Jan. 10, 1961 F. D. ALLEN ET AL 2,967,785

THERMOGRAPHIC COPYING MATERIAL

Filed Aug. 14, 1959

Fig. 1

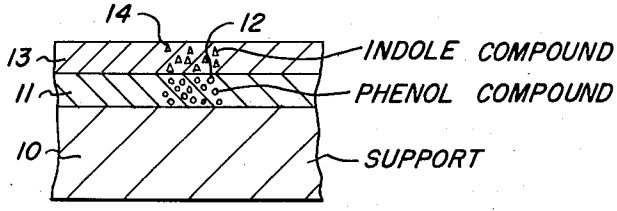


Fig. 2

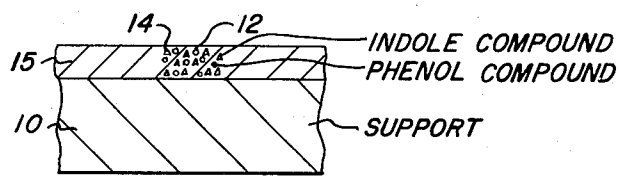
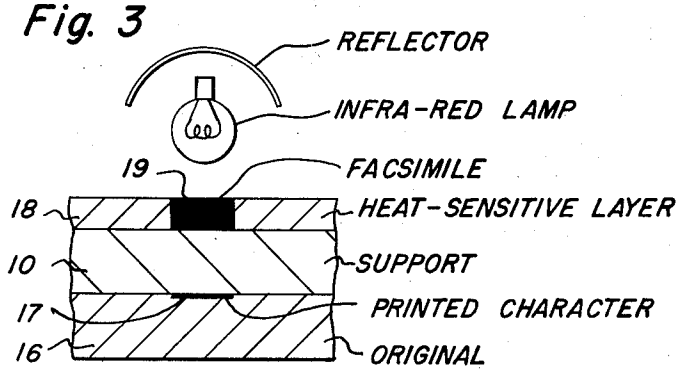


Fig. 3



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United States Patent Office 2,967,785 Patented Jan. 10, 1961

2,967,785

THERMOGRAPHIC COPYING MATERIAL

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Filed Aug. 14, 1959, Ser. No. 833,764

11 Claims. (Cl. 117—36)

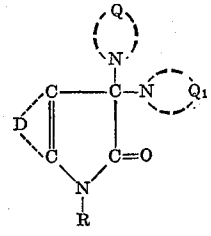
This invention relates to thermographic copying material and to a method of using the same.

Thermographic copying materials and methods have been previously described in a number of domestic and foreign patents. These materials frequently have the advantage of simplicity over certain photographic processes in that they produce a direct positive image of the original upon exposing the heat-sensitive or thermographic copying material in heat conductive association with a graphic original to radiant energy (e.g., infrared radiation). However, certain of these thermographic materials which have been previously used are only slightly sensitive to heat, and, consequently, excessively intense exposures are necessary in order to produce a facsimile copy. Other materials may not suffer from the aforementioned defect, but they are difficult to use, or handle, in that they contain metallic ions which might stain the material upon which the heat-sensitive layer is coated. Other thermographic or heat-sensitive materials have the disadvantage of being excessively sensitive to ordinary light. Other heat-sensitive, copying materials exhibit thermotrophy and lose their developed color when the heat-sensitive material is cooled to room temperature. It is immediately obvious that these heat-sensitive materials have only limited use, and, in certain instances, cannot be used at all if one desires to produce facsimile copies on a commercial scale.

While many of the thermographic methods of reproduction described in the prior art require that the plurality of heat-sensitive ingredients be maintained in physically-distinct relationship, it is not always necessary, according to our invention, to separate physically the heat-sensitive components in our compositions from one another.

The instant invention provides a convenient means of reproducing graphic originals by exposure of such originals in contact with certain heat-sensitive layers. The heat-sensitive layers useful in practicing our invention contain as an essential ingredient at least one indole derivative selected from those represented by the following general formula:

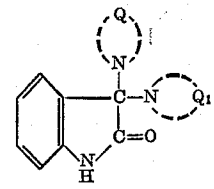
(I)



wherein R represents a hydrogen atom or an alkyl group, such as methyl, ethyl, etc., Q and Q_1 each represents the non-metallic atoms necessary to complete a monocyclic nucleus containing only one nitrogen atom, said nucleus containing an unsubstituted carbon atom in the 3-position with respect to said nitrogen atom, and D represents the atoms necessary to complete a benzene ring, which

