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[54] **THERMAL RECORDING METHOD**

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[52] **U.S. Cl.** ..... **428/500**; 96/115 R; 427/145

[51] **Int. Cl.**[2] **B41M 5/18**

[58] **Field of Search** ..... 117/36.7, 36.8; 96/115 R; 346/1

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[57] **ABSTRACT**

A thermal recording is effected by applying a thermal pattern to a recording member having a recording layer composed of at least a polymer complex to produce a reversible latent image capable of being visualized.

23 Claims, 3 Drawing Figures

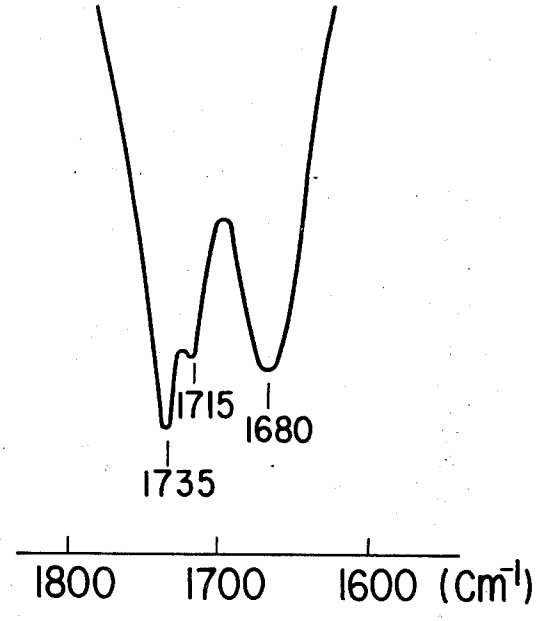


FIG. 1

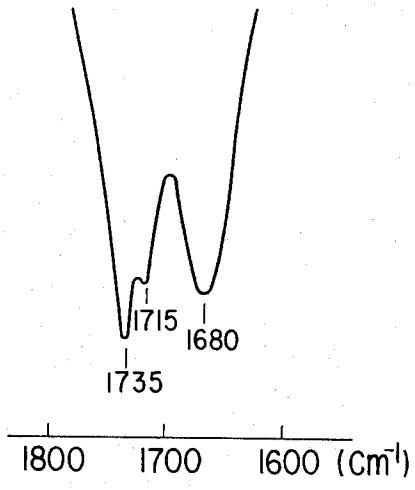


FIG. 2

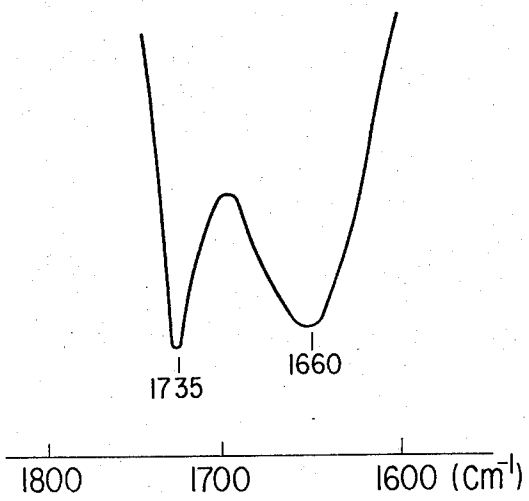
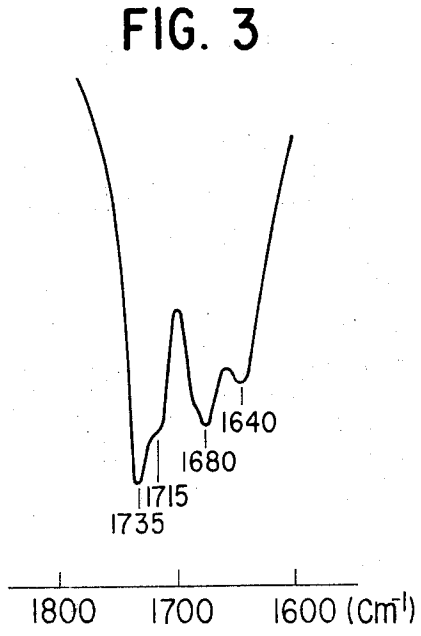


FIG. 3



THERMAL RECORDING METHOD

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a novel thermal recording method. The thermal recording method is a recording method comprising applying heat in the form of an image pattern (hereinafter called "thermal pattern") to a heat sensitive material sheet such as a thermal recording sheet, and converting the resulting image to a visible image.

2. Description of the Prior Art

Heretofore, there have been known many methods for converting a thermal pattern to a useful recording image such as a visible image or printing image. These methods are described in detail in "Insha Kogaku" II, Shingo Henkanron, Chapter 5, Thermal Method, pp. 234–240, edited by Masanobu Wada, published by Kyoritsu Shuppan (1969), in which is described the conversion of a chemical, physical, electrical or magnetic change caused by heat on a recording sheet directly or indirectly to a visible image. Some of them will be explained below somewhat more in detail. There is used a thermal recording sheet produced by coating onto a substrate finely divided particles of a hydrophobic high polymer having a glass transition point of less than 40°C such as polyethylene latex dispersed in a hydrophilic high polymer such as gelatin, casein, polyvinyl alcohol (PVA) and the like. A thermal pattern is applied to this sheet to cause fusing of the hydrophobic resin particles at a high temperature portion resulting in change of various properties of the sheet surface such as mechanical strength, solubility, dye acceptability, inking property and the like. It is also possible to produce relief images or dye images by washing with water or soaking in an aqueous solution of dye after applying a thermal pattern or to use directly as an offset printing plate. The above mentioned thermal recording methods and thermal recording sheets used therefor are disclosed in M. N. Vrancken: "SPBE 2nd Symposium on Unconventional Photographic Systems" (1967) and Japanese Patent Publication No. 1743/1964.

