 26,360).

Anthraquinone dyes are also useful, but like the Azo dyes appear to function better in the presence of small quantities of sulfuric acid. Oil Blue N (C.I. 61,555) is an exemplary useful anthraquinone. However, this dye turns dark blue instead of bleaching, resulting in a blue-print type of copy.

Other dye classes which include useful members are Diphenylmethane (e.g., Auramine O — C.I. 41,000 and Auramine G — C.I. 41,005), Thiazol, Acridine (e.g., Phosphine — C.I. 46,045, Acridine Yellow — C.I. 46,025, Flaveosine — C.I. 46,060, Benzoflavine — C.I. 46,065 and Aurazin G — C.I. 46,030), and Oxazine (e.g., Capril Blue GN — C.I. 51,000, Capril Blue GON — C.I. 51,015, Galleocyanine — C.I. 51,030 and Aminogallamine Blue — C.I. 51,060).

The amount of color forming means utilized will vary depending upon the color and intensity derived in the

final product. The examples set forth hereinafter indicate the amount to be used based on the overall compositions set forth therein. Generally, the yellow dyes such as Tartrazine generally take almost twice as much quantitatively as the reds and blues in order to produce similar results. Nevertheless, those skilled in the art will be able to readily vary these compositions at will based on observations to produce desired results. Also, the selection of the color of the dye may be made dependent upon the particular application. In some instances the color forming composition is bleached out or rendered substantially colorless upon exposure to light after sensitization whereas in other instances it changes from one color to another in exposed areas. Additionally, as will be seen from the embodiments set forth hereinafter, it is possible to mix color forming compositions and thereby reproduce a colored original by a colored copy.

The color forming composition is rendered photosensitive by a suitably selected sensitizing material which is ineffective under ambient light and temperature conditions but becomes effective to photosensitize the color forming material upon heating above a threshold temperature. This desired characteristic is designated herein as "heat activatable" and those skilled in the art will be capable of readily selecting sensitizing means which meet this criteria. Preferable heat activatable sensitizing means for this invention are the substituted thioureas such as thiosinamine, diethylidene thiourea, diethyl allyl thiourea and thiourea dioxide. Other sensitizers such as hydrogen peroxide and anethole may be used with those dye materials known to be sensitive thereto. The sensitizing means may be present together with a color forming means or segregated therefrom only by a heat destructible segregation means such as the heat rupturable capsules similar to those employed in so-called carbonless copy papers made by National Cash Register Company. Alternatively, the sensitizing material may be formed in situ during the copying process when the copy sheet is heated above the threshold temperature, which is then that temperature at which the constituents chemically react to efficiently produce the desired sensitizing material. Thus, thiosinamine may be formed in situ by providing allyl mustard oil in combination with ethanol and ammonia together with the color forming composition in the coating. These constituents, when heated sufficiently will react in situ to form thiosinamine which will then function as the sensitizer for the color forming composition.

The embodiment illustrated in FIG. 1 shows the coating material incorporating both the color forming composition and the sensitizing material as a single layer. However, the support element can conveniently carry the coating material in the form of several separate layers as illustrated in FIG. 2. The structural embodiment of FIG. 2 is suitable where the sensitizing material is to be formed in situ since the reactive constituents can then be maintained in physical proximity to one another to facilitate formation of the sensitizer. The formed sensitizer will then lay adjacent the color forming means and photosensitize it. Where the sensitizing material is present in its final form, same for activation by heat, it may be mixed together with the color forming composition in a single layer as in FIG. 1.

The embodiment of FIG. 3A is particularly suitable when the color forming composition and sensitizing material are to be maintained segregated from one an-

other until the appropriate time by a heat destructible means. Thus, FIG. 3A shows the support element carrying a layer containing the color forming composition and a separate layer containing the sensitizing means in heat rupturable capsule form. The drawing is illustrative only and the sensitizing material layer encapsulation may be formed according to any well known techniques, such as those commonly used in the manufacture of so-called carbonless carbon paper and similar element, for example, that made by National Cash Register Company. The encapsulating medium material should be selected so as to be rupturable or destructible above the desired threshold temperature at which the copy sheet is to be utilized. In most instances this is preferably a temperature greater than about 35°C. Either the color forming composition or sensitizing material may be encapsulated in the heat rupturable material. Also, if desired, one layer with thorough mixing of the color forming composition and encapsulated sensitizing means may be employed. Alternatively, a layer of heat rupturable material such as a film or sheet may be interposed between the color forming composition and the sensitizing material so as to segregate the two as shown in FIG. 3B.