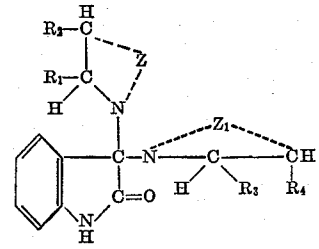
may be substituted by alkyl (e.g., methyl, ethyl, etc.), alkoxyl (methoxyl, ethoxyl, etc.), etc. Especially useful compounds embraced by Formula I above include those represented by the following general formula: :

(II)



wherein Q and Q_1 each have the values given above. Indole compounds embraced by Formula II above include those represented by the following general formula:

(IIa)



wherein R_1, R_2, R_3 and R_4 each represents a hydrogen atom or a lower alkyl group, e.g., methyl, ethyl, etc., and Z and Z_1 each represents the non-metallic atoms necessary to complete a monocyclic ring containing from 5 to 6 atoms in the ring, only one of said atoms in the monocyclic ring being a nitrogen atom. Typical monocyclic nuclei defined by Q, Q_1, Z and Z_1 include pyrrolidine, piperidine, morpholine, etc., as well as substituted derivatives thereof, including alkyl (e.g., methyl, ethyl, propyl, isopropyl, etc.), aryl (e.g., phenyl, tolyl, etc.), etc., derivatives. Our invention is briefly illustrated in the accompanying drawing, wherein

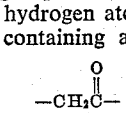
Figure 1 is a graphic reproduction of a heat-sensitive copying material which can be processed according to our invention, while

Figure 2 is a graphic reproduction of a second type of heat-sensitive material which can be processed according to our invention, and

Figure 3 is a graphic reproduction of one method of exposing the heat-sensitive copying material illustrated in Figure 2, the copying material being in heat-conductive association with an original.

Exposure of a copying sheet comprising at least one of the indole compounds represented by Formulas I, II, or II*a* in heat-conductive association with a graphic original as hereinafter described results in a substantially immediate, visible color change. Infrared radiant energy has been found to be particularly useful in practicing our invention, since such energy is readily obtainable from many illuminating sources.

It has been found that especially useful results can be obtained using at least one of the above-formulated indole compounds, if these indole compounds are associated wtih a compound containing a phenolic hydroxyl group, or an organic compound which contains an enolizable ketomethylene group, including 5-pyrazolone compounds containing a hydrogen atom in the 4-position, as well as compounds containing an extracyclic (acyclic)

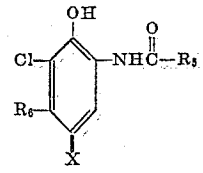


group. Use of one of these compounds containing a hydroxyl group or a potential hydroxyl group makes possible the use of thermographic reaction triggered at lower temperatures.

A particularly useful group of compounds containing

a phenolic hydroxyl group which can be employed in our invention includes compounds represented by the following general formula:

(III)



wherein R_5 represents an alkyl group or an aryl group (either of which may be further substituted by additional organic substituents), R_6 represents a hydrogen atom or an alkyl group such as methyl, ethyl, etc., and X represents a hydrogen atom, a halogen atom (e.g., chlorine, bromine, etc.), or a non-basic organic substituent (e.g., methyl, ethyl, etc.). The term "non-basic" is intended to define substituents other than an amino nitrogen-containing group.

The heat-sensitive material forming the heat-sensitive areas of the copying sheets of our invention can be coated on any suitable support, especially supports having low thermal conductivity, such as paper. In general, we prefer to use ordinary paper as a support for the heat-sensitive materials, and the paper can be transparent, translucent, or opaque. Of course, it is frequently desirable to use a support which transmits the exposing radiation, especially where the graphic original does not transmit such radiation (i.e., at least one of these should transmit radiation).

As indicated above, the indole compounds of Formulas I, II or II*a* can be used alone as the heat-sensitive materials, or they can be used in combination with the phenolic compounds, pyrazolone compounds, or compounds containing an acylic ketomethylene group. When the heat-sensitive indole compounds are used in combination with the phenolic compounds, pyrazolone compounds or compounds containing an acyclic ketomethylene group, the ratio of the components in the heat-sensitive system can vary, depending upon the particular materials, effects desired, etc. In some instances, it is desirable to incorporate the indole compounds in a layer distinct from the layer containing the phenolic compound, pyrazolone compound, or compound containing the acyclic ketomethylene group, since spontaneous color formation may occur if the two components are intimately associated in the same layer. In other instances, particularly with the compounds of Formula III, both components can be dispersed in a common solvent and coated onto the support from the same solution without any spontaneous color formation taking place.

