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PRIMARY AMINE MODIFIED SECONDARY OR TERTIARY AMINE-POLYKETO REACTION PRODUCT IN A HEAT DEVELOPABLE COPY SHEET

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This invention relates to heat marking sheets and processes and provides (1) a novel heat sensitive sheet useful for copying and recording uses, which is characterized by the ability to form a mark of contrasting color when selective areas thereof are heated to an activation temperature, preferably, in the range of about 50–160° C., (2) heat sensitive compounds and compositions for use in making such sheets and (3) methods for making such compounds, compositions and sheets. Sheets of this type are commonly employed in thermographic copying processes, in which a sheet is placed next to a graphic original or master and exposed to infra-red radiation to cause selective heating of the dark areas of the original and hence of the areas of the heat-sensitive sheet adjacent thereto sufficient to form a copy thereof on the heat-sensitive sheet. A more detailed description of this process is set forth in U.S. Patent No. 2,740,896. The sheets of this invention may also be used in recording devices in which marking is accomplished by means of a heated stylus.

U.S. Patent No. 3,076,707 describes heat sensitive sheets and compositions (usually in the form of a coating on a sheet material) containing an indicator or dye forming material, which changes color in the presence of a basic organic amine, in combination with a latent developer, which developer, on heating, yields an amine effective to give a color reaction with the indicator material. The latent developers employed in those sheets and compositions are thermally dissociable complex crystalline molecular compounds consisting of an organic amine in combination with either urea, thiourea, or a bisphenol. Under normal storage conditions, they are solids which exhibit no substantial basic amine characteristics, and may therefore be intimately associated with the indicator material without causing a color reaction. Heating releases the amine for color reaction with the indicator material.

These compositions have the following disadvantages: The complex molecular compounds of the amine and urea, thiourea and the bisphenols are relatively unstable in the presence of moisture and most other liquids and dissociate when dissolved in solvent media. Therefore, they and the indicator must be compounded and coated on the sheet in the form of a dispersion which requires a ball mill or equivalent grinding operation. Also, where a binder is required, only certain limited binder-solvent systems can be used in which the complex compounds will not become dissociated and prematurely activate the coating composition and discolor the coated sheet. The fact that dispersions must be used limits minimum particle size and hence speed of color reaction and the fact that only limited binder-solvent systems can be used prevents the use of the more desirable binders. In addition, the sheets employing these complexes are highly sensitive to humidity and hence have a reduced shelf-life when stored at high humidity. The urea compounds do not dissociate as easily by heat so they are not as desirable as the phenolic compounds but the phenolic compounds have an unpleasant odor which is imparted to the coated sheet. The urea or phenol is an additional compound, the only function of which is to render the amine inactive until heated, which does not enter into the color reaction at all and the use of which adds to the expense of the heat sensitive sheet. Also, the manufacture of the complex constitutes an additional process step.

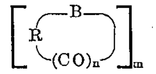
In the generally known copy sheet compositions of this type containing color forming systems, a color is formed when the components of the color forming composition are put into solution. Thus, they are generally coated as intimate mixtures of discrete particles of a plurality of reacting materials and must be kept out of solution, i.e. out of contact with a solvent therefore, at least until heat actuation on the paper. They are kept from reacting by a binder or coating separating them and protecting them from contact with solvents therefor, the binder or coating being melted or vaporized by heat to bring them together and hence form a color. In the case of the urea and bisphenol complexes, the amine is kept from reacting with the color indicator until the complex is dissociated by heat to free the amine. As aforesaid, contact with a solvent will result in premature activation. In other cases, the reactants do not react so long as they are in the form of dry discrete particles. The color is then formed by interaction in the fused state (caused by heating). In all cases, stability is dependent on keeping the reactant particles out of a reactive media.

The present invention is based on a completely different principle. All of the color forming materials may be in solution without any interaction taking place. In a number of cases, only one chemical compound is used, the color being formed by decomposition thereof by heat. These reactive materials may be coated as a solvent solution of the reactant or reactants, as a lacquer solution of the reactant or reactants, or as a pigmented dispersion of the reactant or reactants either in an aqueous or solvent phase. Thus, the invention provides great latitude in compounding and processing. Deposition of the reactants from a solvent system gives a more thermally sensitive sheet than one in which the reactants must be applied as a dispersion. It will be later seen that this invention also offers greater latitude in choice of image and background color. In addition, the thermal sensitivity of the sheet is dependent solely on the decomposition temperature of the reactant or reactants. The chemical compositions of this invention are many and varied in both activation temperatures and reaction colors. Such compositions, in addition to being adapted to be used in solution and being more thermally sensitive, are also highly stable, insensitive to moisture and hence humidity and do not have an unpleasant odor as in the case of the bisphenol complexes.

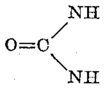
This invention is based upon the discovery that stable, light colored dye intermediates, which are not themselves dyes, can be formed by the reaction of a secondary or tertiary amine with cyclic polyketo compounds under controlled conditions of reaction media, ratios of components and temperatures of reaction. These amine-cyclic polyketo intermediate compounds will decompose at elevated temperatures to give residues which will either interact with themselves or other polyketo compounds to form a highly colored dye. The temperature of decomposition may be controlled by the nature of the parent reactants and the media within which the decomposition takes place. An important advantage of such intermediates is that by mixing them with certain activator compounds their activation temperatures can be varied, e.g. lowered, to provide optimum activation temperatures.

The compositions and sheets of this invention accordingly feature dye-forming materials of the type well-known in the art as cyclic polyketo compounds which have been reacted with a secondary or tertiary amine to form light-colored addition intermediate products, which products are not themselves dyes but which upon heating by themselves or in the presence of other cyclic polyketo compounds or activators form dyes and which are stable under normal conditions of handling and storage. "Normal" conditions is described as conditions of temperature less than about 100° F. or 105° F.

The dye-forming cyclic polyketo compounds are of the well known types such as ninhydrin, hydrindantin, 1,3-indandione, perinaphthindan-1,2,3-trione, perinaphthindan-1,3-dione, alloxan, alloxantin, isatin, and the substituted homologs and analogs normally associated with this class of materials. Most of the compounds in this well known class of compounds have the molecular structure



where n is 2 or more, m is 1 or 2, R is selected from the group consisting of a substituted and unsubstituted aromatic radical (ninhydrin), the radical



(alloxan) and the radical ethylene (benzoquinone) which is part of the ring which includes B and $(CO)_n$, and B is selected from the group consisting of the amino (isatin), methylene (1,3 indandione), ethylene (naphthaquinone), keto (ninhydrin), aromatic (anthraquinone), —C—OH (hydrindantin), and —C—H (bisindane-1,3 dione) groups which is part of the ring which includes R and $(CO)_n$. The substitution groups usually encountered in this class are the nitro, amino, alkyl, alkylene, carbonyl and halogens such as chloro, iodo, etc. These materials are well known as a class for their dye formation in the presence of primary amines, ammonia, or amino-acids, and any of them which are useful in such dye formation can be used in the present invention. Surprisingly enough, however, it has been discovered that when these materials are reacted with an excess of a secondary or tertiary amine (e.g., 1.5 to 10 mols per mol of cyclo polyketo compound) in a non-aqueous (preferably alcoholic), non-acid reaction medium at a temperature below the decomposition point of the intermediate product, preferably, a temperature not greater than 200° F., a stable, light-colored, amine-cyclic keto intermediate addition product is formed, rather than a dye. When an excess of amine is not used, or the amine is a primary amine or ammonia, or the temperature of reaction is above the decomposition point of the intermediate, or an acid or aqueous medium is used, which is the case with the conventional formation of dyes by reaction of the cyclic polyketo compounds and primary amines, a stable intermediate is not formed, but instead, the reaction proceeds to completion with the formation of the dye.