Heating the copy sheet above that threshold temperature which will result in either chemically activating the sensitizing material or destroying the heat destructible segregating means to release the chemically reactive sensitizing material results in the color forming composition becoming photosensitive due to the action of the sensitizing material. However, once the color forming composition has been exposed to light in formation of a copy image it is desirably desensitized and rendered light stable once again. In many instances, it is sufficient to merely reduce the temperature of the copy sheet, after exposure, to below the threshold temperature in order to render the copies stable, particularly stable to ordinary ambient conditions of light and temperature. For example, temperature reduction works well when anethole is the sensitizing material. Copy sheets sensitized with thiourea dioxide can be desensitized by continued heating without the incorporation of any separate desensitizing means. However, where some of the more sensitive dyes are used or the sensitizing means is formed in situ, as previously described, and remains active to continue to sensitize the color forming composition, it is desirable to include a separate desensitizing material. This is accomplished by incorporating certain compounds in the basic composition which render the sensitizer ineffective following the heating and image reproducing process. These desensitizing means may be activated either through the action of light or additional heat.

In a manner similar to that described for the other embodiments of this invention, the desensitizing material can be separated from other constituents of the coating material by segregation means which are heat destructible. Thus, the desensitizing means can be incorporated as a layer of heat rupturable capsules which are destroyed at a preselected temperature which is greater than the temperature necessary to activate the sensitizing material. Alternatively, an intermediate heat destructible layer can be used between the desensitizing means and the remainder of the coating material, this layer also being effectively destroyed at a temperature above that used to sensitize. The temperature differential between that necessary to activate the sensi-

tizing material and that necessary to activate the desensitizing material can conveniently be on the order to 5° to 7°C.

The desensitizing material will be selected so as to be effective with the color forming and sensitizing compositions used. Of wide application as a desensitizer in the compositions of this invention is sulfurous acid either in a capsulated form or separated by heat destructible layer or some other manner from the remainder of the coating material. Sulfurous acid may be present in its final form or formed in situ by incorporating sulfuryl chloride and pyridine in the coating material. With peroxide fast dyes, hydrogen peroxide in the presence of an alkali such as sodium hydroxide can be used as a desensitizing means, particularly with the sensitizers thiosinamine, or diethyl allyl thiourea. Other desensitizing compositions are acetyl chloride dissolved in acetone, for use with thiosinamine, Raney Nickel in alcoholic gelatin, benzoyl peroxide, lead hydroxide, mercuric oxide, ammoniacal silver nitrate, sodium bisulphite, acetic anhydride, alcoholic potassium hydroxide and sodium nitroprusside. Reinecke's Salt with copper irons such as Fehling's Solution A, iodine in ethanol, alkali bromide or iodide compounds, cuprous chloride and ammonium chloride can also be utilized as desensitizers. The foregoing desensitizers are useful for incorporation in coating material in encapsulated or other form which will cause them to be effectively released upon application of higher temperature.

When diethyl thiourea is the sensitizing compound, mercuric oxide is an effective desensitizer since diethyl urea, a relatively ineffective sensitizer, is formed. In the presence of ethylamine, triethylguanidine, an even less effective sensitizer, is formed. Anesole is an effective desensitizer and can be utilized in benzene solution in a gelatin overcoat. Light may be also used to desensitize the copy sheets and this can be done by the addition to the compositions of protoporphyrin when the sensitizing material is a substituted thiourea. The amount of protoporphyrin added is determined by the printing time desired. The substituted thiourea sensitizes the color forming composition causing it to bleach under the influence of light. However, as the light exposure continues the protoporphyrin photo-oxidizes the substituted thiourea to produce a material, which is ineffective as a sensitizer. For example, when thiosinamine is the sensitizer continued light exposure in the presence of protoporphyrin yields allyl formamidine sulfuric acid. In some instances continued radiation that is, irradiation of the basic composition without desensitizing compounds following exposure to light by, x-rays or gamma rays can desensitize by liberating sulfur from the sensitizing phase by a chain reaction.