It is thus apparent that the heat-sensitive layers useful in our invention can be prepared in several ways depending upon the use to which the heat-sensitive copying sheet is to be put. In its simplest form, the invention contemplates the application of a solution of at least one of the above-formulated indole compounds to the support, followed by evaporation of the solvent from the coating solution. In another variation of the invention, a second solution containing the second component (the phenolic compound, pyrazolone compound, or compound containing an extracyclic ketomethylene group) of the heat-sensitive material can be applied to the copying sheet and the solvent evaporated from this second coating solution. Of course, this method of operation cannot be employed if the second component undergoes substantially immediate reaction with the indole compound to produce a color product. Useful results have been obtained where the second solvent is selected so that only one of the components is soluble in that solvent, or the first component has too low a solubility to cause a harmful effect.

If desired, the components of the heat-sensitive system can be incorporated in an inert vehicle by simply adding these components to a solution of the inert vehicle. Useful inert vehicles include esters of cellulose, cellulose ethers (e.g., ethyl cellulose, etc.), polyvinyl resins (e.g., polyvinyl chloride, polystyrene, polymethylmethacrylate, polyvinyl acetate, as well as copolymers of these polymeric materials), etc. In some instances, it may be desirable for the reasons indicated above, to incorporate the components of the heat-sensitive system in separate contiguous layers. It is immaterial which layer is applied to the support first. The heat-sensitive copying sheets of our invention can be treated with solutions designed to provide a protective overcoat for the heat-sensitive layers. For instance, after application of the heat-sensitive material to the copying sheet, a solution of gelatin or other organic material can be applied over the heat-sensitive material. The layers of the heat-sensitive materials can contain inert pigments for the purpose of increasing the contrast of the final copy. For instance, an opaque layer may be applied over the heat-sensitive components, or an opaque layer may be applied on the reverse side of the copying sheet.

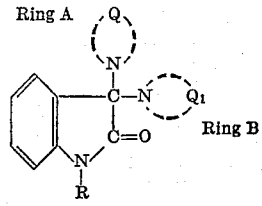
Typical compounds which can be employed together with the indole compounds of our invention in order to lower the reaction temperature include the following:

(1) 2-acetamidophenol
(2) 2-acetamido-4-chlorophenol
(3) 2-acetamido-4,6-dichlorophenol
(4) 2-acetamido-4,6-dichloro-5-methylphenol
(5) 2-benzamido-4,6-dichloro-5-methylphenol
(6) 2 - (2,4 - di - tert. - amylphenoxyacetamino) - 4,6-dichloro-5-methylphenol
(7) 6 - [α - {4 - [α - (2,4 - di - tert. - amylphenoxy)-butyramido]phenoxy} - acetamido] - 2,4 - dichloro-3-methylphenol
(8) 2-[α-(3-pentadecylphenoxy)butyramido]phenol
(9) α - (4 - tert. - amylphenoxy) - 2 - hydroxy - 5 - phenylazobutyranilide
(10) 2 - [α - 2,4 - di - tert. - amylphenoxybutyrylamino]-4,6-dichloro-5-methylphenol
(11) 4 - chloro - 1 - hydroxy - 2 - [α - (2,4 - di - tert.-amylphenoxy)-n-butyl]naphthamide
(12) 4' - (p - tert. - butylphenoxy) - 1 - hydroxy - 4-phenylazo-2-naphthanilide
(13) 1 - p - (p - tert - butylphenoxyphenyl) - 3 - [3 - (p-tert.-amylphenoxy)-benzoylamino]-5-pyrazolone
(14) 1 - (2,4,6 - trichlorophenyl) - 3 - pentadecyl - 4-chloro-5-pyrazolone
(15) 1 - (2,4,6 - trichlorophenyl) - 3 - pentadecyl - 4-bromo-5-pyrazolone
(16) 1 - (2,4,6 - trichlorophenyl) - 3 - [3' - (2'',4'' - di-tert. - amyl - phenoxyacetamido)benzamido] - 4 - (p-methoxyphenylazo)-5-pyrazolone
(17) 1 - (p - tert. - butylphenoxy)phenyl - 3 - α - (p-tert. - butylphenoxy) - propionylamino - 4 - (p - methoxyphenylazo)5-pyrazolone
(18) N - (4 - benzoylacetaminobenzenesulfonyl) - N-(γ-phenylpropyl)-p-toluidine
(19) α - (o - Methoxybenzoyl) - 4 - [α - (2,4 - di - tert.-amylphenoxy)-butyramido]acetanilide
(20) Gentisic acid
(21) Gentisanilide
(22) Tetrachlorohydroquinone
(23) 2,5-dichlorohydroquinone
(24) Monochlorohydroquinone
(25) 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane
(26) 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane
(27) Eethyl gentisate
(28) Methyl gentisate
(29) p-Hydroxybenzaldehyde
(30) Vanillin
(31) Resorcinol
(32) Halogenated phenols (mixture)

Typical indole compounds which can be employed in our invention include those listed in the following table. These indole compounds were prepared by dissolving isatin or an isatin derivative in a suitable organic solvent,

such as methanol, and bringing the solution to a boil. The appropriate secondary heterocyclic amine was added to the solution and the solution warmed on a steam cone until the desired product crystallized. The solution was then cooled to room temperature and the desired product separated by filtration, washed with solvent, such as methanol, and dried. The following table identifies indole compounds of Formula I and give the melting point and chemical analysis thereof.