The dye color achieved upon decomposition of the intermediate product by heating is in many cases different from the dye color achieved when the same keto and amine compounds are reacted to completion in accordance with normal dye forming procedure, which proves that they are different compounds. The (1) stable intermediate product, or (2) a combination of the stable intermediate with other dye-forming cyclo polyketo compounds or with other intermediates, or (3) a combination of the stable intermediate, with or without other dye-forming polyketo compounds, and a modifier or activator for control of decomposition temperature such as a solid acid, anhydride, hydroxy aromatic or ketone compound, is coated or impregnated by any convenient means, either from dispersion or solution, onto or into the desired carrying web of paper or film or other sheet material. This coated or impregnated sheet is then suitable for use in normal thermocopying processes or as a recording sheet for recording instruments using hot stylii since the intermediate compound is sensitive to heat to form a dye.

Preferably, the non-aqueous, non-acidic medium in which the reaction is carried out is an alcohol. Preferred alcohols are low boiling point alcohols such as methyl and ethyl alcohol. The low boiling points of these alcohols keep the reaction mixture from getting too hot. However, other organic media which will not render the system acidic can be used, as for example, aromatic hydrocarbons such as toluene, benzene and xylene. Solvents are preferred in which one of the reactants, i.e. the polyketo compound or the amine, is soluble and, more preferably, solvents in which both reactants are soluble. Cyclic polyketo compounds are believed to be acidic in water—that is why the reaction must take place in a non-aqueous medium. Otherwise, water would not be detrimental since the intermediate is stable in water. Very small amounts of water, although detrimental, can be tolerated. For example, a few percent of water in alcohol can be tolerated but if there is much more than 10% by weight, water the medium will become too acidic. preferably the water content should not eceed much more than 5% of the reaction medium. Aliphatic solvents are not as desirable because neither the cyclic polyketo compounds or amines which have been used are sufficiently soluble in them. Preferred reaction media are those from which the intermediate can be precipitated without undue difficulty. Esters and ethers are less preferred because of the difficulty in precipitating the intermediate therefrom.

Most of the cyclic polyketo compounds are solid. Some of the secondary and tertiary amines are liquids and some solids. So long as one is soluble in the reaction medium, the other can be used as a slurry. In certain cases the solid polyketo compound can be added directly to the liquid amine.

The molar ratio of amine to polyketo compound may range from slightly greater than one, e.g., 1.5, to as high as desired, there being no upper limit except from a practical standpoint. However, the preferred minimum molar ratio is 2, a preferred range being from 2 to 5.

The intermediate compounds are solids. Most of them, but not all, are crystalline in nature and they are precipitated out of the reaction medium.

The temperature of the reacting mixture must be kept below the decomposition temperature of the intermediate formed. Such decomposition temperature can be readily ascertained by carrying out the reaction at a low reaction temperature, e.g., 110° F., and thereafter heating the intermediate formed to its activation or decomposition temperature which is readily observable by the color change. Ordinarily, the temperature should not exceed and is preferably less than 200° F. since the reacting materials tend to react to completion to form a dye above this temperature. Good results have been consistently achieved with reaction temperatures of 110° F. to 180° F. In some cases, reaction occurs at room temperature without heating although in most cases, some heat is required for a short period of time. It is good practice to use as low a temperature as possible to achieve reaction. In some cases, the intermediate precipitates out upon formation but in most cases it crystallizes out on standing at room temperature for a period of time after heating is terminated and can be redissolved or dispersed in either the same liquid medium in which it was formed or another liquid medium for application to the paper. Crystallization may be initiated or accelerated by seeding or scratching the container.

As aforesaid, the intermediate reaction products of the present invention are converted to dye products over a large range of activation temperatures depending on the reactants used, i.e., the keto compound and the amine compound, and the presence of other cyclic polyketo compounds, other intermediates and activators as described in greater detail below. A color shift can be achieved with all of them, when used alone or combined with other keto compounds or other intermediates or activators, within a range of about 50–160° C., which is the temperature range normally achieved with conventional thermocopying machines. Although some of the intermediates do not exhibit a color shift within this temperature range, by adding an activator or another intermediate or a cyclo polyketo compound, a color shift can be achieved within such range. Put in another way, in the case of those compounds which have an activation temperature above that normally used in thermocopying, such temperature can be lowered by the addition of an activator or modifier, as described above and below, or by combination with another or other keto compounds or intermediates. In some cases, there is a shift to one color at one elevated temperature and a shift to another color at a higher elevated temperature.

Although primary amines cannot be used for reaction with the polyketo compounds to form the intermediates since this results in the reaction going to completion to form the dye, intermediates made from secondary and tertiary amines can be further reacted with a primary amine to form another intermediate, which, upon heating, will decompose into a dye different from the dye formed from the intermediate before further reaction with the primary amine. The reaction between the intermediate and the primary amine is carried out in a non-acid medium to prevent dye formation. Preferably, the medium is non-aqueous since some of the final products are hygroscopic and hence are difficult to isolate from the water. Alcohol is a preferred medium. The other solvents present solubility problems. However, otherwise they can be used. At least one mole of primary amine should be used per mol of intermediate. Any greater excess provides no advantage and may pick up water. In many cases this reaction can be carried out at room temperature but in any event, the temperature should not exceed the decomposition temperature of the initial or final intermediate product. Preferably temperatures no greater than 200° F. should be used.

The molecular construction of the intermediates of the present invention is not known for certain. However, it is known from the properties thereof that the molecular construction is different from that of the dyes obtained by reaction to completion of the keto compounds with the amines. For example, such dyes do not exhibit the decompositions and color changes exhibited by the intermediates when heated to the same activation temperatures.

The intermediate compounds may be applied to the sheet material to form the heat sensitive thermocopying sheet as a solution or a dispersion.

Ketones, esters and ethers as well as alcohols, aldehydes and other organic solvents such as aliphatic and aromatic hydrocarbons and halogenated hydrocarbons can be used as a medium for the intermediate compound for application to the sheet material Methyl and ethyl alcohols as well as toluene, butyl acetate, dioxane, di-n-butyl ketone and ethanol-di-n-butyl ketone have proved to be highly satisfactory. Even water can be used as a medium since the intermediates are stable in water. This insensitivity to all kinds of solvent media and water is an important advantage.

If a binder is used, it is dissolved in the medium. Such binder may be any one or more of a large number of common binders, such as Ethocel N–100, an ethyl cellulose sold under that name by Dow Chemical Company, chlorinated rubber, polyvinyl acetal, acrylic ester polymer, polyvinyl acetate, polyvinyl ethyl ether, polyvinyl methylol resin, etc. Such high-melting binders prevent the physical transfer of the intermediate to the belt or screen in the copying machine, but the intermediate will still be activated at the same temperature.

One of the advantages of the intermediates of the invention is that they do not react with the proteins on the hand to form a dye, as is true of the cyclic polyketo compounds. Another of the advantages of such intermediates is that a wide variety of such high melting binders can be used since the intermediates are not activated by the proper solvents for such binders as in the case of the bisphenol-amine complexes.