Various modifications of the compositions can be made by incorporating components which catalyze or promote the systems to either reduced heating time, exposure time or reduced overall processing time.

The following examples are illustrative of the invention.

EXAMPLE 1

A binder is prepared consisting of 1 g of gelatin or nitrocellulose, but preferably a mixture of these two with 15 ml of absolute alcohol, i.e., ethanol. Certain dyes such as Benzopurpin 4B, Thiazol Yellow and Auracin, among others, require the presence of nitrocellulose in the binder.

To the above binder solution is added 1 – 3 mg of the color forming means, specifically for this example, Thionin, dissolved in 5 ml of absolute alcohol and the mix is held at the lowest possible temperature by continual stirring at 30°C.

To the above dye solution is added 5 ml of allyl mustard oil or synthetic allyl mustard oil (N.F. VIII such as manufactured by Magnus, Mabee & Reynard of New York) and 10 ml of 30 percent ammonia.

Paper stock, previously sized with 15 percent gelatin and 5 percent glycerin (although other sizing materials such as pectin sugar or can sugar may be included if desired), is coated with the above mixture and allowed to dry at ordinary room temperatures or below. The sizing basically reduces the porosity of the paper stock, although certain constituents necessary to copying according to the techniques of this invention may be included in the sizing.

EXAMPLE 2

The composition of Example 1 is basically a single layer system for the color forming means and the sensitizing means which acts in accordance with the basic concepts of this invention because the constituents of the thiosinamine require the presence of elevated temperatures in order to react to form the sensitizing means in situ. The stability of such copy sheets under ambient conditions can be further increased by utilizing a multilayer arrangement such as the following:

Fifteen ml of allyl mustard oil or synthetic allyl mustard oil is added to 15 ml alcoholic solution of a 15 percent gelatin. The mixture was run through a homogenizer at 35°C. and coated upon blank paper stock.

Two mg of Thionin in 5 ml of absolute alcohol is added to 10 ml of a 15 percent alcoholic gelatin solution and coated upon the paper which had previously been coated with the mustard oil solution.

Five ml of 30 percent ammonia is added to 10 ml of a 15 percent alcoholic gelatin solution and this in turn was coated on top of the two previous coatings.

EXAMPLE 3

Each of the above Examples incorporates the three basic constituents necessary to the formation of thiosinamine in situ, that is, oil of mustard, alcohol and ammonia. However, to even further stabilize the materials against accidental sensitization of the color forming composition under rather extreme ambient conditions, precursors of three basic constituents mentioned previously can be substituted therefor. For example, the 30 percent ammonia solution can be replaced by a mixture of 3 parts sal ammoniac and 1 part lime or a mixture of other reactable alkali hydroxides and ammonium salts. Upon heating as described for sensitization ammonia is evolved in situ which then reacts with the mustard oil and the alcohol to produce the sensitizing material, thiosinamine.

Alternatively, the ammonia may be replaced by urea in water, methanol or ethanol, a system including this substitution requiring temperatures of up to about 145°C. for approximately 45 seconds to form the sensitizing means to sensitize the color forming composition.

Another substitution for the ammonia is 1 part hexaminecobaltic chloride mixed with 3 parts distilled water. With such a system, the paper is initially stable to light at ordinary ambient conditions, although contin-

ued subjection of a paper including this material to light, especially in the ultraviolet or near ultraviolet region, results in some decomposition of the hexaminecobaltic chloride to yield a photosensitive paper. Thus, although such a paper will be relatively stable to accidental or short time exposure to light, long term storage is preferably in the dark.

A further substitution involves replacing the allyl mustard oil with a mixture of allyl iodide and potassium thiocyanate in absolute ethanol. This, however, requires that heating times be approximately doubled in order to form the sensitizer thiosinamine.

Of course, as hereinbefore disclosed, the thiosinamine may be present in the coating material in the final form, rather than being formed in situ, provided it is separated from the color forming means by a segregation means of the type discussed.