(Formula I)



TABLE

Indole No.	R	Ring A	Ring B	M.P., °C.	Analysis					
					Calcd.			Found		
					C	H	N	C	H	N
1	H	piperidine	piperidine	222-4	72.3	8.4	14.1	72.2	8.4	14.2
2	H	3-methylpiperidine	3-methylpiperidine	150	73.5	8.9	12.9	73.2	8.8	12.6
3	H	4-methylpiperidine	4-methylpiperidine	154.6	73.5	8.9	12.9	73.1	9.0	12.8
4	H	4-ethylpiperidine	4-ethylpiperidine	145	74.4	9.3	11.8	75.2	9.2	------
5	H	4-phenylpiperidine	4-phenylpiperidine	104.7	------	------	------	------	------	------
6	H	morpholine	morpholine	184-5	63.4	7 0	13.8	63.6	7.3	14.1
7	H	pyrrolidine	pyrrolidine	134-6	70.9	7.8	15.5	70.8	8.0	15.6
8	H	morpholine	piperidine	205-8	67.8	7.7	13.9	68.2	7.7	13.7
9	H	pyrrolidine	do	152-5	71.6	8.1	14.7	71.8	8.0	14.9
10	H	do	morpholine	138-40	67.0	7.4	14.6	67.4	7.2	14.9
11	CH_3	morpholine	do	195	64.4	7.3	------	64.5	7.0	------
12	CH_3	piperidine	piperidine	154-7	73.0	8.7	13.4	73.3	8.3	13.4

The following examples will serve to illustrate a convenient method of manufacturing heat-sensitive copying sheets which can be thermographically exposed in heat-conductive association with a graphic original to produce excellent reproductions within a matter of a few seconds.

Example 1

Isatin-3-dipiperidide (Indole No. 1 of the above table) was dissolved in a solution of Vinylite VYLF resin, a copolymer of vinyl chloride and vinyl acetate (containing about 85 to 88% vinyl chloride and having a molecular weight of about 6000). The solution was then coated on a paper support and the solvent evaporated. The dry, heat-sensitive copying sheet was placed with the support side in contact with a graphic original and exposure to infrared radiation was made through the heat-sensitive layer, according to the method described in Miller et al. U.S. Patent 2,844,733, issued July 22, 1958. The graphic original, which contained line copy, such as typewritten characters, developed a heat pattern in those areas containing the line copy and caused the production of a blue image in the associated heat-sensitive copying material. The portions of the copying sheet which were in contact with areas of the original containing no typewritten characters did not undergo any visible change.

It may be desirable to stabilize the images produced according to the above process to ambient radiation. It has been found that the heat-sensitive material can be overcoated with a transparent layer containing an ultraviolet absorbing compound, such as 9-benzalfluorene, 5-benzal-3-n-cetyl - 2 - phenylimino - 4 - thiazolidone, etc., to achieve greater stability.

Example 2

Tetrachlorohydroquinone was dissolved in a solution of Vinylite VYLF in 2-butanone and the solution coated on ordinary paper. After drying, the layer was then overcoated with a polyvinyl butynal layer containing isatin-3-dipiperidide and the coating dried. The coated side of the paper was then exposed through a typewritten sheet to infrared radiation in a thermographic duplicating device of the type described in Miller U.S. Patent 2,740,895, issued December 22, 1953. A copy of the original was obtained as a blue image in a matter of seconds.

Example 3

Dichlorohydroquinone was dissolved in a solution of Vinylite VYLF resin as described in Example 2 and then coated on an ordinary paper support. The dry layer was then overcoated with a methanol solution of polyvinyl butyral resin containing isatin-3-dipiperidide. The coating was then dried and placed in contact with a graphic original and passed through a thermographic copying device as described in Example 2. A copy of the original was obtained as a blue image within a matter of seconds.

Example 4

A heat-sensitive copying paper was prepared exactly as described in Example 3 except that isatin-3-dimorpholide (Indole Compound No. 6) was employed in place of isatin-3-dipiperidide. An excellent copy of the graphic original was obtained as a blue image within a matter of seconds.