As aforesaid, the intermediate is heat sensitive, i.e., when it is applied to a sheet passed through a Thermofax machine, the infra-red heat which collects at the dark areas of the master and hence at the portions of the copying sheet adjacent to such dark areas, will decompose it to form a dye and consequently marks corresponding to the dark areas of the master.

The selection of suitable components for a specific application may be readily made by one skilled in the art and familiar with the principles of this disclosure on the basis of known or readily determined properties. I have found it convenient to use either of two determining tests for the selection of components for a specific application. I have observed the color shift of the intermediates and mixtures of the same with cyclic polyketo compounds, other intermediates and activators, on a Fisher-Johns melting point apparatus to select the types of materials which will give the desired color and temperature of color reaction for the specific application in mind. I have also found it very convenient to intimately mix such components, spread the mixture (or the intermediate alone) on ordinary filter paper, and observe the color shift when heated on a hot-plate for three seconds at 300° F. or some other suitable temperature for the application in mind. I used these procedures in the examples given below.

As aforesaid, a wide variety of image colors, activation temperatures and background colors can be achieved by varying the starting compounds from which the intermediate is formed. Also, the same intermediate can be used to provide a large variety of image and background colors as well as activation temperatures by combining it with a variety of other cyclic polyketo compounds or by combining it with other intermediates or by further reacting it with another amine, including primary amines.

Although certain of the intermediates do not themselves form a dye when heated, when they are combined with other cyclic polyketo compounds, the resulting combination forms a dye when heated.

Representative examples of this invention setting forth the mode presently contemplated for carrying out the invention and preparations of representative types of light-colored, amine-cyclic polyketo compounds which may be used are given below.

A. *Preparation of amine-polyketo reaction products*

(1) 4.0 g. morpholine were added to a solution of 2.0 g. ninhydrin in 20 g. denatured alcohol with warming at 173° F. for 10 minutes. After standing approximately 3 hours at room temperature, scratching with a glass rod induced crystallization. The product was filtered, washed with cold denatured alcohol, and dried. The bright yellow crystals shift to brown-purple at 115–125° C. with some softening but no melt.

(2) 4 g. 2,6-dimethylmorpholine were added to a warm solution of 2 g. ninhydrin in 20 g. denatured alcohol, warmed at 173° F. for 15 minutes, and set aside to crystallize. Crystallization occurred within 24 hours. The product was filtered, washed with cold denatured alcohol, and dried. The very pale yellow crystals became purple-black at 103–108° C. with melting and decomposition.

(3) 4 g. of 1,2,4-trimethylpiperazine were added to a warm solution of 2 g. ninhydrin in 20 g. denatured alcohol, warmed 15 minutes at 173° F., and set aside to crystallize. After 24 hours, the crystalline material was filtered, washed with cold denatured alcohol, and dried. The off-white crystalline material shifts to light lavender at 78° C., changing to purple-black at 103–8° C. with melting and decomposition.

(4) 3.8 g. piperidine were added to a warm solution of 1.8 g. ninhydrin in 20 g. methanol. After warming 5 minutes at 140° F. and scratching with a glass stirring rod, crystallization occurred. The reaction mixture was

allowed to stand 24 hours at room temperature, was filtered, washed with cold methanol, and dried. The yellow-orange crystals shift to purple at 123–6° C. with melting and decomposition.

(5) 3.8 g. N-methylpiperazine were added to a warm solution of 1.8 g. ninhydrin in 20 g. methanol. After warming at 140° F. for 10 minutes, crystals began to form near the top of the beaker. The mixture was allowed to stand 24 hours at room temperature, was filtered, washed with cold methanol, and dried. The yellow crystals shift to light purple at 93° C. becoming brown-black at 110–112° C. with melting and decomposition.

(6) 2 g. dicyclohexylamine were added to a warm solution of 1 g. ninhydrin in 10 g. methanol, warmed 10 minutes at 140° F., and set aside to crystallize. Crystallization started within three hours after intermittent scratching with a glass rod. The mixture was allowed to stand 24 hours at room temperature, was filtered, washed with cold methanol, and dried. The yellow-buff crystals melt at 83–6° C. with decomposition, becoming purple-black at 90–95° C.

(7) 4 g. di-n-butylamine were added to a warm solution of 1 g. ninhydrin in 10 g. methanol, warmed 10 minutes at 140° F., and set aside to crystallize. After 24 hours at room temperature, crystallization was induced by scratching with a glass rod. The mixture was filtered, the filtrate washed with cold methanol, and dried. The off-white crystals melted at 127–9° C. with decomposition, but no color change occurred below 200° C. When mixed with ninhydrin, the color shifted to light purple at 76° C. and became purple-black at 85° C.

(8) 1.4 g. N-ethylcyclohexylamine were added to a warm solution of 0.7 g. ninhydrin in 10 g. methanol, warmed 5 minutes at 140° F., and set aside to crystallize. After 24 hours, the product was filtered, washed with cold methanol, and dried. The cream crystals melt at 153–5° C. with decomposition. No color change was noted below 190° C. When mixed with ninhydrin, the color shift starts at 105° C. becoming purple-black at 135° C. When spread on white filter paper and heated 3 seconds at 300° F., mixed with ninhydrin-purple brown, with a hydrindantin-brown black, with isatin-brown, with alloxan-dark red.

It has been observed that in some cases a different color shade is exhibited on the filter paper (which was white in all the examples) as compared to the Fisher-Johns test at about the same temperature. It is believed that this is due to the difference in background—in the Fisher-Johns test, the background is transparent glass laid on aluminum and a light is shined down onto the sample.

(9) 4 g. N-methylfurfurylamine were added to a solution of 1 g. ninhydrin in 10 g. methanol, warmed 5 minutes with stirring at 140° F., allowed to cool, and crystallized upon scratching with a glass rod. The product was filtered, washed with cold methanol, and dried. The yellow-orange crystals change to purple-black at 93–6° C. with melting and decomposition.

(10) 3.8 g. morpholine were added to a warm slurry of 1 g. hydrindantin in 10 g. methanol. A dark solution formed after warming 10 minutes at 140° F. The solution was allowed to cool and crystallization started within 30 minutes after scratching with a glass rod. The product was filtered, washed with cold methanol, and dried. The yellow crystals became purple-black at 128–138° C. with melting and decomposition.

(11) 3.8 g. piperidine were added to a warm slurry of 1.8 g. hydrindantin in 20 g. methanol and a solution was formed on warming. After 5 minutes at 140° F., precipitation was started by scratching with a glass rod. The product was filtered, washed with cold methanol, and dried. The yellow-orange crystals became purple-black at 134–6° C. with melting and decomposition.

(12) 3.8 g. of 1,2,4-trimethylpiperazine were added to a warm slurry of 1.8 g. hydrindantin in 20 g. methanol and warmed 10 minutes at 140° F. Reaction seemed to take place immediately and a clear solution was never obtained. The product was cooled, filtered, washed with cold methanol, and dried. The off-white crystals became purple at 177–9° C. with melting and decomposition. The product when mixed with ninhydrin became dark brown at 149° C.

(13) 4 g. dicyclohexylamine were added to a warm slurry of 1 g. hydrindantin in 20 g. methanol and warmed 7 minutes at 140° F. with stirring. The solution was set aside to crystallize. After 24 hours, the product was filtered, washed with cold methanol, and dried. The off-white crystals melt at 165–170° C. with decomposition, but no color change. Mixed with hydrindantin, the color shifts to red-brown at 165° C. Mixed with ninhydrin, the color shifts to lavender-brown at 125° C., becoming dark brown at 145° C. with melting.