A yet further substitution can result in the formation, in situ, of the sensitizer diethyldene thiourea. For example, both the allyl mustard oil and the ammonia are replaced by thiourea ethyl oxalate. However, the paper stock must be previously saturated with aldehydeammonia or aldehydeammonia must be incorporated in a gelatin substrate. Heating produces diethyldene thiourea which in turn sensitizes the color forming means to the action of light. Exposure times for the material are preferably fifty percent greater than for the thiosinamine discussed above. Copy sheets having diethyldene thiourea as a sensitizer may exhibit some photosensitivity at ambient temperature after several days storage and thus are desirably used in application where they will not be subject to ambient light and temperature conditions for extended periods.

EXAMPLE 3A

Anethole is a sensitizer particularly useful with dyes such as Erythrosin B, Rose Bengal, Methylene Blue, Crystal Violet and Thionin. Preferably, blank paper stock is first floated in a solution of 15 percent gelatin in water and Thionin. The amount of dye in the system is determined by the shade of coloration desired and light to pale blue is preferred. The paper is then cooled, preferably to or below freezing, while the system dries. While maintaining the paper in the cold state, a coating of 100 percent anethole at or slightly above its melting point is applied by spraying or other suitable methods. The anethole solidifies as it strikes the paper. Several such spray coatings may be employed. Following solidification of the anethole, the paper may be maintained at ambient to cool temperatures until use, at which time, it is heated and exposed to light in the same manner as the copy sheet of Example 1.

The order of the two coatings may be reversed, if desired, but the effectiveness of this system depends upon the degree of separation of the two phases. Thus, an intermediate layer of gelatin or other material may be applied, if necessary, to further segregate the color forming means from the sensitizing means. Additionally, certain materials such as bergamot oil may be added to the anethole to raise its melting point and further stabilize the system.

EXAMPLE 4

Another substituted thiourea which is particularly effective as a sensitizing means according to this invention, due to the fact that it requires the application of heat in order to become effective, is thiourea dioxide.

This material may be prepared by cooling 30 percent hydrogen peroxide to -0.4°C . and slowly adding powdered thiourea until crystals separate from the solution. The crystals are filtered off and dried by air at approximately 25°C . since temperatures higher than about 30°C . at this point tend to render the sensitizer ineffective when subsequently used.

One gram of these crystals is added to 5 ml of distilled water at 20°C . and stirred at this temperature for 15 - 30 minutes. The solution will appear saturated since all of the crystals do not dissolve; however, they are left in solution. Ten ml of alcoholic 15 percent gelatin is added thereto and the temperature is raised to 25°C . Stirring is continued while a color forming means such as an alcoholic solution of 2 mg Thionin (Thiazine dyes are particularly good color forming means with this sensitizer) is added thereto.

Paper stock is coated with the foregoing and dried as quickly as possible at as low temperature as possible. Following low temperature drying, the paper is slowly raised to ambient temperatures. Such paper is stable if stored in a cool dry place and kept from drastic exposures to light or temperatures. Continued exposures to relatively high ambient temperatures will render this paper photosensitive.

EXAMPLE 5

The methods of the various examples set forth previously may be utilized with a mixture of dyes in a manner so as to bleach preferentially according to light reflected from, and passed through, colored matter to yield a colored reproduction resembling the original.

An example of such material could include any of the aforementioned sensitizing phases, but the following formula is given by way of illustration.

To 10 ml of alcoholic gelatin - nitrocellulose (1 gm of each) is added 5 ml of synthetic allyl mustard oil. The mixture is placed in a stirring apparatus and continuously stirred while the remainder of the components, including 10 ml of 30 percent ammonia, are added.

In a separate container, to 5 ml of absolute alcohol is added 4 mg phenanthrophenazonium methyl nitrate (yellow), 2 mg. Rosinduline 2B (magenta) and 2 mg Capril Blue G O N (cyan). When thoroughly dispersed, the dye solution is added to the above mix including the mustard oil and the ammonia. The completed mixture is then passed through a homogenizer and coated upon blank paper stock which is then dried at room temperatures or below.

Exposure to light follows heating at temperatures above about 40°C . at which point the dyes will bleach preferentially according to the color of the exposing light, and following exposure, will reflect according to the degree of bleaching.