Example 5

A solution of 1.25 grams of isatin dimorpholide in 100 cc. of ethanol was added to a solution of 1.8 grams of 2-(2,4-di-tert.-amylphenoxyacetamino) - 4,6-dichloro-5-methylphenol (Phenol No. 6) in 100 cc. of ethanol. The solution remained clear after the addition of the phenol component. To the resulting solution was then added 100 cc. of a 5% solution of Ethocel (ethyl cellulose) in methanol. The resulting viscous solution was then coated on translucent paper stock and allowed to dry. The support side of the dry coating was placed in contact with a graphic original and passed through a thermographic copying device of the type described in U.S. Patent 2,740,895, so that the infrared radiation passed first through the heat-sensitive copying sheet and then to the graphic original. An excellent blue-on-white print of the graphic original was obtained.

Example 6

A solution of 1.25 grams of 3-piperidino-3-morpholino isatin in 100 cc. of methanol was added to 1.8 grams of the same phenol used in Example 5, dissolved in 25 cc. of ethanol. To the resulting clear solution were then added 100 cc. of a 5% solution of polyvinyl butyral in methanol. The resulting viscous solution was then coated on translucent paper stock and allowed to dry. The dry coating was then exposed to a graphic original as described in Example 5, yielding an excellent blue-on-white print.

The contrast of the prints was increased considerably by incorporating baryta or titanium dioxide in the polyvinyl butal coatings or by coating a separate solution of polyvinyl butal containing the white pigment over the heat-sensitive layer. If desired, the pigmented layer can be coated beneath the heat-sensitive layer or on the support side of the supporting surface.

Example 7

The following solutions were prepared:

A. 100 grams of a 10% solution of polystyrene in ethylene chloride.
B. 2.4 grams of indole compound No. 8 in 60 grams of ethylene chloride and 20 grams of methanol.
C. 2.0 grams of phenol compound No. 6 dissolved in 20 grams of ethylene chloride.

To the polystyrene solution were added 2.0 cc. of piperidine followed by the warm solution C. Solution B was warmed on the steam bath and filtered directly into the stirred polystyrene solution A. The mixture was then coated on a suitable translucent paper support and dried.

Exposure of the coating as described in Example 6 gave excellent reproduction of the graphic original as a blue-on-white image.

If desired, platsicizers, such as butylphthalate, or antioxidants, such as butylated hydroxyanisole can be added to the solutions in order to lower the triggering temperature of the thermographic product.

Example 8

The following solutions were prepared:

A. 50 grams of a 10% solution of polystyrene in benzene.
B. 1.2 grams of indole compounds No. 8 in 50 grams of benzene and 15 grams of methanol.
C. 1.0 gram of phenol compound No. 6 in 20 grams of benzene.
D. 1.0 cc. of piperidine.

The above ingredients were combined as described above in Example 7, and the resulting, clear viscous solution was coated on a translucent paper support and the coating dried.

Exposure of the dried coating as described above gave an excellent reproduction of a graphic original as a blue-on-white image. If desired, a matting agent, such as finely-divided silica or dispersed polyethylene, can be added to the above solutions in order to improve the surface characteristics of the product. The addition of these materials can conveniently be made at the time of addition of the piperidine.

Example 9

Component A.—A solution of 100 grams of 2-(2,4-ditert. - amylphenoxyacetamino) - 4,6-dichloro-5-methylphenol (Phenol No. 6) in 400 ccs. of ethyl acetate was filtered while hot and added to a solution of 1000 grams of 10% bone gelatin in water. To the solution were added 300 ccs. of distilled water and 160 ccs. of 5% alkanol B dispersing agent (sodium isobutyl-naphthalene sulfonate) at 40° C. After vigorous stirring, the dispersion was run through the colloid mill three times at a setting of 3 to 5 microns. The dispersion was chill-set at 40° F., noodled and dried on wire screens at 75° F. for two days under a vacuum of 25 inches and for an additional two days at 90° F. under a vacuum of 30 inches.

Component B.—A solution of 40 grams of 3-piperidino-3-morpholinoisatin in 1600 ccs. of 1,4-dioxane and 400 ccs. of methanol was filtered and poured into 8 liters of distilled water containing 80 ccs. of piperidine at a temperature of 8 to 10° C. After stirring for ½ hour, the precipitate was filtered by suction and washed three times on a filter with cold, distilled water, the last water wash containing 1% piperidine. The precipitate was then air-dried at room temperature leaving fine, creamy-white crystals almost uniformly of a size of ½ by 1 micron and melting at 203–206° C. The yield of pure crystals was about 80%.

A coating dispersion was made by reconstituting 100 grams of Component A in 1500 ccs. of distilled water at 40° C., adding 31 grams of reprecipitated Component B, stirring and running three times through the colloid mill at a setting of 2 to 5 microns. Just prior to coating, 5 ccs. of 5% saponin were added. For each 10 square feet of coating, 200 grams of the reconstituted dispersion were weighed out and 0.5 cc. of formalin added.