(14) 2 g. N-isopropylcyclohexylamine were added to a warm slurry of 1 g. hydrindantin in 10 g. methanol. A dark solution formed immediately. This was warmed 5 minutes at 140° F. and set aside to crystallize. After 24 hours, the product was filtered, washed with methanol, and dried. The very light yellow crystals soften at 134° C., melt at 156–163° C. with decomposition, but with no color change. When the product is mixed with hydrindantin, the color shifts to red-brown at 134° C. When the product is mixed with ninhydrin, the color shifts to red-brown at 110° C.

(15) 2 g. N-ethylcyclohexylamine were added to a warm slurry of 1 g. hydrindantin in 10 g. methanol, warmed 10 minutes at 140° F., and set aside to crystallize. After 24 hours, the product was filtered, washed with methanol, and dried. The very light yellow crystals soften at 133° C., melt at 153–8° C. with decomposition, but give no color change. When the product is mixed with hydrindantin, the color shifts to brown at 133° C., with ninhydrin, the color shifts to lavender brown at 105° C. and dark brown at 140° C. When the product is mixed with ninhydrin, spread on filter paper and heated 3 seconds at 300° F., the color becomes purple-brown, with hydrindantin-brown black, with isatin-red brown, and with alloxan-dark red.

(16) 4.4 g. piperidine were added to a hot solution of 2 g. isatin in 50 g. denatured alcohol, warmed 10 minutes at 173° F., and set aside to crystallize. A precipitate formed within one hour. The product was filtered, washed with cold denatured alcohol, and dried. The off-white crystals shifted to blue at 130–140° C. with melting and decomposition.

(17) 4.4 g. morpholine were added to a hot solution of 2 g. isatin in 40 g. methanol, warmed 15 minutes at 140° F., and set aside to crystallize. After 24 hours, the product was filtered, washed with cold methanol, and dried. The off-white crystals shifted to blue at 123–7° C. with melting and decomposition.

(18) 4.4 g. 2,6-dimethylmorpholine were added to a hot solution of 2 g. isatin in 40 g. methanol, warmed 15 minutes at 140° F., and set aside to crystallize After 24 hours, the product was filtered, washed with cold methanol, and dried. The off-white crystals became blue-black at 162–165° C. with melting and decomposition.

(19) 4.4 g. N-methylpiperazine were added to a hot solution of 2 g. isatin in 40 g. methanol, warmed 15 minutes at 140° F., and set aside to crystallize. After 24 hours, the product was filtered, washed with cold methanol, and dried. The pale yellow crystals shifted to brown-black at 142–150° C. with melting and decomposition.

(20) 2.2 g. N-methylfurfurylamine were added to a warm slurry of 1 g. isatin in 10 g. methanol, warmed 10 minutes at 140° F., and set aside to crystallize. After 24 hours, the product was filtered, washed with methanol, and dried. The pale cream crystals became purple-black at 109–114° C. with melting and decomposition.

(21) 2.2 g. pyrrolidine were added to a warm (140° F.) slurry of 1 g. isatin in 10 g. methanol. The reaction and crystallization occurred immediately. The product was cooled, filtered, washed with methanol, and dried. The white crystals became light blue at 112° C., dark blue at 145° C., and dark brown at 148–150° C. with melting and decomposition.

(22) 3.8 g. morpholine were added to a warm solution of 1.8 g. alloxan in 20 g. methanol and warmed 10 minutes at 140° F. After 24 hours, crystallization was started by scratching with a glass rod. The product was filtered, washed with cold methanol, and dried. The white crystals melted at 123-7° C. with decomposition, but no color change. When the product was mixed with ninhydrin, spread on filter paper, and heated 3 seconds at 300° F., the color shifted to purple black, with hydrindantin-purple black, with alloxan-dark red, and with isatin-green black.

(23) 3.8 g. piperidine were added to a warm solution of 1.8 g. alloxan in 20 g. methanol, warmed 10 minutes at 140° F., and set aside to crystallize. After 24 hours, the product was filtered, washed with cold methanol, and dried. The white crystals melted at 154-8° C. with decomposition, but no color change. When the product was mixed with ninhydrin, spread on filter paper, and heated 3 seconds at 300° F., the color shifted to purple-black, with hydrindantin-purple black, with alloxan-red brown, and with isatin-green black.

(24) 3.8 g. 1,2,4-trimethylpiperazine were added to a warm solution of 1.8 g. alloxan in 20 g. methanol, warmed 10 minutes at 140° F., and set aside to crystallize. After 24 hours, the product was filtered, washed with methanol, and dried. The white crystals melted at 156–7° C. with decomposition, but no color change. When the product was mixed with ninhydrin, spread on filter paper, and heated 3 seconds at 300° F., the color shifted to purple-black, with hydrindantin-brown black, with isatin-brown, and with alloxan-reddish purple.

(25) 4 g. 1,2,3,4-tetrahydroquinoline were added to a warm solution of 2 g. alloxan in 20 g. methanol, warmed 10 minutes at 140° F. (light pink solution), and set aside to crystallize After 24 hours, the product was filtered, washed with methanol, and dried. The very light cream crystals became brown, but did not melt below 250° C. When mixed with ninhydrin, the color shifted to light lavender at 105° C., brown lavender at 177° C., and purple brown at 203–5° C., with isatin-orange brown at 177° C., lavender brown at 203–5° C., and with alloxan-light lavender at 177° C. and lavender brown at 203–5° C. When heated 3 seconds on filter paper at 300° F., the product gave no change, mixed with ninhydrin-purple brown, mixed with isatin-dark brown, mixed with alloxan-dark lavender red.

(26) 4 g. dicyclohexylamine were added to a warm solution of 2 g. alloxan in 20 g. methanol, warmed 10 minutes at 140° F. (clear solution), and set aside to crystallize. The product crystallized within an hour of preparation, and was filtered, washed with methanol, and dried. The white crystals shift to light lavender at 143° C. and lavender at 152–160° C. with melting and decomposition. Mixed with ninhydrin, the color shifts to light lavender at 104° C. becoming purple-black at 135–140° C. Mixed with isatin, the color shifts to orange-brown at 143° C. Mixed with alloxan, the color shifts to light lavender at 115° C. and dark lavender at 140° C. When the product is mixed with ninhydrin spread on filter paper and heated 3 seconds at 300 F., the color shifts to purple-black, with isatin-orange brown, with alloxan-dark lavender, and the product alone shifts to reddish lavender.

(27) 4 g. N-ethylcyclohexylamine were added to a warm solution of 2 g. alloxan in 20 g. methanol, warmed 10 minutes at 140° F. (solid formed almost immediately, but redissolved), and set aside to crystallize. Crystallization took place within one hour of preparation. The product was filtered, washed with methanol, and dried. The white crystals shift to light lavender brown at 103° C., becoming brown at 115° C. When mixed with ninhydrin, the product shifts to light lavender brown at 103° C., becoming brown at 115° C. When mixed with alloxan, the color shifts to light lavender at 90° C., becoming dark lavender at 120° C. With isatin, the color shifts to red brown at 142° C. The product melts at 142–146° C. with decomposition. The product spread on filter paper and heated 3 seconds at 300° F. shifts to lavender. When mixed with ninhydrin the color shift is to brown-black, with isatin-red brown, with alloxan-deep lavender.