A manner of using copy sheets formed according to this invention is illustrated schematically in FIG. 4 showing a copying device. The copying device includes a support, base and cover, all indicated generally. The base includes a transparent plate such as a glass plate and a light source therebeneath. Various light sources may be utilized although certain coating composition may provide better copies with different light sources. For example, a conventional 1500 watt sodium iodine lamp has been used quite satisfactorily with the copy sheets described in the examples given below although a 424 watt mercury vapor sun lamp developing ultravi-

olet energy in the spectrum bounded by the lines 2,800 – 3,200 Angstrom units wave length has been shown to provide better results. The type of light source can be readily selected by one skilled in the art depending on the particular coating composition and results desired.

In operation, the original to be copied is placed on the glass plate and a copy sheet superimposed with respect thereto. A heated metal plate is carried by the cover of the copying device and lowered into contact, with the back preferably, of the copy sheet. This function is to hold the copy sheet and original in contact with each other and with the glass plate. The heating means is activated to raise the temperature of the copy sheet and the coating material thereon to the desired threshold temperature which functions to activate the sensitizing material and sensitize the color forming composition. Preferably such temperature is above ordinary room ambient temperature and 35°C may be considered illustrative of a minimum threshold temperature for activation of the sensitizing means. However, the reaction may be speeded by decreasing heating times, and in some instances resolution increased, by utilizing higher temperatures. An optimum temperature for most embodiments of this invention has been found to be approximately 70°C. At this temperature the heating time need not be greater than about 20 seconds and may in some instances be shorter.

Once the sensitizing means has been activated the light source may be energized automatically and the copy sheet thereby exposed to the original and to the selected light pattern. At this temperature the color forming composition will have been sensitized and will change in color in areas exposed to light to produce an image corresponding to the light pattern. If the desensitizing material has been included in the copy sheet, heating plate may be automatically energized subsequent to exposure to raise the temperature slightly to that temperature which will activate the desensitizing means. Alternatively, the heat resulting from energizing the light source may raise the temperature of the copy sheet and material thereon sufficiently to activate the desensitizing means once the sensitizing means has performed its function. The device may be cooled down in conventional manner.

The copy sheets do not require heating to extremely high temperatures which might damage the copy and original and necessitate excessive requirements. Generally, the materials of this invention anticipate heat requirements yielding temperature no greater than about 130°C and in preferred embodiments, less than about 100°C. This enables the use of relatively inexpensive support elements such as ordinary paper and low temperature plastic sheets and economical heating equipment having low power requirements.

The following examples are illustrative of the means and method of using a copy sheet according to this invention.

EXAMPLE 6

A copy sheet formed according to the techniques of Example 1 is placed in contact with an original in a copying device such as is shown schematically in FIG. 4. Since the copy sheet is not light sensitive until its temperature has been elevated, the heated metal plate is energized to raise the temperature above ambient conditions. At approximately 40°C., the paper is preferably heated for approximately 50 seconds, whereas if

the temperature is raised to approximately 70°C., only 20 seconds is required for the heating phase. Utilizing a 1500 watt sodiumiodine lamp, the light source is then energized for approximately 10 seconds to expose the heated copy sheet to a light pattern corresponding to the original, although the time can be further limited or extended for different contrasts. The paper can be removed immediately after the light exposure, or, preferably, can remain in contact with the heating element for an additional 10–20 seconds to insure greater permanency.

The yield is a positive duplicate of the original.

Basically, the system defined hereinabove forms a copy in the following manner. When the composition is mixed and retained at ambient temperatures, the individual constituents remain relatively stable. However, on heating the paper, the oil of mustard, absolute alcohol and ammonia combine to form thiosinamine in situ which in turn sensitizes the dye to the action of the light.

EXAMPLE 7

A copy sheet formed according to Example 4 is utilized for printing by heating for approximately 10 seconds at from about 50° – 90°F. or for about 20 seconds at from about 40° – 50°C. Exposure to light for 20 seconds more or less depending upon the contrast desired will then produce an image corresponding to the exposure time.

With copy sheets formed in this manner, stabilization may be achieved within 5 seconds by bringing the paper to 130°C., by exposing the paper to steam for approximately 10 seconds or by dipping the paper in, or flooding the same with, boiling water. Another method of stabilizing such paper is to coat the same with peracetic acid following exposure, although care must be taken to avoid affecting the dye.