The reconstituted dispersion was coated on an ordinary onion skin paper, 10 inches wide, at the rate of 21 feet per minute. Best results were obtained with an air knife set a ½ inch. The coating averaged about 9 to 10 grams per square foot of emulsion or about 0.8 gram/square foot of solids. Exposure of the dried coating as described above gave an excellent reproduction of a graphic original as a blue-on-white image.

Our invention can be further illustrated by reference to the accompanying drawing in which Figure 1 is a cross-sectional view of a thermographic copying sheet wherein the heat sensitive components are incorporated in separate layers. In Figure 1, a suitable support 10 is coated with a layer 11 comprising a phenol compound 12. Over layer 11 is coated layer 13 comprising particles of indole compound 14.

Figure 2 is a cross-sectional view of a thermographic copying material wherein both heat-sensitive ingredients are incorporated in the same layer. In Figure 2, the copying material comprises a support 10 coated with a heat-sensitive layer 15 having dispersed therein a phenol compound 12 and an indole compound 14.

In Figure 3, there is illustrated an assembly suitable for producing facsimile copies using the particular heat-sensitive material depicted in Figure 2. In Figure 3, a graphic original 16, having printed material 17 thereon, is placed in contact with the uncoated surface of support 10 having coated thereon a heat-sensitive layer 18. Upon exposure of the assembly to infrared radiation supplied by any suitable source, such as an infrared lamp in combination with a suitable reflector, a facsimile copy 19 of the printed character of the original is reproduced as the darkened portion shown in the drawing.

If desired, the source of infrared radiation can be arranged so that the rear surface of the original receives the infrared radiation, although in such cases it may be convenient to have an insulating surface applied to the rear surface of the original in order to minimize loss of the heat generated in the infrared absorbing graphic pattern in the original. Alternatively, the heat-sensitive layer of the copying material can be placed in contact with the printed characters of the original (i.e., 17 of the drawing), and the assembly then exposed either from the side of the original or the rear side of the copying sheet. These adaptations are well understood by those skilled in the art and are illustrated in domestic and foreign patents. See, for example, Miller U.S. Patent 2,663,657, issued December 22, 1953.

When a colloidal binding agent is employed in combination with the indole compounds of our invention, alone or in combination with a phenol compound or a compound containing an enolizable keto-methylene group, the amount thereof can be varied in order to control the contrast of the resulting copy. These effects are well understood by those skilled in the art. Various esthetic effects can be produced by adding inert pigments or colorants to the colloidal dispersion or to one of the protected layers applied to the supporting surface or over the heat-sensitive material, as indicated above.

It has also been found that ninhydrine compounds can be employed in place of certain of the indole compounds of our invention to provide excellent thermographic copies. Such ninhydrine derivatives can be prepared by condensing one of the heterocyclic secondary

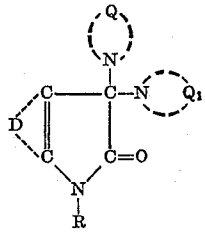
amines mentioned above, such as piperidine, morpholine, etc., together with ninhydrin.

The surface temperatures reached on the recording materials used in our invention can vary considerably, depending upon the particular indole compound employed and the presence or absence of an auxiliary color-forming component, such as a phenol compound, or a compound containing an enolizable ketomethylene group. The heat-sensitive materials used in our invention may undergo a color change at a temperature as low as about 45 to 50° C., or a considerably higher temperature, such as 125° C., may be required in order to effect the desired color change. Of course, where paper or some other support subject to distortion or charring is used, the selection of ingredients should be made so that the desired color change occurs at a temperature below the distortion or charring temperature of the support (which may comprise such materials as cellophane, cellulose acetate film, paper, wood, leather, etc.).

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

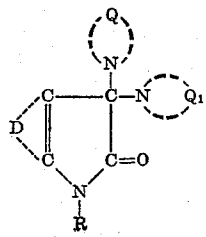
What we claim and desire to secure by Letters Patent of the United States is:

1. A heat-sensitive, copying sheet comprising a support and coated on said support a heat-sensitive area containing a compound selected from the class represented by the following general formula:



wherein R represents a member selected from the class consisting of a hydrogen atom and an alkyl group, Q and Q_1 each represents the non-metallic atoms necessary to complete a monocyclic nucleus containing only one nitrogen atom, said nucleus containing an unsubstituted carbon atom in the 3-position with respect to said nitrogen atom, and D represents the atoms necessary to complete a benzene ring, said heat-sensitive area being disposed on said support so that upon exposure of said heat-sensitive area to radiant energy in heat-conductive association with a pattern containing portions highly absorptive of said radiant energy and portions substantially nonabsorptive of said radiant energy, said heat-sensitive area undergoes a rapid color change only in those areas in heat conductive association with those areas highly absorptive of said radiant energy, said heat-sensitive, copying sheet being stable at room temperature, being substantially insensitive to visible radiations and being non-sticking at 125° C.