(28) 4 g. N-methlpiperazine were added to a warm solution of 2 g. alloxan in 20 g. methanol, and warmed at 140° F. A pink solution formed, which crystallized within a minute of starting the reaction. The product was cooled, filtered, washed with methanol, and dried. The white crystalline product shifts to light brown at 163° C., brown at 180° C., and dark brown at 230° C., but no melt. With ninhydrin, the color shifts to light lavender at 93° C., becoming lavender at 132° C., with isatin the color is brown-black at 180° C., with alloxan the color shifts to light lavender at 132° C., becoming dark lavender at 180° C. When spread on filter paper and heated 3 seconds at 300° F., the product shifts to dark red brown, mixed with ninhydrin-purple black, mixed with isatin-brown, mixed with alloxan-deep lavender.

(29) 4 g. diethylamine were added to a warm solution of 2 g. alloxan in 20 g. methanol, warmed at 140° F.; a precipitate formed within 1 minute and did not go back into solution. The product was cooled, filtered, washed with methanol, and dried. Very hygroscopic light lavender crystals became dark lavender at 120° C. with heavy gassing. Spread on filter paper and heated 3 seconds at 300° F., the product became red lavender, mixed with ninhydrin-deep purple, mixed with isatin-brown black, and mixed with alloxan-deep lavender.

(30) 4 g. di-n-propylamine were added to a warm solution of 2 g. alloxan in 20 g. methanol, warmed at 140° F. A precipitate formed within 1 minute and did not redissolve. The product was filtered, washed with methanol, and dried. The very light lavender crystals became lavender at 114–122° C. and melted with decomposition. Mixed with ninhydrin, the color shifted to purple-black and melted at 96–100° C. Mixed with isatin, the color shifts to green-brown at 128° C. becoming dark brown at 170° C. Mixed with alloxan, the color shifts to lavender at 90° C., becoming purple-brown at 135–140° C. Spread on filter paper and heated 3 seconds at 300° F., the product shifted to lavender, mixed with ninhydrin-purple black, mixed with isatin-dark brown, mixed with alloxan-lavender.

(31) 4 g. diisopropylamine were added to a warm solution of 2 g. alloxan in 20 g. methanol, warmed 10 minutes at 140° F. (formed yellow solution which became colorless), and set aside to crystallize. After 24 hours, the product was filtered, washed with methanol, and dried. The white crystals soften at 128° C. becoming light lavender, and give clear melt with some decomposition at 180–3° C. When mixed with ninhydrin, color shifts to light brown at 90° C., becoming dark brown at 110–118° C., and a molten black at 130° C. Mixed with isatin, there is no color change. Mixed with alloxan, the color shifts to light lavender at 90° C. and dark lavender at 130° C. When spread on filter paper and heated 3 seconds at 300° F., the product shifts to a light pink brown, mixed with ninhydrin-purple black, with isatin-orange brown, and with alloxan-dark lavender.

(32) 2 g. piperazine were added to a warm solution of 1 g. ninhydrin in 10 g. methanol. A precipitate was formed which did not redissolve after 5 minutes at 140° F. The mixture was set aside to cool, and the product was then filtered, washed with methanol, and dried. The

light blown crystals became light lavender at 93° C. and black at 150° C. No melt was obtained below 200° C. Mixed with ninhydrin-light green at 93° C., lavender at 113° C., and purple brown with melting at 180° C. With isatin-light brown at 153° C., and brown black at 180° C. With alloxan-light lavender at 95° C., blue at 113° C., brown at 162° C., and green-brown at 180° C. When spread on filter paper and heated 3 seconds at 300° F., it turned purple black, mixed with ninhydrin-green, then purple black, with isatin-brown black, and with alloxan-brown black.

(33) 2 g. piperazine were added to a slurry of 1 g. of isatin in 20 g. methanol. A solution formed on warming 5 minutes at 140° F. Scratching with a glass rod caused crystal formation on the side of the beaker. The mixture was cooled and the product was filtered, washed with methanol, and dried. The yellow-buff crystals became light brown at 170° C. and black at 208–215 C. with melting and decomposition. Mixed with ninhydrin-light green at 94° C., green lavender at 113° C., brown purple at 147° C., and purple black at 180° C. with melting. With isatin-purple black at 170° and melted. With alloxan-buff-purple at 157° C. On filter paper 3 seconds at 300° F., it turned brown black, mixed with ninhydrin-purple green, with isatin-brown black, and with alloxan-purple brown.

(34) 2 g. piperazine were added to a warm solution of 1 g. alloxan in 10 g. methanol, warmed 5 minutes at 140° F., and set aside to crystallize. The product was filtered, washed with methanol, and dried. The light lavender crystals became lavender at 157° C., with no melt below 220° C. Mixed with ninhydrin-light green at 93° C., blue green at 110° C., purple at 157° C., and black at 173° C. With isatin-brown at 173° C. and black at 185° C. With alloxan-lavender at 157° C. and lavender brown at 173° C. On filter paper 3 seconds at 300° F. it turned purple, mixed with ninhydrin-green black, with isatin-brown black, and with alloxan-lavender brown.

(35) 1 gram example 22, 10 g. methanol, and 1 g. ethylene diamine (primary amine) were stirred and heated 5 minutes at a hotplate temperature of 170° F. A solution was formed which was set aside to crystallize. After six days, the crystalline product was filtered, washed with methanol, and dried. The yellow crystals melt at 150–170° F. with gassing and become light brown. Mixed with ninhydrin-light purple at 105° C., purple at 130° C., and purple-black and melting at 154° C. with isatin, the shift is to brown at 168° C. with melting, and with alloxan-light lavender at 130° C., lavender brown at 154° C. Heated 3 seconds at 300° F. on filter paper, the sample became light brown, with ninhydrin-purple black, and with isatin-brown black.

(36) 2 grams of cyclohexylamine (primary amine) were added to a slurry of 1 g. example 22 in 10 g. methanol and warmed 7 minutes at a hotplate temperature of 170° F. The reaction seemed to occur immediately, and a solution was never formed. The mixture was set aside to cool. The white crystals become lavender at 152–7° C. with melting and decomposition. Mixed with ninhydrin-light tan at 85° C., purple at 107° C. with melting, and green at 134° C. With isatin-orange brown at 128° C. with melting and brown at 138° C. With alloxan-light lavender at 91° C., lavender at 115° C., and lavender brown at 150° C. Spread on filter paper and heated 3 seconds at 300° F., the sample becomes lavender, mixed with ninhydrin-dark green, with isatin-brown, and with alloxan-lavender.

(37) 2 grams n-hexylamine were added to a slurry of 1 g. example 22 in 10 g. methanol. A solution formed cold. After warming 7 minutes at a hotplate temperature of 170° F., the solution became cloudy and was set aside to crystallize. The white crystals melted at 111–115° C. with no color change, mixed with ninhydrin-purple lavender at 67° C., dark purple at 83° C. with melting, and purple black at 86° C., with isatin-orange brown and melting at 90° C., and brown at 111° C., and with alloxan-lavender at 80° C. and dark lavender at 111° C. Spread on filter paper and heated 3 seconds at 300° F., sample did not change, with ninhydrin-blue black, with isatin-dark brown, and with alloxan-purple brown.

(38) 2 grams alpha methylbenzylamine were added to a slurry of 1 g. Example 22 in 10 g. methanol. A solution formed on mixing. The solution was warmed 7 minutes at a hot-plate temperature of 170° F. and set aside to crystallize. When the waxy white solid product was spread on filter paper and heated 3 seconds at 300° F., there was gassing but no color change, mixed with ninhydrin-purple black, with isatin-green black, and with alloxan-dark lavender.

