Aug. 30, 1960 E. G. HOWARD, JR 2,950,987

THERMALLY-SENSITIVE RECORDING ELEMENTS

Filed Oct. 28, 1958

FIG. 1



FIG. 2

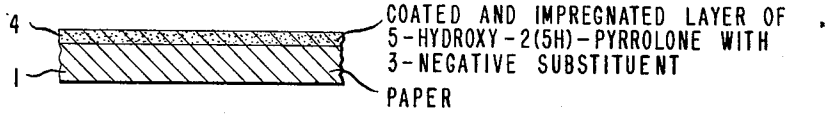


FIG. 3



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THERMALLY-SENSITIVE RECORDING ELEMENTS

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4 Claims. (Cl. 117—36)

This invention relates to new and improved thermally-sensitive recording elements including flexible elements which are especially useful for the direct formation of positive images.

A need exists for improved materials useful for the direct production of positive facsimile images, for instance, in the duplication of business correspondence, and the like. Considerable research effort has been given to the development of such processes, some of which are commercially practical. However, these new processes still have certain disadvantages. For instance, the diazo process is satisfactory only where relatively small numbers of copies are required. Furthermore, copies fade rather quickly and reproduction speed is relatively slow. In addition, only translucent originals with text on one side can be copied. Finally, damp processing or ammonia vapor is required.

A recently developed process is based on a sensitized dye-containing paper master which is selectively acted upon by light passed through the back thereof and reflected from the light and dark areas of the original. Duplication from the master hinges on transfer of dye by pressure after the exposed master has been activated in a suitable solution. Only a few copies can be made and critical judgment by the operator is required in determining proper exposure time, developing time, and roller pressure. The sensitive layer contains silver salt and consequently the paper is expensive.

Another process has been developed recently in which an electrically-charged, selenium-coated plate is substituted for a photographic film in a camera and an exposure made of the matter to be copied. Because of the photoconductive nature of the selenium, the plate in the exposed areas is no longer electrically charged, i.e., the charge leaks off in these areas. The exposed plate is then treated with a black, resinous developing powder which is preferentially taken up in the non-exposed, still charged areas. The powder is then transferred in this pattern to a sheet of paper and the final print fixed or fused by heat or solvent treatment. Certain disadvantages include the tendency of particles to adhere to the blank areas of the copy paper, resulting in dirty background and non-uniform areas, especially with large, solid colored areas. Since the process is basically electrostatic in nature, changes in humidity cause electrical leakage and loss of static charge on the plate or copy.

In another process, matter to be duplicated is placed in contact with a paper coated with a heat-activatable, color-forming composition and the combination is then exposed to infrared radiation. Since the printed or written

matter being duplicated is dark, it selectively absorbs and converts the light rays to heat. The special paper is thus heated, and the original printed or written matter is in effect burned into the copy paper. While this process is simple and has had considerable commercial use, it has certain significant limitations. For instance, the copy paper used in this process contains a sensitive layer which includes at least two interreactive solids in the form of fine particles—see, for instance, U.S. Patents 2,663,364, -5, -6, and -7. Since these materials must be maintained as discrete particles until heat from the copy causes at least one of the solids to melt and react with the other, the conditions permitted in application to the paper are rather limited.

Thus, it is substantially impossible to impregnate paper throughout with the materials, short of adding them to the paper-making compositions before the paper is made, which again, because of the necessity of maintaining separate particles of the interreactive solids, is exceedingly difficult. Accordingly, for practical reasons, the sensitive color-forming materials are deposited in a surface coating on preformed paper. Any solvent or binder compositions or the like involved in obtaining the surface coating of the sensitive layer must be chosen with care and an overall careful balance of properties maintained to avoid interaction of the color-forming particulate solids before the desired time.

Also, since the light-sensitive material in this process is necessarily present in a surface coating, a serious limitation as to the permitted quality of the support paper arises. Thus, in copying material containing text matter on both sides, the so-called "reflex copy method" must be used. In this method the copy paper is inserted between the source of illumination and the original with the light-sensitive side of the copy paper in direct contact with the surface of the original carrying the matter to be reproduced. The activating radiation passes through the copy sheet support and the sensitive coating, strikes the text matter of the original which is thereby heated as the infrared radiation is converted to heat, and the thus heated text prints back on the color-forming layer on the copy sheet. The copy sheet support must be substantially transparent to infrared radiation to permit formation of the copy, and to visible radiation to permit reading of the copy obtained. Papers with such properties are not only expensive but are flimsy or limp, making the copy difficult to handle and store. Since the papers should be visually highly transparent, in order to provide sufficient visual contrast they should contain a visually opaque coating over the sensitive layer. This double coating obviously adds to the cost.