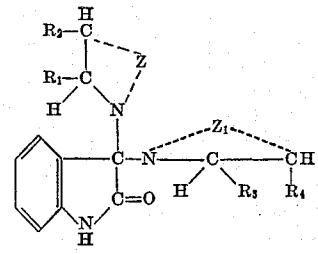
2. A heat-sensitive, copying sheet comprising a support and coated on said support a heat-sensitive area containing (*a*) a compound selected from those represented by the following general formula:



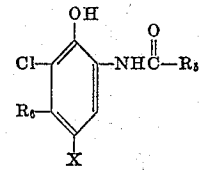
wherein R represents a member selected from the class consisting of a hydrogen atom and an alkyl group, Q and Q_1 each represents the non-metallic atoms necessary to complete a monocyclic nucleus containing only one nitrogen atom, said nucleus containing an unsubstituted carbon atom in the 3-position with respect to said nitrogen atom, and D represents the atoms necessary to complete a benzene ring and (*b*) a compound selected from the class consisting of phenols and compounds containing an enolizable keto group, said compounds (*a*) and (*b*) being maintained in physically-distinct relationship, so that upon exposure of said heat-sensitive area to radiant energy in heat-conductive association with a pattern containing portions highly absorptive of said radiant energy and portions substantially nonabsorptive of said radiant energy, said heat-sensitive area undergoes a rapid color change only in those areas in heat conductive association with those areas highly absorptive of said radiant energy, said heat-sensitive, copying sheet being stable at room temperature, being substantially insensitive to visible radiations and being non-sticking at 125° C.

3. A heat-sensitive copying sheet comprising a support and coated on said support a heat-sensitive area containing (*a*) a compound selected from those represented by the following general formula:

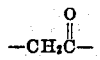
(IIa)



wherein R_1, R_2, R_3 and R_4 each represents a member selected from the class consisting of a hydrogen atom and a lower alkyl group, and Z and Z_1 each represents the non-metallic atoms necessary to complete a monocyclic ring containing from 5 to 6 atoms in the ring, only one of said atoms being a nitrogen atom, said ring containing an unsubstituted carbon atom in the 3-position with respect to said nitrogen atom, and (*b*) a compound selected from the class consisting of (1) those represented by the following general formula:



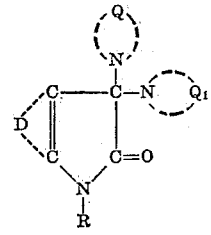
wherein R_5 represents a member selected from the class consisting of an alkyl group and an aryl group, R_6 represents a member selected from the class consisting of hydrogen atom and an alkyl group, and X represents a member selected from the class consisting of a hydrogen atom, a halogen atom, and a non-basic organic substituent, (2) a 5-pyrazolone compound containing a hydrogen atom in the 4-position and (3) a compound containing an acyclic



group, said compounds (*a*) and (*b*) being maintained in physically-distinct relationship, so that upon exposure of said heat-sensitive area to infrared energy in heat-conductive association with a pattern containing portions highly absorptive of said infrared energy and portions substantially nonabsorptive of said infrared energy, said heat-sensitive area undergoes a rapid color change only in those regions in heat-conductive association with those regions highly absorptive of said infrared energy, said

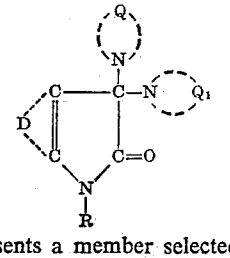
heat-conductive, copying sheet being stable at room temperature, being substantially insensitive to visible radiation and being non-sticking at 125° C.

4. A heat-sensitive, copying sheet comprising (1) a fibrous support and (2) a heat-sensitive colloid layer having dispersed therein particles of (*a*) a compound selected from those represented by the following general formula:



wherein R represents a member selected from the class consisting of a hydrogen atom and an alkyl group, Q and Q_1 each represents the non-metallic atoms necessary to complete a monocyclic nucleus containing only one nitrogen atom, said nucleus containing an unsubstituted carbon atom in the 3-position with respect to said nitrogen atom, and D represents the atoms necessary to complete a benzene ring, and particles of (*b*) a compound selected from the class consisting of phenols and compounds containing an enolizable keto group, said particles (*a*) and (*b*) being maintained in a physically-distinct relationship, so that upon exposure of said heat-sensitive, copying sheet to radiant energy in heat-conductive association with a pattern containing portions highly absorptive of said radiant energy and portions substantially non-absorptive of said radiant energy, said heat-sensitive copying sheet undergoes a rapid color change only in those areas in heat-conductive association with those areas highly absorptive of said radiant energy, said heat-sensitive copying sheet being stable at room temperature, being substantially insensitive to visible radiation and being substantially non-sticking at 125° C.