There are commercially available products produced according to the above methods. For example, a polyester sheet covered with a hydrophobic resin emulsion and a pigment dispersed in an aqueous resin is exposed to a thermal pattern and washed with water wherein the portion subjected to high temperature to form a pigment image.

Also known is a thermal recording sheet capable of producing a visible image only by applying a thermal pattern without a developing treatment. Usually, such thermal recording sheets have a thermal recording layer composed of at least two kinds of solid reaction components capable of releasing active components as the result of melting or decomposing at a temperature corresponding to a high temperature portion of the thermal pattern, dispersed in a binder resin, and capable of producing a colored matter by reaction when heated. These reaction components are physically separated so that no reaction occurs at room temperature. However, when one of them is heated to the melting point or decomposition temperature, there is caused contact between both of them or the released active components to initiate the reaction and produce a colored matter. There have been known many kinds of reaction components and combinations thereof. A Representative one is a combination of a long chain fatty acid metal salt with a chelating agent or an organic reducing agent. Representative chelating agents are tannic acid, pyrogallol and spiropyrans, and a representative reducing agent is hydroquinone. As the result of mutual reaction, there is formed a visible image composed of metal chelate or metal.

The above-mentioned prior arts have many drawbacks. The image is composed of a pigment, metal chelate, metal and the like so that it is not possible to obtain transparency, light color and high purity. These drawbacks are disadvantageous especially when the thermal recording sheet is used for a overhead projector or regeneration of color by a thermal recording method.

On the other hand, there is a drawback common among thermal recording sheets for converting a physical or chemical change caused by a thermal pattern to a visible image. This common drawback is that the production of the thermal recording sheet is carried out at a temperature lower than the heat response temperature (heat sensitive temperature) of the sheet. The heat sensitive temperature is a temperature which is sufficient to produce a visible image and generally ranges from 60°C to 150°C, preferably from 80°C to 120°C. For example, when a thermal recording sheet having a heat sensitive temperature of 80°C is produced, the coating and drying should be naturally carried out at 15° – 60°C for safety. In general the heat sensitive temperature when wetted with a solvent is lower than that of the dried coating so that it is more necessary to operate at low temperatures. The above difficulty is mainly due to irreversibility of response of the thermal recording sheet to heat or thermal response. There are known thermal recording methods and sheets having reversible thermal response. For example, a dielectric high polymer film is uniformly charged and then exposed to a thermal pattern. There occurs a rapid lowering of electric resistance at a temperature higher than the secondary transition temperature of the high polymer film and the electrostatic charge is decayed at a high temperature portion of the thermal pattern to produce an electrostatic pattern, which is then developed with a charged toner to produce a visible image. This method is published in P. M. Cassiers: Photogr, Sci, & Eng., 4, p. 199 (1960) and is called electrothermography. Most electrothermography or other thermal recording sheets utilizing electric and magnetic changes which show reversible thermal response and therefore such difficulty as mentioned above is not present and high temperature coating is also possible. However these thermal recording methods need an additional operation such as charging, magnetization and the like and therefore the apparatus is disadvantageously complicated. The above-mentioned drawbacks are the cause of the high cost of commercially available thermal recording sheets.

The present inventors have now found that a thin film composed of a certain kind of high polymer complex shows a peculiar thermal behavier. This thin film is uniform and transparent and can not be dyed with a dye liquid developer at room temperature, but when heated at a temperature higher than a certain temperature, it can accept a dye from the dye liquid developer and be dyed. This property can be directly used for production of the thermal recording sheet and the thermal recording method. The high polymer complex thin film pro-

vided on a support is used as a thermal recording sheet and a thermal pattern is applied to the surface and then the sheet is contacted with a dye liquid developer to produce a visible image accepting selectively the dye at the high temperature portion of the thermal pattern. Suprisingly it has been found that the acceptability of the portion subjected to high temperature by the thermal pattern disappears gradually and completely loses such acceptability. In other words the heat response of the thermal recording sheet according to the present invention is reversible. The image portion capable of accepting a dye when exposed to a high temperature is hereinafter called a latent image in the present invention. It has also now been found that the latent image and other portions of the sheet exhibit differences in solubility and differences in gas permeability as well as dye acceptability.

SUMMARY OF THE INVENTION

An object of this invention is to provide a novel thermal recording method and a novel thermal recording sheet therefor.

Another object of this invention is to provide a novel method of converting a thermal pattern to a visible image and a recording sheet therefor.

A further object of this invention is to provide a novel method of converting a thermal pattern applied to a thermal recording sheet to a reversible latent image and then converting the resulting reversible latent image to an everlasting image.

Still another object of this invention is to provide a novel method of producing a transparent, light and highly pure color image.

A still further object of this invention is to provide a novel thermal recording method and a material therefor for producing multicolor images.

Still another object of this invention is to provide a novel thermal recording method and a material therefor for regenerating a continuous tone.

A still further object of this invention is to provide a novel thermal recording method and a material therefor for applying a thermal pattern to a thermal recording sheet and then forming a latent image which can be eliminated if desired.

Still another object of this invention is to provide a novel thermal recording method and a material therefor in which add-on is possible.

A still further object of this invention is to provide an inexpensive thermal recording sheet and a process for production thereof.

According to one aspect of this invention, there is provided a thermal recording method which comprises applying a thermal pattern to a recording member having a recording layer composed of at least a polymer complex to produce a reversible latent image capable of being visualized.

According to a further aspect of this invention, there is provided a thermal recording method as mentioned above in which the polymer complex has a weak bond capable of being dissociated at a temperature ranging from 50°C to 120°C.