(39) 2 grams tert. butylamine were added to a slurry of 1 g. Example 22 in 10 g. methanol. The solids changed and formed a jelly-like substance in the cold. A solution was formed on warming 7 minutes at a hot-plate temperature of 170° F. The mixture was set aside to crystallize. The white crystals melted at 121–7° C. with decomposition and became lavender, mixed with ninhydrin-lavender at 90° C., purple lavender at 103° C. and melting, purple black at 121° C., with isatin-brown and melting at 121° C., with alloxan-light lavender at 90° C., and lavender at 121° C. Spread on filter paper and heated 3 seconds at 300° F., the sample became red-lavender, with ninhydrin-purple black, with isatin-dark brown, and with alloxan-purple brown.

(40) 2 grams isopropylamine were added to a slurry of 1 g. Example 22 in 10 g. methanol. A solution formed cold. The mixture was heated 7 minutes at a hot-plate temperature of 170° F. and set aside to crystallize. The white crystals melt at 141–4° C. with gassing but no color change, mixed with ninhydrin-purple and melting at 90° C., dark green at 98° C., with isatin-brown and melting at 130° C., with alloxan-light lavender at 90° C., lavender at 105° C. and lavender purple and melting at 130° C. Spread on filter paper and heated 3 seconds at 300° F., the sample gave no color change, with ninhydrin-dark green, with isatin-brown, and with alloxan-dark lavender.

(41) 2 grams tert. octylamine (Rohm & Haas) were added to a slurry of 1 g. Example 22 in 10 g. methanol. A solution formed on stirring. The mixture was warmed 7 minutes at a hot-plate temperature of 170° F. and set aside to crystallize. The white crystals soften at 120° C. becoming light lavender and melt at 130–6° C. with gassing. Mixed with ninhydrin-light lavender at 90° C., lavender and melting at 100° C., and purple brown at 120° C., with isatin-red brown at 145° C., with alloxan-light lavender at 90° C., lavender at 120° C., and purple and melted at 145° C. Spread on filter paper and heated 3 seconds at 300° F., the sample turned red lavender, with ninhydrin-lavender purple, with isatin-brown, and with alloxan-lavender.

(42) 2 grams n-amylamine were added to a slurry of 1 g. Example 21 in 20 g. methanol. A solution formed at room temperature. The mixture was warmed 5 minutes at 170° F. hot-plate temperature and set aside to crystallize. The white crystals melt at 193–5° C. with no color change, mixed with ninhydrin-light purple at 96° C., purple and starting to melt at 133° C. with isatin-brown and started to melt at 160° C., with alloxan-salmon lavender at 160° C. Spread on filter paper and heated 3 seconds at 300° F., the sample gave no change, with ninhydrin-purple, with isatin-green brown, and with alloxan-lavender pink.

(43) 4 grams di-n-butylamine were added to a warm solution of 2 g. alloxan in 20 g. methanol, warmed 10 minutes at a hot-plate temperature of 170° F., and set aside to crystallize. The white crystals (some hygroscopy) melt at 113–6° C. with heavy gassing but no color change, mixed with ninhydrin-light brown at 80° C., purple and melting at 92° C., black and melted at 96° C., with isatin-orange brown and melted at 105° C., with alloxan-red lavender and melting at 105° C. Spread on filter paper

and heated 3 seconds at 300° F., the sample did not change, mixed with ninhydrin-greenish purple black, with isatin-dark brown, and with alloxan-lavender.

(44) 4 grams 1,2,3,4-tetrahydroquinoline were added to a warm solution 1 g. ninhydrin in 20 g. methanol, warmed 10 minutes at a hot-plate temperature of 170° F., and set aside to crystallize. The yellow orange crystals melt at 168–170° C. gassing and becoming brown, mixed with ninhydrin-light brown at 99° C., purple and melting at 163° C., with isatin-brown and melting at 145° C., with alloxan-yellow lavender at 142 C., lavender brown and melting at 153° C. Spread on filter paper and heated 3 seconds at 300° F., the sample turns blue and becomes colorless on cooling (thermochromic). Mixed with ninhydrin-black, with isatin-brown, and with alloxan-purple.

(45) 4 grams indoline were added to a solution of 2 g. alloxan in 20 g. methanol, warmed 10 minutes at a hot-plate temperature of 170° F., and set aside to crystallize. The off-white colored crystals became light pink at 114° C., pink at 140° C., lavender at 180° C., but no melt below 210° C. Mixed with ninhydrin-purple and starting to melt at 140° C. and purple-black at 180° C. With isatin-dark brown and melting at 177° C., and with alloxan-brown at 180° C. Spread on filter paper and heated 3 seconds at 300° F., the sample became purple, with ninhydrin-purple black, and with isatin-brown black.

(46) 4 grams indoline were added to a slurry of 2 g. 1,3-indanedione in 20 g. methanol, warmed 10 minutes at a hot-plate temperature of 170° F., and set aside to crystallize. The product precipitated in less than 2 hours. The green crystals melt at 195–200° C. with no color change, mixed with ninhydrin-a purple sublimation at 130° C., with isatin-dark brown and melting at 167° C., and with alloxan-blue green at 200° C. Spread on filter paper and heated 3 seconds at 300° F., sample-no change, with ninhydrin-purple, with isatin-brown, with alloxan-blue green.

(47) 4 grams 1-phenylpiperazine were added to a warm solution of 2 g. ninhydrin in 20 g. methanol. Crystallization started within 1 minute. The light buff crystals become light purple and soften at 110° C., dark green at 125° C., and melt becoming green-black at 142–5° C. Mixed with ninhydrin-purple at 125° C. and purple black at 163° C., with isatin-brown at 125° C. and dark brown and melting at 143° C., with alloxan-lavender brown at 160° C.

(48) 4 grams 1-phenylpiperazine were added to a slurry of 2 g. isatin in 20 g. methanol, warmed 10 minutes at a hot-plate temperature of 170° F. and set aside to crystallize. A precipitate formed in less than two hours. The light cream crystals become light brown at 111° C. and brown-black at 145–6° C. with melting. Mixed with ninhydrin-light purple at 81° C., purple and melting at 105° C. and purple black at 111° C., with isatin-dark brown at 148° C., with alloxan-dark brown at 145° C. Spread on filter paper and heated 3 seconds at 300° F. the sample turned brown black, with ninhydrin-black, with isatin-dark brown, and with alloxan-red black.

(49) 4 grams 2,6-dimethylpiperidine were added to 2 g. alloxan in 20 g. methanol, warmed 10 minutes at a hot-plate temperature of 170° F., and set aside to crystallize. A precipitate formed within 2 hours. The white crystals become lavender pink at 145–8° C. and melt with decomposition. Mixed wih ninhydrin-green at 105° C., purple brown at 130° C., and purple black with melting at 141° C., with isatin-brown and melting at 150° C., with alloxan-lavender and melting at 130° C. Spread on filter paper and heated 3 seconds at 300° F., the sample became lavender, with ninhydrin-purple black, with isatin-brown, and with alloxan-lavender.