There are two other methods of obtaining right reading positive copies from such copy papers. These involve positioning the original with text side down between the light source and the copy paper with coated side down, or positioning the original with text side up between the light source and the copy paper also with coated surface up. In both these variations, however, formation of the copy image requires transmission of the heat induced in the text matter either through the original support or through the copy support. In both instances, because of the necessary heat conductivity of both support materials, the copy images formed are either of unsatisfactorily low optical density or exhibit unsatis-

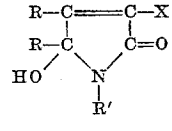
factory definition and fidelity, i.e., the image is either weak or else it is "spread." These techniques are not useable with originals carrying text matter on both sides.

An object of this invention is to provide new thermally-sensitive recording elements useful for the recording of data, indicia, images, etc. Another object is to provide such elements, e.g., films and papers, from which good positive images can be formed directly. Yet another object is to provide such elements which can be used to reproduce images from various image-bearing materials including process negatives, semi-opaque copy materials including paper with drawings, type matter or typewritten matter thereon. A further object is to provide such material which utilizes commercially available and economical chemicals. Still further objects will be apparent from the following description of the invention.

The novel thermally sensitive recording elements of this invention comprises a flexible sheet support embodying a stratum containing in an amount from 10 to about 500 mg./dm.^{2} a 5-hydroxy-2(5H)pyrrolone having in the 3-position a negative, i.e., a strong electron attractive, amino hydrogen-free group which, when attached to a carbon atom of a benzene ring, exerts a positive electrostatic polarizing effect on the adjacent carbon-to-carbon double bond of said benzene ring of at least 0.84×10^{-4} dynes, i.e., is strongly meta-directing (greater than 50%)—see Price, Chem. Rev. 29, 58 (1941) and pages 13–29, "Reactions at Carbon-Carbon Double Bonds," Price, Interscience (1946).

Especially useful 5-hydroxy-2(5H)-pyrrolones for the elements of this invention are those wherein the ring nitrogen is hydrogen-bearing, the negative functional group in the 3-position is carboxyl or a group hydrolyzable thereto, and any substituents in the 4- and 5-positions are hydrocarbyl radicals wherein the alpha-carbon of each such radial carries at least two hydrogens. The preferred elements comprise paper in any of the normal forms having distributed therethrough from 10 to 500 mg./dm.^{2} of a 3-cyano-2(5H)-pyrrolone wherein the 4- and 5-positions are linked directly to hydrocarbyl radicals wherein the alpha-carbon of each such radical carries at least two hydrogens, which radicals may be joined together, an outstanding substituted pyrrolone being 3-cyano-5-hydroxy-4,5-dimethyl-2(5H)-pyrrolone.

The 5-hydroxy-2-pyrrolones having a negative substituent in the 3-position useful in accordance with the invention can be represented by the general formula:



wherein X is a negative substituent selected from the group consisting of quaternary onium and inium salts and carboxyl groups and groups hydrolyzable thereto, R' is a member selected from the group consisting of hydrogen and monovalent hydrocarbon radicals of no more than 10 carbon atoms, the R's when separate can be the same or different and are each selected from the group consisting of hydrogen, alkyl of 1 through 10 carbon atoms, cycloalkyl of 4 through 6 carbon atoms, aryl of 6 through 10 carbon atoms and alkaryl of 7 through 10 carbon atoms and the R's when together constitute a single divalent hydrocarbon radical that forms with the 4- and 5-carbon atoms of the pyrrolone ring a carbocyclic radical of 5 to 7 ring atoms, said substituted pyrrolones being further characterized in that only one of the 4- and 5-carbon atoms have an aromatic substituent.

Compounds having the above structural formula are disclosed in and can be prepared by the method described in Howard U.S. Patent 2,824,110 of Feb. 18, 1958.

The flexible support of the thermally sensitive permanent image-recording elements of the invention can vary widely in constitution but should not be a good conductor of heat because the image is produced thermally and a heat-conductive support, e.g., a metal foil or a self-supporting film or layer containing an appreciable quantity of powdered metal, would prevent the formation of a sharp image. In general, the flexible support can be composed of an organic polymeric material having a softening point above the temperature at which the thermographic image is formed, e.g., about 150–225° C. Suitable such polymeric materials include paper, thin cardboard, self-supporting films composed of cellulose and regenerated cellulose; cellulose ethers, e.g., methyl cellulose, ethyl cellulose of low substitution; cellulose esters, e.g., cellulose triacetate; synthetic macromolecular polymers, including polyvinyl acetals, e.g., polyvinyl formal; polyvinyl esters, e.g., polyvinyl acetate of low acetate content, and proteins, e.g., gelatin. Instead of films the foregoing synthetic polymers can be layers on paper or another support. The supports can be used in the form of films and in the form of felted sheets made from fibers of the cellulosic or other polymeric materials referred to above. Flexible supports made from the foregoing materials as is well known, are not good conductors of heat but have low heat conductivity.