According to a further aspect of this invention, there is provided a thermal recording method as mentioned above in which the resulting latent image is visualized with a dye liquid developer.

According to a further aspect of this invention, there is provided a thermal recording method as mentioned above in which the latent image is visualized by utilizing difference of solubility.

According to a further aspect of this invention, there is provided a thermal recording method as mentioned above in which the resulting latent image is visualized by utilizing difference of gas permeability.

According to a further aspect of this invention, there is provided a thermal recording method which comprises applying a thermal pattern to a recording member having a heat sensitive layer comprising a complex of polymers which are selected from polymers and copolymers of N-vinyl lactams, N-vinyl cyclic carbamates, N-vinyl imidazoles, 2-vinylpyridine, alkylene oxides, 4-vinyl-pyridine and acrylamide, to form a reversible latent image capable of being visualized.

According to a further aspect of this invention, there is provided a thermal recording method as mentioned above in which the resulting latent image is visualized with a dye liquid developer.

According to a further aspect of this invention, there is provided a thermal recording method as mentioned above in which the resulting latent image is visualized by utilizing difference of solubility.

According to a further aspect of this invention, there is provided a thermal recording method as mentioned above in which the resulting latent image is visualized by difference of gas permeability.

According to a further aspect of this invention, there is provided a thermal recording member used for the thermal recording method as mentioned above which comprises a heat sensitive layer containing, as an active component, a polymer complex having a weak bond capable of being dissociated at a temperature ranging from 50°C to 120°C.

According to a further aspect of this invention, there is provided a thermal recording member used for the thermal recording method as mentioned above which comprises a heat sensitive layer containing a complex composed of a low molecular weight compound or a polymer with a polymer selected from polymers and copolymers of N-vinyl lactams, N-vinyl cyclic carbamates, N-vinyl imidazoles, 2-vinyl pyridines, alkylene oxides, 4-vinyl pyridines and acrylamide.

According to a further aspect of this invention, there is provided a thermal recording member used for the thermal recording method as mentioned above which comprises a heat sensitive layer containing a polymer complex and a proton acceptor or a proton donor.

According to a further aspect of this invention, there is provided a thermal recording member used for the thermal recording method as mentioned above which comprises a heat sensitive layer containing a proton acceptor or proton donor and a complex composed of a low molecular weight compound or a polymer with a polymer selected from polymers and copolymers of N-vinyl lactams, N-vinyl cyclic carbamates, N-vinyl imidazoles, 2-vinyl pyridines, alkylene oxides, 4-vinyl pyridines and acrylamide.

According to a further aspect of this invention, there is provided a thermal recording member used for the thermal recording method as mentioned above which comprises a heat sensitive layer containing an aliphatic or aromatic ketone which is non-volatile at room temperature and a complex composed of a low molecular weight compound or a polymer with a polymer selected from polymers and copolymers of N-vinyl lactams, N-vinyl cyclic carbamates, N-vinyl imidazoles, 2-vinyl

pyridines, alkylene oxides, 4-vinyl pyridines and acrylamide.

According to a further aspect of this invention, there is provided a thermal recording member used for the thermal recording method as mentioned above which comprises a heat sensitive layer containing benzophenone and a complex composed of a low molecular weight compound or a polymer with a polymer selected from polymers and copolymers of N-vinyl lactams, N-vinyl cyclic carbamates, N-vinyl imidazoles, 2-vinyl pyridines, alkylene oxides, 4-vinyl pyridines and acrylamide.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 shows a combination of an infrared absorption spectrum of PVP and that of ES-425 at a range of 1600 – 1800 cm^{-1};

FIG. 2 shows an infrared absorption spectrum of a complex of PVP and ES-425; and

FIG. 3 shows an infrared absorption spectrum directly after heating the complex in FIG. 2.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to the present invention there is provided a thermal recording method which comprises applying a thermal pattern to a thermal recording sheet to form a latent image, and contacting with a dye liquid developer, washing off with a solvent, or utilizing the difference of gas permeability to convert the latent image to a visible image. The thermal pattern may be applied by a known method.

Representative methods for applying a thermal pattern are as follows.

1. Mechanical method

A thermal recording sheet surface is partly and selectively heated by a heat stylus, a heat typewriter, a thermal printing head, or a scanning beam such as laser and electron beam. For example, a stylus heated by a nichrome wire is driven in accordance with an input signal to scan the surface of the thermal recording sheet and there is obtained a recording corresponding to the trace of the stylus. A thermal printing head is composed of a matrix of minor heating dots and the dots are selectively heated by applying an electric current from a controlling circuit. A thermal recording sheet contacting the head is heated in accordance with the letter or sign pattern to produce a record. Details and specifications of such thermal printing heads are disclosed in U.S. Pat. No. 3,161,457 (National Cash Register) and Japanese Patent Publication No. 23520/1970. These thermal printing heads may be used in the thermal recording methods of this invention.

2. Radiation heating method

An original having a letter or sign pattern capable of absorbing a radiation is placed in contact with a thermal recording sheet in a thermal conductive position and irradiated with a strong radiation such as an incandescent tungsten lamp. The letter or sign portion of the original absorbs more radiation than the background portion and is more heated to raise the temperature and thereby there is formed a thermal pattern, which is then transferred to a thermal recording sheet by conduction of heat.

When a thermal recording sheet having a radiation absorption property is used and subjected to an extremely strong radiation for a short time by using a flashing discharging lamp as the radiation source for heating, there can be effected a negative-positive reproduction. In other words, when such a thermal recording sheet is contacted with a negative image of a silver salt film and exposed to a flash discharging lamp on the film side, the radiation passing through transparent portions of the film is converted to heat in the thermal recording sheet to produce a thermal pattern. Upon producing a thermal pattern by laser beam scanning as mentioned in the mechanical method above, it is preferable to use a thermal recording sheet having radiation absorption property (absorbing said laser light wave length in this case).