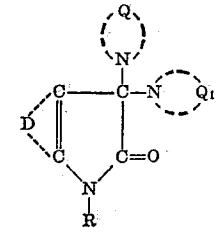
5. A heat-sensitive, copying sheet comprising (1) a thin paper support having low thermoconductivity, (2) a colloid layer having dispersed therein discrete particles of a compound selected from those represented by the following general formula:



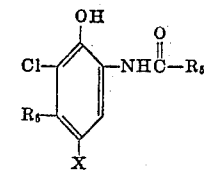
wherein R represents a member selected from the class consisting of a hydrogen atom and an alkyl group, Q and Q_1 each represents the non-metallic atoms necessary to complete a monocyclic nucleus containing only one nitrogen atom, said nucleus containing an unsubstituted carbon atom in the 3-position with respect to said nitrogen atom, and D represents the atoms necessary to complete a benzene ring, and contiguous to said colloid layer (2), a colloid layer having dispersed therein discrete particles of a compound selected from the class consisting of phenols and compounds containing an enolizable keto group, so that upon exposure of said heat sensitive copying sheet to radiant energy in heat-conductive association with a pattern containing portions highly absorptive of said radiant energy and portions substantially non-absorptive of said radiant energy, said heat-sensitive copying sheet undergoes a rapid color change only in those areas in heat-conductive association with those areas highly absorptive of said radiant energy, said heat-sensitive, copying sheet being stable at room temperature,

being substantially insensitive to visible radiation and being non-sticking at 125° C.

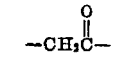
6. A heat-sensitive, copying sheet comprising (1) a thin paper support having low thermoconductivity and (2) a heat-sensitive colloid area having dispersed therein (*a*) discrete particles of a compound selected from those represented by the following general formula:



wherein R represents a member selected from the class consisting of a hydrogen atom and an alkyl group, Q and Q_1 each represents the non-metallic atoms necessary to complete a monocyclic nucleus containing only one nitrogen atom, said nucleus containing an unsubstituted carbon atom in the 3-position with respect to said nitrogen atom, and D represents the atoms necessary to complete a benzene ring, and (*b*) discrete particles of a compound selected from the class consisting of (A) those compounds represented by the following general formula:



wherein R_5 represents a member selected from the class consisting of an alkyl group and an aryl group, R_6 represents a member selected from the class consisting of a hydrogen atom and an alkyl group, and X represents a member selected from the class consisting of a hydrogen atom, a halogen atom, and a non-basic organic substituent, (B) a 5-pyrazolone compound containing a hydrogen atom in the 4-position, and (C) a compound containing an acyclic



group, said particles (*a*) and (*b*) being maintained in physically-distinct relationship, so that upon exposure of said heat-sensitive copying sheet to infra-red energy in heat-conductive association with a pattern containing portions highly absorptive of said infrared energy and portions substantially non-absorptive of said infrared energy, said heat-sensitive copying sheet undergoes a rapid color change only in those areas in heat-conductive, association with those regions highly absorptive of said infrared energy, said heat-conductive, copying sheet being stable at room temperature, being substantially insensitive to visible radiation and being non-sticking at 125° C.

7. A heat-sensitive, copying sheet, as defined in claim 4, wherein said particles (*a*) comprise isatin-3-dipiperidide and said particles (*b*) comprise tetrachlorohydroquinone.

8. A heat-sensitive, copying sheet, as defined in claim 4, wherein said particles (*a*) comprise isatin-3-dipiperidide and said particles (*b*) comprise dichlorohydroquinone.

9. A heat-sensitive, copying sheet, as defined in claim 4, wherein said particles (*a*) comprise isatin-3-dimorpholide and said particles (*b*) comprise 2-(2,4-di-tert.-amylphenoxyacetamino)-4,6-dichloro-5-methylphenol.

10. A heat-sensitive, copying sheet, as defined in claim

4, wherein said particles (*a*) comprise 3-piperidino-3-morpholinoisatin and said particles (*b*) comprise 2-(2,4-di-tert.-amylphenoxyacetamino)-4,6 - dichloro-5-methylphenol.

11. A heat-sensitive, copying sheet, as defined in claim 4, wherein said heat-sensitive copying sheet is provided with a protective outer layer which is substantially non-heat-sensitive at the temperatures employed in producing visible copies from said heat-sensitive copying sheet.

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