For some uses the flexible sheet support should be infrared-transparent to permit the formation of the color image in depth and in, for instance, reflex copying to permit the satisfactory development of the image on the reverse surface or within the sheet. For other uses, for instance, recording paper for a suitably driven hot stylus, the flexible sheet support can be infrared opaque. The flexible sheet support can be transparent or opaque to visible light. For contrast purposes, it is generally desirable that the flexible sheet support be somewhat opaque to visible light and, ideally, should exhibit a contrast color to the color of the thermographic image.

The 5-hydroxy-2(5H)-pyrrolone carrying a strong electron attractive group in the 3-position, can be brought into the necessary operative association with the flexible sheet support by any of the various conventional coating and impregnating procedures. When the flexible sheet support used is a film of a polymer which is not easily penetrated by the thermographic agent or solutions thereof, for instance, a preformed sheet of a condensation polymer, e.g., polyhexamethyleneadipamide, the hydroxypyrrolone in solution in a suitable solvent at the desired concentration and in combination with a suitable protective binder which is preferably adherent to the substrate, e.g., gelatin, is topcoated on the polyhexamethyleneadipamide base and the solvent allowed to evaporate. There is thus obtained a polyhexamethyleneadipamide base with a layer of the desired thickness of the functionally substituted 5-hydroxy-2(5H)-pyrrolone protected by the gelatin binder. A convenient way to achieve a "deep" image is to dissolve the polymeric material forming the flexible sheet support in a suitable solvent and to add thereto the required amount of the functionally substituted 5-hydroxy-2(5H)-pyrrolone to give the desired concentration at the desired thickness and then to cast the solution by conventional film-casting techniques and allow the solvent to evaporate. Various binders can be used in place of gelatin. Suitable binders include natural and synthetic organic colloids having protective colloid properties, e.g., casein, polyvinyl alcohol, polyvinyl acetals and esters containing unsubstituted vinyl alcohol units, and polyvinyl pyrollidone.

In those instances where the flexible sheet support is absorbent of, or easily penetrated by, suitable solvents for the 3-substituted 5-hydroxy-2(5H)-pyrrolone, for instance, in the case of most of the commercially available paper stocks, it is necessary only to dip the paper stock in a solution of the 3-substituted 5-hydroxy-2(5H)-pyrrolone at the desired concentration and allowed the

solution to impregnate and be absorbed by the paper. Upon evaporation of the solvent, the 5-hydroxy-2(5H)-pyrrolone will be substantially uniformly and homogeneously distributed throughout the thickness of the paper. The resultant thermographic image obtained from such an impregnated paper is "deep" in that it is formed throughout the thickness of the paper. Thus, a conventional onionskin paper can be used instead of the thin translucent type required in the prior art method where the sensitive coating is on the back surface of the sheet. The higher visual opacity of the onionskin paper as well as its greater stiffness makes the copies much more attractive than previous types.

Representative thermally-sensitive image recording elements described above and in the following examples are shown in the attached drawing which forms a part of this application. In the drawing

Fig. 1 is an enlarged sectional view of a flexible paper base element bearing a gelatin/barium sulfate coating and a layer of a substituted pyrrolone;

Fig. 2 is a similar view of another element comprising flexible paper coated and impregnated with such a pyrrolone; and

Fig. 3 is a similar view of a flexible polymeric film bearing a coating of gelatin containing such a pyrrolone.

Referring now to the drawing, in Fig. 1 the flexible paper support **1** has on its upper surface a barium sulfate/gelatin coating **2** which in turn is coated with a layer **3** of a 5-hydroxy-2-(5H)pyrrolone having a negative substituent in the 3-position.

In Fig. 2 a flexible paper support **1** is coated and impregnated with a 5-hydroxy-2-(5H)pyrrolone having a negative substituent in the 3-position to form layer **4**.

The film element of Fig. 3 has a flexible polymeric film support **5** bearing a layer **6** composed of gelatin containing 5-hydroxy-2-(5H)pyrrolone having a negative substituent in the 3-poistion.

The following examples in which the parts given are by weight are submitted to illustrate further but not to limit the present invention.

EXAMPLE I

A 1.5% solution of 3-cyano-4,5-dimethyl-5-hydroxy-2(5H)-pyrrolone in water was applied to gelatin-barium sulfate-coated photographic paper stock to give a coating weight of 30 mg. of the pyrrolone/dm.^{2} of paper surface. The coating did not change the appearance of the paper in any way. A portion of the coated paper was pressed for five seconds onto a copper electrotype heated to 185–200° C. A clean, sharp magenta image of the type matter on the electrotype was thereby obtained. At 185° C. the color was a pink-magenta, while at 200° C. a darker, more bluish magenta was obtained.

To test the light stability of the colored form, a portion of such an image was shielded with aluminum foil and the unshielded portion exposed to the radiation from a commercial, transformer operated 100-watt mercury vapor sunlamp for six hours at a distance of four inches. In this time the original bluish magenta had faded somewhat to a brownish magenta and the white background, i.e., the portions having no thermal image, had become a cream color. The image was still sharp and easily legible, however.