Conversion of a latent image to a visible image is explained below. A thermal pattern is applied to a thermal recording sheet of the present invention by a method as mentioned above to produce a reversible latent image and then the resulting latent image is converted to a visible image within a period of life time. The life time of the latent image is a parameter showing reversibility of the latent image and is defined as a period of time from applying a thermal pattern to the maximum time at which any substantial lowering of density is not observed when developed, or a period of time from the application of a thermal pattern to a time at which the latent image is almost eliminated down to a fog density. One of these two definitions is used for each particular purpose.

A thermal recording sheet is contacted with a dye liquid developer to convert a latent image to a visible image. For example, the sheet is soaked in a dye liquid developer, or the sheet surface is wetted with a sponge, felt, roller or belt impregnated with a liquid developer, or a liquid developer is sprayed onto the sheet surface. It is also desirable to use a simple developing device such as a wet diazo copying machine and a developing device for a copier of a diffusion transferring reversing method, which may be used without any particular modification.

Necessary developing time varies depending upon the type, composition or temperature of the liquid developer or the mechanical conditions.

The developing time may be selected with a considerable latitude, but is in general, about 5 seconds taking into consideration rapid and access or about one minute for the purpose of reproduction of a continuous tone in the following examples.

At completion of development the image is already produced at a portion corresponding to the high temperature portion of the thermal pattern.

The recording is finished with or without washing with water to remove excess liquid developer. If desired, additional treatments of the images such as drying, chelating the dye image to improve the durability may be applied.

Latent images on one thermal recording sheet may be developed with two or more dye liquid developers to form each different colored image.

It is also possible to develop only the necessary portion of the latent images without developing the unnecessary portion thereof. The latent image not developed disappears by standing and said portion may be used again to reproduce other images.

In addition, the latent image may be visualized by utilizing a difference of solubility in a solvent or a difference of gas permeability. Increase in solubility in a certain solvent of the latent image portion according to the present invention is observed.

Furthermore, increase in gas permeability is also observed. Therefore, it is possible to form a relief image or colored image by washing off with a solvent after formation of the latent image.

Alternatively, it is also possible to form a visible image by placing the recording sheet in a gas such as ammonia gas after forming the latent image and forming color of a visible image forming component, in or under the recording layer, capable of forming color by alkali. The visible image forming component capable of forming color by alkali may be a pH indicator or a combination of an aromatic diazo compound and a coupler.

The thermal recording sheet may be produced by providing on a support a thin film composed of a high polymer complex having a weak bond capable of being dissociated at 50°C – 120°C.

By "polymer complex" is meant a complex compound of at least two kinds of polymer compounds, or at least one polymer and at least one low molecular weight compound having a moiety as described in Table 1 and Table 3 and there exists a "weak bond" between these components, and further, physical or chemical property of one or more of the components is remarkably changed. If there exists no bond among such components at all, the physical property of the mixture of the components is a simple sum of the physical or chemical properties of each component. The weak bond changes the physical or chemical properties of the components, but does not change the intrinsic chemical structure of each component substance.

In addition, the polymer complex includes a polymer having at least two kinds of moieties as shown in Table 1 and Table 3 in the same molecular chain. Such a polymer shows physical or chemical properties similar to a complex produced by mixing polymers having each moiety.

In other words, the polymer complex in the present invention may be defined as follows:

1. complex composed of a proton donative polymer and a proton acceptive polymer,
2. complex composed of a proton donative polymer and a proton acceptive low molecular weight compound,
3. complex composed of a proton acceptive polymer and a proton donative low molecular weight compound, and
4. polymer having a proton donative group and a proton acceptive group.

In items (1) – (4) above, the proton donative moiety and the proton acceptive moiety are selected from moieties as shown in Table 1 and Table 3.

The cause of the weak bond has not yet been determined, but it is considered that the weak bond is caused by the complicated combination of electrostatic forces between ions, hydrogen bonds, van der Waals forces, electrostatic forces caused by partial transferring of electric charge or a spacial intertwinement of high polymer chains and segments.

In any event, it is essential that the bond be broken or relaxed at 50°C – 120°C.

It is considered that an important factor of the complex of the present invention is hydrogen bonding or a spacial configuration based on entwinement of hydrogen bonding and molecular chains.

Table 1 illustrates atoms and atomic groups participating in the formation of the hydrogen bond. When the proton donative compounds are combined with proton acceptive compounds, there may be formed complexes.

Table 1

Atoms and Atomic Groups participating in the formation of hydrogen bond	
Proton donative group	—OH, —COOH, $\geq$ NH, —SH, $\geq$CH—
Proton acceptive atoms or atomic group	—OH, —OR, $\geq$ C=O, —COOR, $—NO_2$, $—NH_2$, —NHR, $—NR_2$, —N=N—, —C $\equiv$ N, $—N_3$, —F, —Cl, —Br, —I, —SH, —SR, unsaturated bond, and aromatic ring (R is alkyl and/or aryl.)

According to the present invention, one or both of the proton donative compound or proton acceptive compound are polymers. It is preferable that both of them are polymers. Further, there may be used a system of a low molecular weight compound dispersed in a polymer matrix.

The above mentioned matters suggest that the shape of the molecule and its spacial configuration as well as hydrogen bonding are important and effective in the present invention. The polymer chains (intertwinement effect) probably delay the thermal dissociation speed of the weak bond to extend the life of the latent image enough to retain the life up to the developing step, and when the latent image is maintained at a temperature higher than the temperature at which the polymer chain is frozen the latent image disappears gradually as the result of Brownian motion of the polymer chain. Room temperature is generally higher than the polymer chain freezing temperature.