B. *Preparation of thermocopies*

a. A hot 2 percent solution of Example 26 (alloxan-dicyclohexylamine) in methanol was coated onto 20 pound S. D. Warren tissue grade paper, dried, overcoated with a hot 2 percent solution of ninhydrin in methanol, and dried. The combined dry weight of coating was less than 2 lb./3000 sq. feet. The dry copy paper was passed with a master through a model 45 Thermofax machine to give a legible reflex copy of brown purple on an off-white background.

b. Plain white notepad paper was coated with a hot 2 percent solution of Example 22 (alloxan-morpholine) in di-n-butyl ketone, dried, then top-coated with

(1) A 1 percent solution of ninhydrin in methanol and dried. The total combined dry weight coat was less than 2 lb./3000 sq. feet. When run through a model 45 Thermofax machine with a master, a legible direct copy of the master was obtained, purple on a white background;

(2) A hot 1 percent solution of alloxan in methanol to give a combined weight coat of less than 2 lb./3000 sq. feet. The dry sheet was run through a model 45 Thermofax machine to give a legible direct copy of red on a light pink background;

(3) A hot 1 percent solution of isatin in methanol-di-n-butylketone to give a combined dry weight coat of less than 2 lb./3000 sq. feet. The dried sheet was run through a Thermofax model 45 machine to give a legible direct copy of brown on an orange background;

(4) A hot solution (1%) of Example 19 (isatin-N-methylpiperazine) in methanol-di-n-butylketone to give a combined weight-coat of less than 2 lb./3000 sq. feet. The dry sheet was run through a model 45 Thermofax machine to give a legible copy of brown on a light buff background;

(5) A hot one percent solution of Example 10 (hydrindantin-morpholine) in methanol-di-n-butylketone to give a total weight coat of less than 2 lb./3000 sq. feet. The dry sheet was run through a model 45 Thermofax machine to give a legible copy of purple brown on a very light buff background;

(6) A hot one percent solution of Example 21 (isatin-pyrrolidine) in methanol-di-n-butylketone to give a combined dry weight coat of less than 2 lb./3000 sq. feet. The dry sheet was passed through a model 45 Thermofax machine to give a legible direct copy of blue on a light yellow background;

(7) A hot one percent solution of Example 9 (ninhydrin-N-methylfurfurylamine) to give a combined dry weight-coat of less than 2 lb./3000 sq. feet. The dry sheet was passed through a model 45 Thermofax machine to give a legible direct copy of brown-black on a light yellow brown background;

(8) A one percent solution of Example 16 (isatin-piperidine) in methanol for a combined dry weight coat of less than 2 lb./3000 sq. feet. The dry sheet was passed through a model 45 Thermofax machine to give a legible direct copy of blue-green on yellow.

c. A 2 percent solution of Example 9 (ninhydrin-N-methylfurfurylamine) in methanol was coated on ordinary white notepad paper to give a dry weight-coat of less than 2 lb./3000 sq. feet. The dry sheet was passed through a model 45 Thermofax machine to give a legible direct copy of purple-black on a light lavender background.

It was noted that in some cases a pale background color was developed, as compared to the original color, by passage through the machine. This is normal in this type process. However, good contrast between copy and background was in every case achieved. Such contrast was better than in known thermocopy sheets. Such background development is reduced by decreasing activation temperature (increasing machine speed.)

d. A hot 2 percent solution of Example 10 (hydrindantin-morpholine) in methanol was coated on ordinary white note-pad paper to a dry weight-coat of less than 2 lb./3000 sq. feet. The dry sheet was passed through a model 45 Thermofax machine to give a legible direct copy of purple-brown on a light yellow background.

e. A hot 2 percent solution of Example 11 (hydrindantin-piperidine) in methanol was coated on ordinary white note-pad paper to a dry weight-coat of less than 2 lb./3000 sq. feet. The dry sheet was passed through a model 45 Thermofax machine to give a legible direct copy of purple on a yellow background.

f. A hot 2 percent solution of Example 12 (hydrindantin-1,2,4-trimethylpiperazine) in methanol was coated on ordinary white note-pad paper to a dry weight-coat of less than 2 lb./3000 sq. feet. The dry sheet was passed through a model 45 Thermofax machine to give a legible direct copy of purple-black on light lavender.

g. A hot 2 percent solution of Example 1 (ninhydrin-morpholine) in methanol was coated on ordinary white note-pad paper to a dry weight-coat of less than 2 lb./3000 sq. feet. The dry sheet was passed through a model 45 Thermofax machine to give a legible direct copy of brown on light yellow.

h. A hot 2 percent solution of Example 2 (ninhydrin-2,6-dimethylmorpholine) in methanol was coated on ordinary white note-pad paper to a dry weight-coat of less than 2 lb./3000 sq. feet. The dry sheet was run through a model 45 Thermofax machine to give a legible direct copy of brown on yellow.

i. A hot 2 percent solution of Example 5 (ninhydrin-N-methylpiperazine) in a 5 percent solution of Ethocel N–100 (binder) in methanol was coated onto ordinary white note-pad paper to a dry weight-coat of less than 2 lb./3000 sq. feet. The dry sheet was passed through a model 45 Thermofax machine to give a legible direct copy of purple on a yellow-orange background.

j. A hot 2 percent solution of Example 1 (ninhydrin-morpholine) in a 5 percent solution of Ethocel N–100 in methanol was coated on ordinary white note-pad paper to a dry weight-coat of less than 2 lb./3000 sq. feet. The dry sheet was passed through a model 45 Thermofax machine to give a legible direct copy of brown on a light pink background.

k. A hot 2 percent solution of Example 2 (ninhydrin-2,6-dimethylmorpholine) in a 5 percent Ethocel N–100 solution in methanol was coated onto ordinary white note-pad paper to a dry weight-coat of less than 2 lb./3000 sq. feet. The dry sheet was passed through a model 45 Thermofax machine to give a legible direct copy of brown on a yellow background.

l. A hot 2 percent solution of Example 3 (ninhydrin-1,2,4-trimethylpiperazine) in a 5 percent Ethocel N–100 solution in methanol was coated onto ordinary white note-pad paper to a dry weight-coat of less than 2 lb./3000 sq. feet. The dry sheet was passed through a model 45 Thermofax machine to give a legible direct copy of brown-orange on a cream background.

m. A 1 percent solution in ethyl alcohol was made from each of the following: ninhydrin, Example 17, Example 5, Example 10, Example 22 and Example 21. When these were mixed in equal proportions in the following combinations, coated onto S. D. Warren paper at a weight-coat of less than 2 lb./3000 sq. feet, dried, and run through the model 45 Thermofax machine to obtain reflex copies, the following results were obtained:

21–5 brown copy on yellow-orange background
10–22 lavender purple copy on light salmon background
10–5 lavender purple copy on yellow background
10-ninhydrin lavender copy on light salmon background
10–21 dark blue copy on pink background
5–22 purple copy on white background
5–17 dark blue copy on yellow background
22–21 dark blue copy on yellow background
22–17 dark blue copy on yellow background
5-ninhydrin purple copy on off-white background
21-ninhydrin green copy on red-brown background
22-ninhydrin purple copy on light lavender background
21–17 blue copy on yellow background
17-ninhydrin red-lavender copy on tan background
10–17 blue-purple copy on tan background.

n. Ethylene diamine, diethylene triamine and cyclohexylamine (all primary amines) were each added to separate alcoholic solutions of Example 5 in methanol. There was no color reaction, as occurs when such amines are added to the unreacted cyclic polyketone. This proved that the intermediate does not react with a base to form a color and that the intermediate is a different compound from the starting polyketo compound. These solutions were quite stable and were lighter in color than the original untreated Example 5 solution after 24 hours aging. They were coated onto S. D. Warren thermocopy grade tissue paper and reflex copies were made on the model 45 Thermofax machine. When only a small amount of amine was used, the color of the image was shifted from purple to red-brown and the background from yellow orange to yellow. When more amine was used, no reflex copies could be obtained. In this way, color of image and background can be shifted, if desired, by judicious use of an amine additive.

o. Molecular compounds were made from bisphenol A with ethylene diamine, diethylene triamine and cyclohexylamine according to the teaching of US 3,076,707. Hot solutions of the molecular compounds in methanol were coated onto S. D. Warren thermocopy grade tissue paper, dried, and overcoated with alcoholic solutions of Examples 17, 10, 22 and 20. When the bisphenol complex was dissolved it dissociated to liberate amine but the amine did not activate the overcoat intermediates of the examples whereas they immediately react with an overcoating of the polyketo compounds themselves. As aforesaid, no activation was obtained, whereas where the overcoat comprises the compositions of the above patent, the entire sheet is activated immediately upon overcoating due to the amine released in the undercoat.