EXAMPLE II

Aqueous solutions of 3-cyano-4,5-dimethyl-5-hydroxy-2(5H)-pyrrolone ranging in concentration from approximately 2% to 16% were applied by brush to additional samples of the photographic paper stock of Example I to give pyrrolone coating weights in the range 25–400 mg./dm.^{2}. A powdery layer of the hydroxypyrrolone crystals was present on the surface of the dry sheets with coating weights in excess of 200 mg./dm.^{2}. At lower coating weights the hydroxypyrrolone appeared to be completely absorbed into the gelatin-barium sulfate surface of the paper. Strips of the various coatings were pressed against a nickel-surfaced electrotype for approximately five seconds at temperatures ranging from 100° to over 200° C. and the appearance of the image noted. Little or no color showed at temperatures below 130° C. Data are given in Table 1, following.

Table I

Coating Weight mg./dm.^{2}	Temperature, ° C.	Image Appearance
25	146	Faint trace of magenta.
	154	Do.
	165	Light magenta.
	177	Dark. magenta
	202	Do.
50	140	Faint magenta.
	146	Do.
	154	Magenta.
	165	Deep magenta.
	177	Do.
100	146	Faint brownish magenta.
	154	Brownish magenta.
	165	Dark bluish magenta.
	177	Do.
200	146	Brownish magenta.
	154	Do.
	165	Blue-black.
	177	Do.
400	134	Irregular brown-black.
	146	Do.
	165	Blue-black.
	177	Do.

EXAMPLE III

Other 3-functionally substituted 5-hydroxy-2(5H)-pyrrolones listed in Table II below were applied from ethanolic solution to additional samples of the barium sulfate-gelatin surfaced photographic paper stock of Example I to give coating weights of approximately 50 mg./dm.^{2}. The dry coatings were then pressed against a heated electrotype for five seconds at various temperatures with the results as indicated in Table II. The negative result with 3-cyano-4,5-diphenyl-5-hydroxy-2(5H)-pyrrolone shows the selectivity of the nature of the invention.

Table II

Compound	Color of Coating	Marking Temp., °C., 5 Sec.	Appearance of Image Text
3-Ethoxycarbonyl-5-hydroxy-4, 5-dimethyl-2 (5H)-pyrrolone	Colorless	162	Barely perceptible.
		175	Faint brown.
		183	Do.
		195	Deep brown.
3-Cyano-5-hydroxy-4,5-pentamethylene-2 (5H)-pyrrolone	do	162	Barely perceptible.
		175	Faint reddish brown.
		183	Brick red—low contrast.
		195	Brick red—high contrast.
3-Thiocarbamoyl-5-hydroxy-4, 5-dimethyl-2 (5H)-pyrrolone	Pale yellow	162	Barely perceptible.
		175	Faint gray.
		183	Gray.
		195	Dark gray-violet.
3-Pyridinium-5-hydroxy-4,5-dimethyl-2(5H)-pyrrolone chloride	Colorless	162	Barely perceptible.
		175	Faint brown.
		183	Light brown.
		195	Light brown—improved contrast.
3-Cyano-5-hydroxy-4,5-dimethyl-2(5H)-pyrrolone	do	146	Barely perceptible pinkish.
		154	
		165	Faint magenta.
		195	Deep magenta.
3-Cyano-5-hydroxy-4, 5-diphenyl-2(5H)-pyrrolone	do		Do.
			No image up to temperatures which cause browning of the paper stock itself.

EXAMPLE IV

A solution of one part of 3-cyano-4,5-dimethyl-5-hydroxy-2(5H)-pyrrolone dissolved in 20 parts of a 5% aqueous solution of low molecular weight, completely hydrolyzed polyvinyl alcohol was coated onto smooth onionskin paper (substance 9) so that the coating weight of the hydroxypyrrolone was approximately 40 mg./dm.^{2}. The coated paper, after drying, was essentially unchanged in appearance except for a slight gloss. When this paper was pressed onto a hot electrotype for five seconds at 195° C., a deep magenta image of the type matter was formed. A piece of the paper with its coated side against a printed text was placed in a commercial thermographic copying machine so that the uncoated side of the paper was toward the light source. No image was obtained at the regular scanning rate, but when the machine was modified to reduce the rate to about ⅓ of normal so as to increase the exposure about threefold, a magenta image of the printed text was visible on the coated paper. Because of the penetration of the paper by the hydroxypyrrolone, the image was formed within the paper fibers as well as on the surface adjacent to the original. This allowed a right-reading image to be visible on the uncoated side without the use of an expensive tracing paper stock for the support.