Table 2 shows energy of typical hydrogen bonds. Since the energy value is about several Kcal./mole, it is clear that the bond can be easily cut by thermal energy.

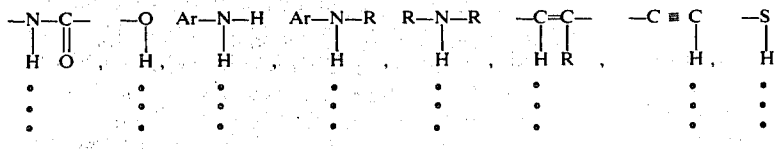
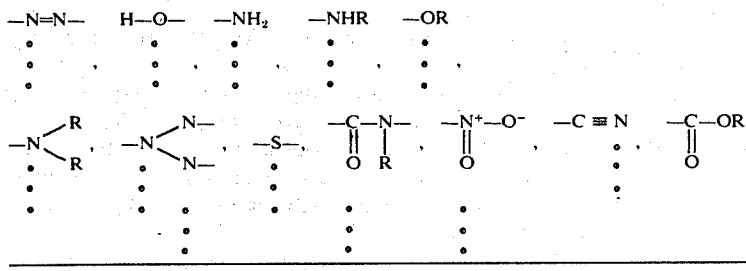
Table 2

Bond Energy of Hydrogen Bond			
Type of hydrogen bond		Measured value Kcal/mole	Average value Kcal/mole
F-H	F	6.8 – 27	7
O-H	O	2.4 – 7.6	6
O-D	O	7.0 – 8.0	7.5
C-H	O	2.6 – 2.7	2.6
O-H	σ-electron system	2.0 – 4.0	3.0
N-H	O	2.3	2.3
N-H	N	1.3 – 4.0	3.0
N-H	F	5	5
O-H	Cl	1.7 – 2.8	2.3

From a quantitative point of view, the equilibrium constant of dissociation of many hydrogen bond complexes usually increases as the temperature is raised. In other words, this means that the complexes are dissociated to each component substance as the temperature is elevated. Table 3 illustrates some examples of fundamental structures of compounds capable of forming a hydrogen bond complex.

According to the thermal recording method of the present invention, a latent image is effectively produced by applying a thermal pattern at 50° – 120°C. Therefore, it is considered that the weak bond is dissociated at this temperature range (cf. "Insha Kogaku" II, as mentioned above).

Table 3

Fundamental Structure of Compound of Forming Hydrogen Bond Complex
Proton donative (donor) group:

Proton acceptive (acceptor) group:


where R is hydrogen, alkyl and/or aryl.

Has not yet been clearly proven that the bond of the polymer complex used in this invention is a hydrogen bond only, but to say the least, the combination of compounds having the moiety as shown in Table 1 and Table 3 is effective in the present invention.

According to an embodiment of the present invention, the thermal recording sheet of the present invention may be produced by providing on a support a thin film composed of at least a polymer (A) selected from polymers and copolymers of N-vinyl lactams, N-vinyl cyclic carbamate, N-vinyl imidazole, 2-vinyl pyridines, 4-vinyl pyridines, alkylene oxides and acryl amide and a polymer (B) capable of forming a complex with the polymer (B). The polymer (A) as mentioned above can form a complex with other many substances.

When there are mixed the solutions of the polymer (A) and the polymer (B) in solvents such as water, alcohols, lower ketones, dioxanes and the like, there occurs a remarkable increase of the viscosity or formation of gel. When the polymer (A) and the polymer (B) are mixed and a thin film is produced from the mixture, dye acceptability of the polymer (A) in the thin film thus produced is masked and therefore, this thin film can not be dyed by a dye liquid developer capable of dyeing the polymer (A). The resulting film shows such a peculiar physical property, but when the film is treated with an acid or alkali or the pH is changed, the original components, that is, the polymer (A) and the polymer (B), can be recovered again from the thin film or gel. This fact indicates the presence of a weak bond.

The polymer (B) capable of forming such a weak bond with the polymer (A) may be selected from many high polymers as mentioned later. The formation of the complex may be judged based on the above mentioned matter upon selecting polymer (B).

When the above mentioned complex is heated to a temperature higher than a certain temperature, the complex can be dyed by the liquid developer. This mechanism is not yet clear, but may be considered as follows. The polymer complex composed of a polymer (A) and a polymer (B) is stable at room temperature and the dye acceptability of the polymer (A) is masked and cannot be dyed by the dye liquid developer. However, the complex is dissociated to each component substance at a certain temperature or higher than said temperature and the physical properties of each component substance appear again to recover the dye acceptability of the polymer (A). The dissociation to each component seems to be accompanied simultaneously by separation of micro phase. The high polymer components thus dissociated coagulate each other by the self coagulation force and there is formed an island structure of one of them in a sea of the other (sea-island structure of a blend polymer), and thereby there is provided a surface sufficient to accept a dye from the dye liquid developer.

Each component dissociated at a high temperature returns again to a stable complex structure as the temperature is lowered and the dye acceptability is lost. The reversibility of the latent image of the thermal recording sheet of the present invention seems to be due to the above-mentioned reason. Rearrangement of the polymer segments requires a certain period of time so that the latent image can be present for a certain period of time.

The above mentioned explanation of the mechanism is given for the purpose of enabling one skilled in the art to understand this invention, but should not be construed as a limitation of the present invention.