Various modifications may be made of the disclosed composition to catalyze or promote the system thereby reducing either the heating time or the exposure time, and in other instances thereby reducing the overall processing time while still producing an acceptable copy.

The composition of Example 1 can be further modified by inclusion in the gelatin sizing layer or in the gelating binder of 5 ml of 50.4 grams of rhombic sulfur dissolved in 100 grams of carbon disulfide. This additive promotes the reaction of the system, cutting all times by approximately 25 percent. Alternatively, if one gram of monomethylparamidophenyl sulfate is added to the coating mixture with the dye solution, the exposure time, with the system of Example 1, is decreased by about 50 percent to approximately 5 seconds.

With the system of Example 3A, particularly when the color forming means in Methylene Blue, Crystal Violet or Thionin, the addition of 0.5 g of sodium or potassium hydroxide to the dye phase will decrease light exposure time by about 30 percent. Generally, the inclusion of 1 – 5 grams of zinc oxide in the coating composition or in the sizing, of the various disclosed systems of this invention, decreases both the heating times and the exposure times by 15 – 20 percent.

Thus there has been disclosed herein copy sheets, processes and means for manufacturing and for utilizing the same in reproduction techniques, having advantages over the prior art.

I claim:

1. An ordinarily light stable copy sheet capable of being rendered sensitive to light upon heating above a predetermined threshold temperature comprising a support means having thereon a coating including a photo-sensitizable color forming organic dye insensitive to light at ambient temperatures without a sensitizing means but sensitive to light at ambient temperatures with a sensitizing means, a sensitizing means selected so as to be capable of sensitizing said color forming organic dye only upon the application of heat to the copy sheet, said sensitizing means being physically kept from effective contact with the color forming organic dye until the application of the heat to the copy sheet by a physical segregation means which is heat destructible at the threshold temperature and a desensitizing means for rendering the copy sheet light stable upon an application of heat greater than that necessary for sensitization.

2. An ordinarily light stable copy sheet capable of being rendered sensitive to light upon heating above a predetermined threshold temperature comprising a support means, a color forming means including an organic dye selected from the group consisting of xanthene, thiazine, triarylmethane, azine, azo, anthraquinone, diphenylmethane, thiazole, acridine and oxazine or a combination thereof and a composition which upon heating above the predetermined temperature will form, in situ, a photosensitizing material including a substituted thiourea selected from the group consisting of thiosinamine, diethylidene thiourea, diethyl allyl thiourea and thiourea dioxide, all carried on the support means.

3. A copy sheet as claimed in claim 2 further including a promoting composition which effectively reduces the time necessary to expose the copy sheet to light for producing an acceptable copy by 25 to 50 percent.

4. A copy sheet as claimed in claim 2 further including a desensitizing composition effectively activatable

at a temperature greater than the temperature which effectively activates the photosensitizing material and which renders the color forming means stable upon the application of heat to yield such greater temperature.

5. An ordinarily light stable copy sheet capable of being rendered photosensitive upon heating above a predetermined threshold temperature comprising a support means, a color forming composition including an organic dye selected from the group consisting of xanthene, thiazine, triarylmethane, azine, azo, anthraquinone, diphenylmethane, thiazole, acridine and oxazine and a photosensitizing material capable of becoming effectively active upon the application of heat including a component selected from the group consisting of substituted thioureas selected from the group consisting of thiosinamine, diethylidene thiourea, diethyl allyl thiourea and thiourea dioxide, hydrogen peroxide and anethole, all carried on the support means.

6. A copy sheet as claimed in claim 5 wherein the photosensitizing material is maintained segregated from sensitizing contact with the color forming composition by a heat destructible means which is effectively destroyed as a segregating means upon heating to a temperature just above the threshold temperature.

7. A copy sheet as claimed in claim 6 further including a desensitizing composition effectively activatable at a temperature greater than the temperature which effectively activates the photosensitizing material and which renders the color forming composition light stable upon the application of heat to yield such greater temperature.

8. A copy sheet as claimed in claim 7 wherein the desensitizing composition is sulfurous acid.

9. A copy sheet as claimed in claim 5 further including a promoting composition which effectively reduces the time necessary to expose the copy sheet to light for producing an acceptable copy by 25 to 50 percent.

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