EXAMPLE V

A solution of one part of low-viscosity polyvinyl butyral and three parts of 3-cyano-4,5-dimethyl-5-hydroxy-2(5H)-pyrrolone in 31 parts of ethanol was applied to an essentially grainless tracing paper stock to give a pyrrollone coating weight of 75–100 mg./dm.^{2}. The coating gave a glossy surface to the paper. Pressing the coated paper onto a heated electrotype for 15 sec. at temperatures of 145–180° C. gave brownish to brownish-black reproductions of the text on the electrotype. There was a slight tendency for the butyral carrier to stick to the electrotype. When tested in a commercial thermographic copying machine modified to reduce the scanning rate to about 20% of the original, a brownish black image was obtained. Again there was some sticking because the temperature attained exceeded the softening point of the polyvinyl butyral binder.

EXAMPLE VI

Solutions were prepared as follows: A—water, 100 parts; 3-cyano-4,5-dimethyl-5-hydroxy-2(5H)-pyrrolone, 3 parts; and B—water, 100 parts; the pyrrolone, 3 parts; and urea, 3 parts. These solutions were coated onto smooth finish onionskin paper to give a pyrrolone coating weight of 50 mg./dm.^{2}. The dry sheets were essentially the same in appearance as the unmodified paper.

Strips were cut from the coated sheets and pressed onto an electrically heated melting point bar for 10 sec. at temperatures ranging from 100–200° C. The exact temperature at the pressing area was determined by means of a thermocouple. Three strips of each coating were pressed at each temperature. The strips coated with solution A gave marks with a magenta cast, while the marks on the strips coated with solution B were black. The reflection density of the marks was determined by means of the reflection density probe (no filter) of a Welch "Densicron" densitometer. The readings at each temperature were averaged to obtain the data shown in Table III below. When these data are plotted with the reflection density values along the ordinate axis and temperature values along the abscissa, a typical S-shaped curve was obtained similar to a Hurter and Driffield type curve for a photosensitive material wherein optical density is plotted against exposure. In addition to the change in image color, the urea sensitizer shifted the curve 10–15° toward the lower temperature range.

Table III

Temperature	Reflection Density	
	A	B
100	.14	.15
110	.14	.16
120	.14	.14
130	.14	.19
140	.14	.29
150	.15	.20
160	.23	.63
170	.58	1.06
180	.35	.95
190	1.05	1.13
200	1.23	1.15
210	1.26	1.29
220	1.25	1.24

EXAMPLE VII

A mixture of 50 parts of water, 40 parts of methanol, 10 parts of glycerol, five parts of urea, and five parts of 3 - cyano-4,5-dimethyl-5-hydroxy-2(5H)-pyrrolone was applied to sheets of regenerated cellulose (uncoated cellophane) to give a hydroxypyrrolone coating weight of approximately 50 mg./dm.^{2}. The coated cellophane was dried under tension to prevent wrinkling. The treated cellophane was unchanged in appearance. Thermal image-forming tests were carried out by pressing the treated sheets onto a hot electrotype for 10 sec. at temperatures from 110–172° C. At the lower temperature range a light gray image was obtained, but at the higher temperatures the image was a deep black. Tests in a modified commercial thermographic copying machine showed that excellent copies of an original containing both printed matter and penciled notations could be obtained with scanning rates ⅓ to ⅛ those ordinarily used. The image color ranged from gray in the faster rates to jet black at the slowest rate.

EXAMPLE VIII

A mixture of 8 parts of xylene, 30 parts of acetone, 2.5 parts of chlorinated rubber, and 2.5 parts of 3-cyano-3,4-dimethyl-5-hydroxy-2(5H)-pyrrolone was applied to photographic paper stock and allowed to dry. The pyrrolone coating weight was approximately 55 mg./dm.^{2}. The dry coating was colorless with no noticeable increase in gloss over the uncoated paper. Portions of the dry coating were pressed for 2–3 seconds against a hot electrotype at temperatures ranging from 148–188° C. At 148° C. a pale magenta image was obtained. As the temperature was increased the color of the image obtained deepened until at temperatures of 165° C. and above sharp, dark magenta, almost black images were obtained.

EXAMPLE IX

PREPARATION OF NEW 3-FUNCTIONALLY SUBSTITUTED 5-HYDROXYL-2(5H)-PYRROLONES

Several new 3-substituted 5-hydroxy-2(5H)-pyrrolones not described in detail in U.S. Patent 2,824,110 were prepared by methods like those given in the reference patent.

Thus, to a stirred mixture of 10 parts of 1-phenyl-1,2-propanedione, 5.7 parts (equimolar on the diketone) of cyanoacetamide, 30 parts of water, and about 15 parts of ethyl alcohol was added dropwise about 0.50 part of 10% aqueous NaOH solution. The temperature of the reaction mixture rose from 25° C. to 39° C. as the reagents dissolved. Within 1–2 minutes of solution, the reaction solution turned cloudy, and almost immediately thereafter a white solid product precipitated from solution in quantities such that the reaction mixture became almost solid. The resultant solid product was separated by filtration and dried in air. After recrystallization from methanol, there was obtained 5.1 parts (35% of theory) of 3-cyano-5-hydroxy-5-methyl - 4 - phenyl-2(5H)-pyrrolone as white crystals melting at 154–155° C. The position of the methyl and phenyl substituents was deter-

mined by comparison of the ultraviolet spectrum with those for the 4,5-dimethyl- and 4,5-diphenyl-3-cyano-5-hydroxy-2(5H)-pyrrolone.