(16) One percent solutions of Examples 1, 16, 17 and 19 were made in a one percent solution of Ethocel N–100 in methanol and blended separately in equal amounts of each with separate solutions of 1 percent of Examples 43 and 40 in 1 percent Ethocel N–100 in methanol. These mixed solutions were coated on S. D. Warren tissue thermocopy paper and reflex copies were made on the model 45 Thermofax machine. All made legible copies at the settings for white Thermofax paper.

The above examples are intended only to illustrate the versatility and working of the invention and are not meant to limit the scope of the invention in any manner.

The parent compounds of the cyclic polyketo compounds were used as illustrations, but anyone skilled in the art and familiar with this disclosure will realize that homologs and analogs of these parent compounds can be used. As aforesaid, any of the cyclic polyketo compounds commonly used in making dyes by reaction with ammonia or a primary amine can also be used to make the intermediate compounds of the present invention. Examples in addition to those referred to above are 1,4-naphthoquinone; 2,5-dichloronaphthoquinone; 2-amino-1,4-naphthoquinone; tetrachlorobenzoquinone; 2 methyl-1,4-naphthoquinone; 1-nitroanthraquinone; 1,5-dinitroanthraquinone; 1-nitro-2-carboxy-anthraquinone; 9,10-dioxyanthracene; indane-1,2-dione; bis-indane-1,3-dione; 2-hydroxy-indane-1,3-dione; and 2-phenylindane-1,3-dione.

The types of amines used in the examples show the general breadth of the invention. Any secondary amine can be used including alkyl, aryl, alicyclic, alkyl aryl, aralkyl, alkyl alicyclic, aryl alicyclic and heterocyclic amines. Heterocyclic amines are preferred.

The above mentioned inumerable combinations of components illustrate the versatility with regard to color of image and background and also flexibility in choosing the temperature of activation.

It has been discovered that solid aromatic hydroxy compounds, solid acids, solid anhydrides, solid keto compounds, solid aldehydes and other similar solid acidic activator compounds will increase the copying speed from

10 to over 100 percent by decreasing activation temperature when incorporated with the amine-polyketo compounds of the present invention.

Examples of such compounds are as follows:

- Aromatic hydroxy compounds—
  - beta naphthol (mono hydroxy)
  - dihydroxy aromatics such as hydroquinones, e.g., hydroquinone monoethyl ether
  - trihydroxy aromatics such as pyrogallol
- Solid aliphatic, aryl, alicyclic, aryl aliphatic, alicyclic aliphatic and aryl alicyclic acids—
  - fatty acids such as azelaic, stearic, docosanoic, lauric, myristic, glutaric, etc. acids;
  - aromatic acids such as ortho and meta toluic acids, benzoic acid, phenoxy acetic and phenyl acetic acids, etc.
  - alicyclic acids such as 2-furoic acid.
- Solid ketones—benzil
- Anhydrides of the solid acids referred to above—
  - itaconic anhydride
  - benzoic anhydride
  - cis 4-cyclohexene, 1,2-dicarboxylic anhydride.

These activators must be solid since in liquid form the acidic nature thereof would cause premature dye formation.

These activators can be screened very simply by mixing the potential activating or accelerating compound with the amine-polyketo compound as dry powders, spreading on paper along with the amine-polyketo compound alone and exposing to the direct copy process on the Thermofax machine. When the activator is effective, a higher setting can be used to obtain the same copy as obtained by the amino-polyketo compound alone. As aforesaid, these activators are effective to reduce the activation temperature of the amine-polyketo compound.

When the reaction products of the following examples were mixed with the following activators in a ratio of 1 to 1, the activation temperatures were reduced to the following temperatures:

Example	Activator	Activation Temperature, ° C.
9	B-naphthol	65
16	do	85
9	Azelaic acid	52
16	do	74
9	m-Toluic Acid	53
16	do	70
2	2-Furoic Acid	57
9	Itaconic anhydride	55
16	do	58
2	do	61
9	Cis-4-cyclohexene-1,2-dicarboxylic anhydride.	61
16	do	82
2	do	77
9	Alpha benzylhydrocinnamic acid	60
16	do	73
2	do	73
9	Benzil (ketone)	72
16	do	93
2	do	95

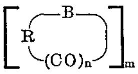
The proportions of activator to intermediate are not particularly important so long as such proportions do not form a eutectic liquid mixture under normal conditions described above since this causes premature dye formation.

I claim:

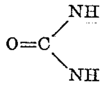
1. A heat developable copy sheet containing a reaction product of a primary amine of the group consisting of an alkyl amine, an alkylene polyamine, a cycloalkyl amine and a furfuryl amine reacted in a non-acid medium and at a temperature below the decomposition temperature of said reaction product, with an intermediate reaction product of (1) an amine selected from the group consisting of a secondary and a tertiary amine and (2) a solid cyclic polyketo compound of the type normally used to form a dye by reaction with a primary amine, reacted with an excess of said amine in a non-acid medium at a temperature below the decomposition temperature of said intermediate reaction product.

2. A sheet according to claim **1**, said reaction temperatures being not greater than 200° F.

3. A sheet according to claim **2**, said polyketo compound having the molecular structure



where *n* is 2 or more, *m* is 1 or 2, R is selected from the group consisting of a substituted and unsubstituted aromatic radical, radical



and radical ethylene, which is part of the ring which includes B and $(CO)_n$, and B is selected from the group consisting of the amino, methylene, ethylene, keto, aromatic, —C—OH and —C—H groups, which is part of the ring which includes R and $(CO)_n$.

4. A sheet according to claim **3**, said amine being a secondary heterocyclic amine.

5. A sheet according to claim **1**, also containing in addition to said reaction product a solid cyclic polyketo compound. different than that used to make said intermediate reaction product.

6. A sheet according to claim **1**, said polyketone being selected from the group consisting of an isatin, ninhydrin, hydrindantin, 1,3 and 1,2-indandione, 1,3-bisindandione, alloxan, alloxantin, perinaphthindan-1,2, 3-trione and perinaphthindan-1, 3-dione, 1,4-naphthaquinone, benzoquinone, anthraquinone and 9,10-dioxyanthracene, unsubstituted and substituted by a radical of the group consisting of nitro, amino, alkyl, alkylene, carbonyl and halogen, said amine of said intermediate reaction product being a secondary heterocyclic amine.

7. A sheet according to claim **6**, said cyclic polyketo compound being isatin and said primary amine being an aliphatic amine.

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