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HEAT-SENSITIVE COPYING SHEET

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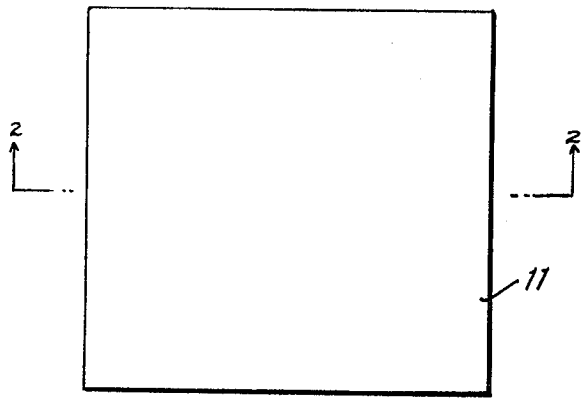


FIG. 1



FIG. 2

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HEAT-SENSITIVE COPYING SHEET

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This invention is concerned with a novel heat-sensitive copying sheet. More specifically, it relates to a novel composition, which coated onto a base sheet forms a thermally activatable reproduction material.

Heat-reactive copying sheets are well-known in the arts. They may be classified broadly into two types. In one type, an opaque surface is made transparent through the application of heat. The transparentized surface coating exposes a coloured background. If the transparentized areas are limited to those equivalent to the original image, then a satisfactory reproduction has been achieved. The second type of heat-reactive copy sheet employs a chemical reaction initiated by heat.

It is an object of my invention to provide a novel heat-reactive copying sheet of the chemical type. It is a further object of my invention to provide a novel heat-reactive copying sheet devoid of the many shortcomings of the products of the prior art. It is a further object of my invention to provide a heat-sensitive copying sheet with improved heat sensitivity. Another object of my invention is to provide a heat-sensitive copying sheet with improved storage life. It is a further object of my invention to provide a heat-sensitive copying sheet of excellent image reproducibility. It furthermore is a principal object of my invention to provide new methods for producing a heat-sensitive copying sheet. Said novel methods are designed to eliminate the many difficulties associated with the preparation of prior art products.

To better appreciate the novel features of the present invention, it is necessary to critically evaluate the main features of the prior art. We are concerned here exclusively with one sub-class of the chemical type of heat-sensitive reproducing sheets, namely that class comprising at least one organo-metallic reactant. The many patents issued for this type of reaction deal both in their disclosures as well as their claims with a coating comprising two or more solid reactants which are potentially chemically capable of irreversible and rapid reaction at normal room temperature to produce a visibly different reaction product. These solid reactants are kept in physically distinct relationship and prevented from so reacting with one another. Upon application of heat the physically separated reaction products melt and thus come in contact with one another. This basic idea of having two reactants in close contact with one another and yet physically distinct from one another, has been presented in many patents such as U.S. 2,663,654, 2,663,656, 2,899,334, 3,108,896 and many others. The disadvantages of this idea are manifold. The solid reactants must be reduced to a minimum size by mechanical means. This entails grinding for many hours and sometimes even for days. Since the solid reactants must be maintained physically separated, each reactant must be ground individually. Thus the preparation of reactants is both costly and time consuming. There are mechanical limitations to the size to which the reactants can be reduced. Thus heat-sensitive copying sheets of the prior art have a definite grainy and rough appearance. One can both see and feel the solid particles. The size of the individual particle furthermore limits the resolution

of the reproduced image. The larger the particle the poorer the resolution. However, even the smallest size particle available from mechanical grinding yields relatively poor resolution.

The objective of keeping solid reactants physically distinct is usually achieved with the aid of a binder. The binder, a polymeric material, serves the dual function of adhering the solid particles to the substrate as well as separating the two potential reactants from one another. This second function requires a coating composition comprising as much as 20% of a non-reactive binding material. In the prior art product, it is therefore necessary to apply heavy coats of the reactant material in order to compensate for the presence of 20% of non-reactive binder. Further difficulties were encountered with prior art products upon prolonged storage or exposure to even slightly elevated temperatures. The physically separated reactants have a tendency to fuse if given enough time or slight encouragement by even slightly elevated temperatures.