Analysis.—Calcd. for $C_{12}H_{10}O_2N_2$: C, 67.3%; H, 4.7%; N, 13.1%. Found: C, 67.0%; H, 4.8%; N, 13.0%.

In a similar manner from equimolar proportions of 1,2-diisopropyl-1,2-ethanedione, i.e., 2,5-dimethyl-3,4-hexanedione, and cyanoacetamide, 3-cyano-5-hydroxy-4,5-diisopropyl-2(5H)-pyrrolone was obtained as white crystals melting at 165–170° C. Yield 80% of theory crude; 42% of theory after recrystallization from methanol.

Analysis.—Calcd. for $C_{11}H_{16}O_2N_2$: C, 63.4%; H, 7.7%; N, 13.5%. Found: C, 63.9%; H, 7.7%; N, 13.3%.

In a similar manner from 1,2-di(alpha-furyl)-1,2-ethanedione and cyanoacetamide, there was obtained 3-cyano-4,5-di(alpha-furyl)-5-hydroxy-2(5H)-pyrrolone as white crystals melting at 203–205° C. Yield 68% of theory crude; 45% of theory after recrystallization from methanol.

Analysis.—Calcd. for $C_{13}H_8O_4N_2$: C, 61.0%; H, 3.2%; N, 10.9%. Found: C, 61.1%; H, 3.2%; N, 10.9%.

In a similar manner from 2,3-pentanedione and cyanoacetamide, there was obtained 3-cyano-4,5-(ethyl, methyl)-5-hydroxy-2(5H)-pyrrolone as white crystals melting at 151.5–152.0° C. The respective positions of the ethyl and methyl substitutent in the 4- or 5-positions are not known but it is believed that the methyl substituent is in the 5-position and the ethyl substituent in the 4-position. Yield 64% of theory crude; an analytical sample was recrystallized from ethonol.

Analysis.—Calcd. for $C_8H_{10}O_2N_2$: C,57.8%; H, 6.0%; N,16.9%. Found: C,58.0%; H, 6.1%; N,16.8%.

The thermographic properties of the above four new 3-functionally substituted 5-hydroxy-2(5H)-pyrrolones, and in addition the 1-allyl-3-cyano-5-hydroxy-4,5-dimethyl-2(5H)-pyrrolone and the 3-acetyl-5-hydroxy-4,5-dimethyl-2(5H)-pyrrolone of U.S. 2,824,110, were evaluated as follows: 8½ x 11" sheets of onionskin paper were impregnated from aqueous alcoholic solution with the six respective hydroxy-pyrrolones at such concentration that the six treated papers exhibited a coating weight of the respective hydroxy-pyrrolones of about 50 mg. of the pyrrolone/dm.^{2} of paper surface. The coated papers were pressed against a heated copper electrotype at controlled temperatures, resulting in colored images or imprints of the text in the electrotype. The data are summarized in Table IV below.

EXAMPLE X

A solution of 3-cyano-5-hydroxy-4,5-dimethyl-2(5H)-pyrrolone in warm water was applied to filter paper and the paper then air-dried. When a hot spatula was pressed on the treated paper, a dark line resulted. The spatula was not hot enough to char the untreated paper or to mark it, as evidenced by a simultaneous test on a separate piece of untreated filter paper.

As indicated above, the thermographic materials used in accordance with this invention are 5-hydroxy-2(5H)-pyrrolones (*a*) wherein any substituents on the 1-, 4-, and/or 5-positions are monvalent hydrocarbon radicals of no more than ten carbons each, with the proviso that the 4- and 5- substituents can be together joined to form with the 4- and 5-carbons of the pyrrolone ring to form carbocycles of from five to seven ring-members and the further proviso that at most one of the 4- and 5-carbons can carry an aromatic substituent, and (*b*) wherein the 3-carbon is directly and singly covalently linked to a quaternary onium or inium salt group, such as the quaternary phosphonium, sulfonium, and ammonium salt groups, or through functional carbon thereof to carboxyl or groups hydrolyzable thereto or to a carboxylic acid, e.g., cyano, carboxyl, carboxyester, i.e., hydrocarbyloxycarbonyl, carbamoyl, mono- and di-substituted carboxamido and carbacyl. Specific examples of these thermographic compounds, in addition to those already illustrated in the foregoing examples, includes those 5-hydroxy-2(5H)-pyrrolones carrying an electron attractive amino-hydrogen-free functional substituent on the 3-carbon wherein: the 3-substituent is a quaternary onium salt group, such as 3-dimethylsulfonium-5-hydroxy-4-,5-diisobutyl-2(5H)-pyrrolone bromide, 3-dimethyldodecylammonium-5-hydroxy-4,5-dimethyl-2(5H)-pyrrolone chloride and 3-quinolinium-5-hydroxy-4-phenyl-2(5H)-pyrrolone methyl sulfate; and the preferred compounds wherein the 3-substituent is carboxyl or a group hydrolyzable thereto or to a carboxylic acid, such as 3-cyano-5-hydroxy-4,5-tetramethylene-2(5H)-pyrrolone or more properly 9-cyano-8-keto-6-hydroxy-7-azabicyclo[4.3.0]-9-nonene, 3-propionyl-5-hydroxy-4-phenyl-2(5H)-pyrrolone, 3-cyano-5-hydroxy-4,5-dibenzyl-2(5H)-pyrrolone, 3-cyano-5-hydroxy-1-cyclohexyl-4,5-dicyclohexylmethyl-2(5H)-pyrrolone and 3-cyano-5-hydroxy-1-decyl-4,5-dimethyl-2(5H)-pyrrolone.