Representative polymers (A) in this invention are:

1. N-vinyl lactam polymer

Polymers such as N-vinyl pyrrolidone, N-vinyl-3-methyl pyrrolidone, N-vinyl-5-methyl pyrrolidone, N-vinyl-3,3,5-trimethyl pyrrolidone, N-vinyl-3-benzylpyrrolidone, N-vinyl piperidone, N-vinyl-4-methyl piperidone, N-vinyl caprolactam (N-vinylhexahydro-2H-adipin-2-one), N-vinyl capryllactam, N-vinyl-3-morpholinone, N-vinyl thiopyrrolidone, N-vinyl-2-pyridone and the like.

The above-mentioned monomers are known materials and processes for the polymerization thereof are also known. Particularly important and commercially available homopolymers are poly-N-vinyl pyrrolidone, poly-N-vinyl piperidone, poly-N-vinyl caprolactam and poly-N-vinyl morpholinone. Copolymers of said monomers with each other or of said monomers with other vinyl monomers are also useful. The other vinyl monomer may be methacrylates, acrylates, acrylamides, acrylonitrile, vinyl ethers, vinyl acetate, vinylimidazoles,

ethylene and the like. Particularly, copolymers with vinyl acetate are commercially available. Also, the copolymer may include graft-copolymers, for example graft-copolymers of monomers such as formaldehyde, vinyl chloride, acrylamide, vinyl pyridine and the like onto poly-N-vinyl pyrrolidone.

2. N-vinyl cyclic carbamate polymer

Polymers of monomers such as N-vinyl-2-oxazolidone, N-vinyl-5-methyl-2-oxazolidone, N-vinyl-5-ethyl-2-oxazolidone, N-vinyl-4-methyl-2-oxazolidone, N-vinyl-2-thiooxazolidone, N-vinyl-2-mercaptobenzothiazole and the like.

Homopolymers of the above mentioned monomers or copolymers of the above mentioned monomers with styrene, vinyl acetate, methacrylate, vinyl ether, N-vinylpyrrolidone and the like are also included. Homopolymers of monomers such as N-vinyl-2-oxazolidone and N-vinyl-5-methyl-2-oxazolidone, or copolymers of these monomers with vinyl acetate are particularly important.

3. Polymers of N-vinyl imidazoles

Copolymers of monomers such as N-vinyl imidazole, N-vinyl-2-methyl imidazole and N-vinyl-4-methyl imidazole, with other vinyl monomers such as styrene, acrylonitrile, methyl methacrylate, N-vinylpyrrolidone and the like.

4. 2-, or 4-Vinylpyridine polymer

5. Alkylene oxide polymer

Polyethylene oxide, polypropylene oxide and the like.

6. Acrylamide polymer

Homopolymers or copolymers of methacrylamide and other alkyl or N-alkyl derivatives. There may be mentioned, for example, polyacrylamide, -methacryl amide, poly-N-methyl acrylamide, poly-N-normal butyl acrylamide, poly-N-benzyl acrylamide and N-methyl acrylamide / N-butyl acrylate (1 : 1 copolymer).

A thin layer of a homopolymer of N-vinyl lactam, N-vinyl cyclic carbamate, N-vinylimidazoles, 2- or 4-vinylpyridine, alkyleneoxide or acryl amide as mentioned above can be dyed by a dye liquid developer of this invention. In the case of a copolymer of the monomer with other vinyl monomers, the type of partner monomer and the composition ratio should be carefully selected to impart a suitable capacity of accepting a dye from a dye liquid developer. In the case of monomer such as vinyl acetate, giving a water insoluble polymer, the developing speed by a dye liquid developer in the copolymer is retarded. Therefore, for example, in the case of a copolymer of N-vinyl lactam the composition ratio of N-vinyl lactam/vinyl acetate preferably ranges from about 60 / 40 to 90 / 10. On the contrary, when N-vinyl imidazole, N-vinyl pyridine and the like are copolymerized with N-vinyl lactam, the developing speed by a dye liquid developer is accelerated.

In this manner, the developing speed or image density and the like may be controlled by appropriately selecting the partner monomer in copolymerization.

Polymers of N-vinyl lactam, N-vinyl cyclic carbamate, N-vinyl imidazole, 2- or 4-vinyl pyridine, alkylene oxide or acrylamide as aforementioned are made into a thin layer by combining with a polymer (B) forming the complex. Polymer (B) may be selected from high polymers of various kinds. Particularly, high polymers having carboxylic acid radicals, sulfonic acid radicals or OH radicals are preferable. Combination of polymer (A) and polymer (B) may be effected based on a standard that a complex is formed between them (the examination of complex formation is disclosed previously). It is desirable to satisfy at least the following conditions.

1. The high polymer complex obtained is soluble in usual solvents. This property enable one to form a thin layer of the complex from the solvent solution.
2. When the high polymer complex solution is coated and dried on a support, a homogeneous and substantially transparent layer is formed without separating the components from each other.

The examination whether the above mentioned conditions are satisfied may be carried out easily by those skilled in the art.

Further, the examples of useful polymer (B) in this invention are shown as below.

1. Polymer having carboxylic acid radical; for example:

A. Polyesters obtained by reacting an excess of aliphatic polyhydric carboxylic acid such as citric acid, tartaric acid and the like with diols such as ethylene glycol, 1,4-butanediol, diethylene glycol, dipropylene glycol and the like.