The basic features of my invention are such as to have eliminated all of the aforementioned objections. The "physically distinct" specification has been discarded altogether.

The invention will be further described by reference to the accompanying drawings which are made a part of this specification.

FIG. 1 is a plan view of a heat-sensitive copying sheet made in accordance with this invention.

FIG. 2 is a cross-sectional view taken along lines 2—2 of FIG. 1.

A detailed description of this invention will now be set forth having reference to the specific form thereof as set forth in the accompanying drawings. In this connection, however, the reader is cautioned to note that the specific forms of the instant invention as set forth in the drawings and specification herein are for illustrative purposes and for purposes of example only. Various changes and modifications may obviously be made within the spirit and scope of this invention.

Now referring to the drawings herein for a detailed description of this invention.

The novel heat-reactive reproducing sheet of the present invention **11** comprises a substrate and deposited thereon a heat reactivatable coating **13**. The substrate **12** may be paper or plastic film, or any other suitable material. The coating comprises two reactants, a pH modifier, and a binder.

The two reactants are selected from (a) organo-metallics and (b) aromatic reducing agents. They are furthermore selected on the basis of yielding no coloured products when reacting with one another under either acid or neutral conditions. The two reactants may therefore be dissolved in a common solvent without discolouring the solution.

The pH modifier may be chosen so as to react with either of the two reactants. The complex thus formed must be stable at ordinary room temperature but must decompose, librating the pH modifier, at temperatures between 60–120°. The pH modifier may alternatively be complexed with some other product. The critical requirement being that said complex be stable at room temperature and heat decomposable between 60–120° centigrade. The pH modifier exerts little influence over the pH at room temperature. However, at elevated temperature the

complex decomposes liberating the modifier causing a considerable change in pH.

The binder may be selected from amongst that many commercially available film-forming polymers. The desirable physico-chemical properties of said binder being:

(a) Good adhesion to the substrate
(b) Chemical inertness towards the reactants
(c) A softening point higher than 150° centigrade
(d) Good heat and light stability

Examples of such satisfactory binders are: Ethyl cellulose, styrene homo and copolymers, butyl rubber, and many others.

The aforementioned as well as many other features of my invention will become apparent from an examination of the following examples:

EXAMPLE 1

	Parts by weight
Mercuric palmitate	710
Resorcinol	110
o-Toluidene acetate	88
Saran	90
Methyl ethyl ketone	2000

The mercuric palmitate is prepared in a manner well-known in the arts. A mercury salt is reacted with either palmitic acid or an alkali salt of palmitic acid. The o-toluidene acetate is prepared by adding to a cooled sample of o-toluidene equimolar quantities of acetic anhydride. The crystals formed are washed with toluene and dried under vacuum. Saran is a vinylidine chloride-acrylonitrile copolymer. The grade employed in this example was that manufactured by the Dow Chemical Company of Midland, Michigan under its trade name of "Saran Resin F220." The Saran is dissolved in the methyl ethyl ketone to yield a 10° resin solution. The remainder of the solvent is required for the solution of the metallic soap, the resorcinol, and the pH modifying o-toluidine acetate. The quantity of solvent employed may be varied in order to modify the viscosity of the solution. The quantity of binder may also be increased if the coating operation demands considerably higher viscosity. The solution is coated onto glassene-type paper or transparent plastic film by any one of the many well-known coating processes. The solvent is evaporated in an air current at temperatures not to exceed 100° F.

The dry coated material has a slight buff colour and gives excellent reproductions of printed material if placed in contact with same and passed through one of the commercially available thermo reproducing devices.