Production of the thermographic image in the new elements of the present invention can be achieved in any way whereby the element comprising the flexible sheet support and in operative association therewith the necessary 3-negatively substituted 5-hydroxy-2(5H)-pyrrolone is selectively exposed to the required color-developing temperatures to form the desired pattern. For instance, the thermographic element can be pressed with a heated stylus operated manually or mechanically as the recording or copy arm of a sensing system driven by a photoelectric scanning beam. In a similar fashion, heated type characters, slugs, or complete composed plates may be pressed directly in contact with the thermographic element. Alternatively, the thermographic images can be prepared by suitable selective infrared radiation absorption. Thus, a master to be reproduced will generally have a dark text on a white background. Accordingly, on exposure to infrared radiation or to normal actinic light, the black areas are selectively warmer than the white areas by virtue of the selective absorption of the infrared radiation in the dark areas. With light of sufficient intensity directed on such an original held in contact with one of the thermographic elements of the present invention, the original is heated in the dark areas to temperature ranges wherein the thermographic reaction

Table IV

THERMOGRAPHIC PROPERTIES OF PYRROLIN-2-ONES

3-Functionally Substituted Hydroxypyrrolone	Temp. Producing Best Image	Lowest Temp. at Which Image Appears	Color of Image
3-acetyl-5-hydroxy-4,5-dimethyl-2(5H)-pyrrolone	176° C./30 sec.	151° C./15 sec.	brown.
3-cyano-4,5-(ethyl, methyl)-5-hydroxy-2(5H)-pyrrolone	200° C./5 sec.	150° C./15 sec.	violet.
3-cyano-5-hydroxy-5-methyl-4-phenyl-2(5H)-pyrrolone	180° C./30 sec.	165° C./15 sec.	dark blue.
3-cyano-5-hydroxy-4,5-diisopropyl-2(5H)-pyrrolone	180° C./15 sec.	165° C./15 sec.	brown.
3-cyano-4, 5-di(alpha-furyl)-5-hydroxy-2(5H)-pyrrolone	200° C./5 sec.	170° C./15 sec.	violet (yellow compound).
1-allyl-3-cyano-5-hydroxy-4,5-dimethyl-2(5H)-pyrrolone	175° C./30 sec.	130° C./30 sec.	brown (poor).

occurs in the thermographic element, thereby producing a colored direct positive duplicate of the original.

The temperatures to which these thermographic elements must be brought in order to develop the thermographic image will vary with the nature of the functionally substituted 5-hydroxy-2(5H)-pyrrolone, the nature of the support, and the relative concentration of the hydroxypyrrolone. Generally satisfactory colored images are obtained when the thermographic element is brought to temperatures between about 150° C. and about 225° C. A generally satisfactory average temperature would thus be in the neighborhood of about 175–200° C. The times at which these thermographic elements must be selectively held at such temperatures in order to develop satisfactory image quality likewise vary with the nature of the substituents on the 5-hydroxy-2(5H) - pyrrolone and in part with the nature of the support in the sense of the optical contrast qualities thereof. An approximate shortest color development time at these temperatures is in the neighborhood of about 0.1–2.0 seconds; whereas, with some of the less reactive pyrrolones reaction times of up to 30–45 seconds or even a few minutes or longer are needed. Generally speaking, an average color development time at the average development temperature of about 200° C. will be about 1.0 to 2.0 seconds.