B. Acid cellulose derivatives shown in the following Table 4.

Table 4

Polymers	Total of substitution	Acidity of substitution
Cellulose-propionate / hydrogen sebacinate	2.0	1.0
Cellulose-acetate / methacrylate / hydrogen succinate	2.5	0.8
Cellulose-acetate / crotonate / hydrogen phthalate	2.6	0.9
Cellulose-benzoate / hydrogen terephthalate	2.1	1.2
Cellulose-cyclohexane carboxylate / hydrogen oxalate	2.1	1.0
Cellulose-nptrate / hydrogen phthalate	2.6	0.8
Methyl cellulose-hydrogen phthalate	2.3	0.7
Cyclohexyl cellulose-hydrogen succinate	2.1	0.8
Cyanoethyl cellulose-hydrogen succinate	2.5	0.8
Ethyl cellulose-acetate / hydrogen succinate	2.8	0.8
Cyanoethyl cellulose-stearate / hydrogen phthalate	2.2	1.0
Benzyl cellulose-hydrogen succinate	2.3	1.0
Hydroxyethyl cellulose-acetate / hydrogen succinate	2.5	0.7
Cellulose-butyrate / hydrogen succinate / hydrogen phthalate	2.0	1.0
Ethyl cellulose-hydrogen succinate / hydrogen maleate	2.8	1.0

C. Acid polyvinyl polymer

(The process for producing them is disclosed in Japanese Patent Application No. 8495/1960 by DuPont Co. Ltd.)

There may be mentioned, for example, polyvinyl hydrogen oxalate, polyvinyl hydrogen malonate, polyvinyl hydrogen glutarate, polyvinyl hydrogen adipate, polyvinyl hydrogen suberate, polyvinyl hydrogen maleate, polyvinyl hydrogen undecenyl succinate, polyvinyl hydrogen isophthalate, polyvinyl hydrogen terephthalate, polyvinyl hydrogen hexahydrophthalate, polyvinyl-0-carboxymethylphenyl acetate, polyvinyl-P-carboxymethylphenyl acetate, polyvinyl-0-carboxyphenyl acetate, polyvinyl hydrogen succinate / polyvinyl hydrogen phthalate (90/10), polyvinyl hydrogen oxalate / polyvinyl hydrogen isophthalate (50/50), polyvinyl hydrogen maleate / polyvinyl hydrogen adipate (10/90), polyvinyl acetate / polyvinyl hydrogen succinate

(70/30), polyvinyl benzoate / polyvinyl acrylate / polyvinyl hydrogen succinate (41/4/55), polyvinyl formate / polyvinyl hydrogen terephthalate (65/35), polyvinyl propionate / polyvinyl hydrogen phthalate (40/60), polyvinyl alcohol / polyvinyl hydrogen phthalate (10/90), polyvinyl alcohol / polyvinyl hydrogen succinate (19/81), polyvinyl alcohol / polyvinyl hydrogen glutarate (29/71), polyvinyl alcohol / polyvinyl hydrogen maleate (65/35), polyvinyl alcohol / polyvinyl acetate / polyvinyl hydrogen isophthalate (10/60/30), polyvinyl alcohol / polyvinyl propionate / polyvinyl hydrogen maleate (15/45/40), polyvinyl alcohol / polyvinyl acetate / polyvinyl hydrogen maleate (30/10/60), polyvinyl alcohol / polyvinyl acetate / polyvinyl hydrogen maleate (29/34/37), polyvinyl alcohol / polyvinyl acetate / polyvinyl hydrogen succinate (16/13/71), polyvinyl chloride / polyvinyl acetate / polyvinyl hydrogen succinate (25/25/50), polyvinyl chloride / polyvinyl acetate / polyvinyl methacrylate / polyvinyl hydrogen succinate (20/15/5/60), polyvinyl chloride / polyvinyl butyrate / polyvinyl hydrogen maleate (30/30/40), polyvinyl alcohol / polyvinyl chloride / polyvinyl acetate / polyvinyl hydrogen phthalate (5 / 10/15/70), ethylene / vinyl acetate / vinyl hydrogen succinate copolymer (4/42/54), ethylene / vinyl benzoate / vinyl hydrogen succinate copolymer (5/40/55), propylene / vinyl acetate / vinyl hydrogen maleate copolymer (4/46/50), ethylene / vinyl acetate / vinyl hydrogen glutarate copolymer (15/40/45), ethylene / vinyl alcohol / vinyl acetate / vinyl hydrogen succinate copolymer (5/5/40/50), ethylene / vinyl alcohol / vinyl acetate / vinyl hydrogen phthalate copolymer (2/22/9/67), polyvinyl formal / polyvinyl hydrogen glutarate (50/50), polyvinyl butyral / polyvinyl hydrogen allylsuccinate (60/40), polyvinyl propional / polyvinyl hydrogen maleate (65/35), polyvinyl formal / polyvinyl acrylal / polyvinyl hydrogen succinate (50/10/40), polyvinyl butyral / polyvinyl hydrogen adipate (50/50), polyvinyl benzal / polyvinyl hydrogen phthalate (50/50), polyvinyl benzoate / polyvinyl-P-carboxybenzal (40/60), polyvinyl butyral / polyvinyl hydrogen phthalate (40/60), polyvinyl formal / polyvinyl acetal / polyvinyl hydrogen terephthalate (40/30/40), polyvinyl formal / polyvinyl butyrate / polyvinyl carbonate / polyvinyl hydrogen succinate (40/10/10/40), polyvinyl formal / polyvinyl methylether / polyvinyl hydrogen phthalate (40/10/50), polyvinyl acetate / polyvinyl ethylether / polyvinyl hydrogen succinate (60/10/30), polyvinyl benzal / polyvinyl methylether / polyvinyl hydrogen diglycolate (45/30/25), polyvinyl butyral / polyvinyl hydroxyether / polyvinyl hydrogen glutarate (60/10/30), polyvinyl alcohol / polyvinyl formal / polyvinyl β-cyanoethylether / polyvinyl hydrogen phthalate (5/20/25/50), poly-N-vinyl-N-methylformamide / vinyl acetate / vinyl hydrogen succinate (30/30/40), poly-N-vinyl-N-methylformamide / vinyl acetate / vinyl hydrogen phthalate (15/40/45), poly-N-vinyl-N-methylformamide / vinyl acetate / vinyl hydrogen glutarate (40/15/45), poly-N-vinyl-N-methylacetamide / vinyl acetate / vinyl hydrogen succinate / vinyl hydrogen maleate (30/30/30/10), poly-N-vinylphthalamide / vinyl methacrylate / vinyl acetate / vinyl hydrogen succinate (5/25/30/40), poly-N-vinyl caprolactam / vinyl acetate / vinyl hydrogen phthalate (20/30/50), poly-N-vinyl-N-methylformamide / vinyl formal / vinyl acetal / vinyl hydrogen succinate (20/30/20/30), poly-N-vinyl-N-methylacetamide / vinyl methacrylate / vinyl acetate / vinyl acetal / vinyl hydrogen phthalate (10/10/20/20/40), poly-N-vinyl-N-methylbenzamide / vinyl acetate / vinyl formal / vinyl hydrogen succinate / vinyl hydrogen maleate (10/25/15/40/10), poly-N-vinylpyrrolidone / vinyl acetate / vinyl formal / vinyl hydrogen succinate (10/20/30/40), poly-N-vinyl-N-methylformamide / vinyl alcohol / vinyl acetate / vinyl hydrogen succinate (20/5/35/40), poly-N-vinyl-N-methylformamide / vinyl alcohol / vinyl acetate / vinyl hydrogen phthalate (10/25/15/50) and the like.