EXAMPLE 2

	Parts by weight
Copper stearate	635
Hydroquinone-piperazine	196
Ethyl cellulose	40
Ethyl acetate	1600

The copper stearate is prepared by methods well-known in the art. A copper salt is reacted with stearic acid or an alkali salt of stearic acid. In this example the pH modifier and reducing agent have been combined into one reactant. Equimolar quantities of hydroquinone and piperazine are dissolved in methyl ethyl ketone and upon addition form a buff coloured crystallin product. This addition compound protects the hydroquinone from premature oxidation. It furthermore provides a latent pH modifier. In the absence of piperazine, the copper stearate and the hydroquinone will not form a coloured reaction product. With excessive heat or prolonged periods of exposure to oxygen, the hydroquinone will oxidize and a minor colour change will be noticeable. The said colour change, however, is insufficient to produce legible copy.

Only at a pH of 8 or higher will copper stearate and hydroquinone react to yield a dark coloured product. The piperazine hydroquinone addition compound then has a dual function, namely to protect the hydroquinone from undue oxidation during storage and furthermore upon application of heat to liberate piperazine, a base, which will create the necessary environmental conditions to permit the copper stearate to react with the hydroquinone and yield a coloured reaction product.

This same consideration applies to all the examples cited. In the previous Example 1, resorcinol does not react with a mercuric salt to yield a coloured product except at a pH of 8 or higher. The pH modifier employed in that example, o-toluidine acetate, upon heating decomposes to yield a strong base, o-toluidine. Thus an otherwise colourless reaction is made to yield a coloured product by the introduction of a heat labile pH modifier.

The ethyl cellulose of this formula is a grade sold by the Dow Chemical Company of Midland, Michigan under their trade name of "Ethocel" having an epoxy range of 48.0 to 49.5% and a viscosity of approximately 200 centipose in a 5% solution at 25° centigrade in a solvent mixture consisting of 80 parts toluene and 20 parts ethyl alcohol.

The ethyl cellulose is dissolved in the ethyl acetate to yield a 10% solution. The copper stearate and hydroquinone-piperazine complex are each individually dissolved in the ethyl acetate solvent. The three solutions are combined and solvent added to adjust the viscosity to meet coating requirements. Coating and drying procedures are identical with those outlined in Example 1.

EXAMPLE 3

	Parts by weight
Copper palmitate	535
Hydroquinone-piperazine complex	196
Ethyl cellulose	50
Ethyl acetate	1500

This example serves to illustrate that salts of several fatty acids may be employed to yield identical results.

EXAMPLE 4

	Parts by weight
Magnesium palmitate	547
Catechol-p-phenylenediamine	218
Ethyl cellulose	75
Toluol	3200

The magnesium palimitate is prepared in a manner well-known in the art. The catechol-piperazine addition compound is prepared by dissolving catechol and p-phenylenediamine each separately in chloroform and thereafter combining the two solutions. The white addition compound separating is filtered and vacuum dried. The grade of ethyl cellulose employed in this example was identical to that in Example 2.

The examples cited are not to be construed as limiting my invention. They are rather illustrations of an almost infinite variety of metallic soaps, reducing agents, and thermally activated pH modifiers.

What I claim is as follows:

1. A heat-sensitive copying sheet for making clear and sharp copies of a graphic subject matter by methods involving a brief application of a heat pattern corresponding to said graphic subject matter, said copying sheet being visibly stable at normal room and storage temperatures and under exposure to light, said copying sheet including a flexible substrate and coated thereon a visibly heat-sensitive layer comprising a metallic soap and a reducing agent, said reactants yielding no coloured reaction products at a pH lower than 7, where at least one of the two reactants has a melting point between 60 and 120° C., and thirdly a latent pH modifier, said modifier selected from the class consisting of o-toluidine acetate, hydroquinone-piperazine complex, and catechol-p-phenylene diamine, all of the above in unimolecular contact with

one another and adhered onto the flexible substrate with the aid of a non-reactive binder.

2. A heat sensitive copying sheet as described in claim 1, said pH modifier being o-toluidine acetate.

3. A heat sensitive copying sheet as described in claim 1, said pH modifier being hydroquinone-piperazine complex.

4. A heat sensitive copying sheet as described in claim 1, said pH modifier being catechol-p-phenylene diamine.

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