While the thermographic images are readily developable of themselves in systems comprising only the flexible sheet support and the hydroxypyrrolone, for some particular uses, e.g., with the light weight, non-coated, less rugged paper stocks, the development temperatures required of the unmodified systems are undesirably close to the decomposition or char point of the flexible sheet support of this type. Accordingly, it is desirable in such uses to activate the systems. A suitable means of doing this is to supply in operative association with the thermographic element an activator for the thermographic reaction of the 5-hydroxy-2(5H)-pyrrolone. Suitable activators for the thermographic, i.e., thermal color-forming, reaction will be found among those materials or mixtures of materials which are capable of releasing a base with increasing temperature, i.e., thermal base-generating compositions. Probably the most common of such materials and systems are those which with increasing temperature generate ammonia or amines. Suitable specific examples of such material include the ammonium bases of weak acids, e.g., ammonium cyanate and the like, as well as urea and simple substituted ureas, e.g., the lower alkyl-substituted ureas described in U.S. Patent 2,732,299. These base-generating activators will be in operative association with the thermographic element in amounts ranging from one-tenth to two to three times the weight of the thermographic material, i.e., the substituted 5-hydroxy-2(5H)-pyrrolone. For reasons of convenience and for increased efficiency, the base-generating activators are preferably dispersed throughout the thermographic element and are conveniently obtained by being applied to the flexible sheet support in conjunction with the pyrrolone by treatment of the support with a solution of the hydroxypyrrolone and the base-generating activator in a mutual solvent. However, the activator can obviously be applied separately on or within, or both, either the flexible sheet support alone or the flexible sheet support already containing the thermographic material.

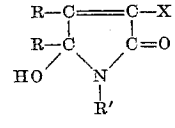
Suitable images of adequate density are obtained when the hydroxypyrrolone is present in concentrations ranging from 10 to about 500 mg./dm.^{2} of flexible sheet support surface. Higher loadings can readily be achieved, but at levels above approximately 200 mg./dm.^{2} the hydroxypyrrolone tends to crystallize out on the surface of the coated sheet. Without some sort of suitable topcoat protective binder, the hydroxypyrrolone as it crystallizes out of the higher concentrations tends to be physically removable by abrasion. Accordingly, loadings much above this approximate 200 mg./dm.^{2} figure will not normally be used nor needed. Decreased cost as well as avoidance of the above problems make coating weights in the range from 25 to 100 mg./dm.^{2} preferred. However, if heavier coatings are needed for some particular reason in the copy process, a suitable protective topcoat colloid will be applied. If such an element is intended for use in reflex copying, this topcoat obviously must be infrared transparent and likewise visibly transparent in order that (1) the thermographic image can be obtained, and (2) once obtained can be seen.

An advantage of the present invention is that it provides the art with a new class of thermally sensitive image recording elements which are economical to make and easy to use in making positive images directly. The novel elements do not require skilled operators or technicians when used to make positive images. A large number of reproductions can be made rapidly from any printed or other material to be copied. Still other advantages will be apparent to those skilled in the art of image formation or reproduction.

The novel thermally-sensitive recording elements of this invention have advantages when used in charts to be marked with a stylus over prior art materials. The latter generally employ a dark-colored paper with a white, opaque coating that becomes clear on application of heat, thereby producing a dark area on a white background. Typical coatings of this type are based on opaque, waxy, or crystalline materials, blushed resin coatings (see U.S. Patent 2,519,660) or plastic films containing microscopic voids (see U.S. Patent 2,739,909). Waxy coatings stick to adjacent layers and because of their softness are easily damaged. The blushed resin coatings must be applied under carefully controlled conditions to avoid variations in opacity of the coatings. The third type of film—that containing the microscopic voids—is widely used, but careful balancing of ingredients is required to produce a film which can be marked at available temperatures but at the same time is not unduly sensitive to pressure. All of these types of coatings must be applied to a colored base, which is generally paper carrying a dark pigmented coating. In addition, volatile organic solvents are necessarily employed in the production of all three types.

What is claimed is:

1. A thermally-sensitive image-recording element comprising a flexible sheet support of low heat conductivity and a stratum containing, in an amount from about 10 to about 500 milligrams per square decimeter, a 5-hydroxy-2-pyrrolone covered by the general formula



wherein X is a negative substituent selected from the group consisting of quaternary onium and inium salts, and carboxyl groups and groups hydrolyzable thereto, R′ is a member taken from the group consisting of hydrogen and monovalent hydrocarbon groups of no more than 10 carbon atoms, the radicals are each selected from the group consisting of hydrogen, alkyl of 1 through 10 carbon atoms, cycloalkyl of 4 through 6 carbon atoms, aryl of 6 through 10 carbon atoms and alkaryl of 7 through 10 carbon atoms and the radicals R when taken together constitute a single divalent hydrocarbon radical that forms with the 4- and 5-carbon atoms of the pyrrolone ring a carbocyclic radical of 5 to 7 ring atoms, said substituted pyrrolones being further characterized in that when substituted with the members recited not more than one of the 4- and 5-carbon atoms have an aromatic substituent.

2. An element as defined in claim 1 wherein said support is paper.

3. An element as defined in claim 1 wherein said 3-substituted 5-hydroxy-2-pyrrolone is in a layer of an organic colloid of high molecular weight and possessing protective colloid properties.

4. An element as defined in claim 1 wherein said pyrrolone is 3 - cyano - 5 - hydroxy-4,5-dimethyl-2(5H)-pyrrolone.

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