D. Acrylic acid and methacrylic acid polymer

There may be mentioned, for example, polyacrylic acid, partially hydrolyzed product of polymethacrylic acid-n-butyl, partially hydrolyzed product of polyacryl-N-n-propylamide and the like.

E. α,β-Unsaturated acid polymer

There may be mentioned, for example, polymers of α,β-unsaturated acids such as maleic anhydride, itaconic anhydride, citraconic anhydride, diester fumarate and the like, or copolymers of the α,β-unsaturated acid as mentioned above with other vinyl monomers. Vinyl monomers to be copolymerized with the acid anhydride monomer preferably include vinyl esters such as vinyl acetate and the like and vinyl ethers. Vinyl monomers to be copolymerized with diester fumarate is preferably include acrylamide, vinyl esters, vinyl ethers, ethylene, styrene, acrylic esters and the like.

The above mentioned polymer is disclosed in Murahashi, Inoue and Tani, "Gosei Kobunshi [III]", Asakura Shoten, 1971, pages 250–257 and pages 374–380. Among them, a particularly useful polymer is maleic anhydride copolymer since it is not expensive. A carboxylic acid radical existing in the copolymer forms the derivatives such as the mono ester of dicarboxylic acid, mono amide and the like by reacting with a compound having active hydrogen such as alcohol, ammonia, primary and secondary amines and the like. Also, the derivatives thereof are useful in this invention. Processes for producing some of them are disclosed in the following U.S. Patents.

Partner monomers of α,β-unsaturated acid anhydride	U.S. Patent Nos.	Applicants
Unsaturated monoolefine such as ethylene, propylene and the like	2,378,629	E. I. Dupont
Alicyclic terpene such as dipentene and the like	2,118,925	Hercules Powder
Ternary copolymer comprising terepene and styrene or indene	2,383,399	E. I. DuPont
Vinyl ester	2,047,398	I. G. Farben
Vinyl ether	3,161,538	General Aniline and Film Corp.

2. Polymers having a sulfonic acid group

For example,

A. Acid cellulose derivatives

Table 5 shows some representative examples.

Table 5

Polymers	Total of substitution	Acidity of substitution
O-ethyl cellulose-acetate / hydrogen succinate / hydrogen phthalate	2.6	0.9
Cellulose-acetate / hydrogen sulfate / hydrogen phthalate	2.65	0.85
Ethyl cellulose-hydrogen-O-sulfobenzoate	2.2	0.5
O-P-sulfonbenzile cellulose-	2.6	0.8

Table 5-continued

Polymers	Total of substitution	Acidity of substitution
acetate O-ethyl,O-P-sulfoethyl cellulose-acetate	2.4	0.6

The process of preparation thereof is disclosed in Japanese Publication No. 5093/1960 (DuPont Co. Ltd.).

B. Acid polyvinyl alcohol derivatives

For example, polyvinyl-0-sulfobenzoate, polyvinyl-β-sulfopropionate, polyvinyl-δ-sulfovarate, polyvinyl-P-sulfophenyl acetate, polyvinyl acetate / polyvinyl-0-sulfobenzoate (50/50), polyvinyl benzoate / polyvinyl-γ-sulfopropionate (50/50), polyvinyl acetate / polyvinyl crotonate / polyvinyl-2-sulfo-4-carboxybenzoate (40/30/30), polyvinyl formal / polyvinyl butyral / polyvinyl-p-sulfobenzal (10/60/30), polyvinyl formal / polyvinyl acetate / polyvinyl-0-sulfobenzal (60/20/20), polyvinyl alcohol / polyvinyl acetate / polyvinyl formal / polyvinyl-0-sulfobenzal (5/40/30/25), poly-N-vinyl-N-methylformamide / vinyl acetate / vinyl-0-sulfobenzoate (30/30/40), poly-N-vinyl-N-methylacetamide / vinyl acetate / vinyl-β-sulfopropionate (40/30/30), poly-N-vinyl-N-methylformamide / vinyl alcohol / vinyl acetate / vinyl-0-sulfobenzoate (10/20/40/30) and the like.

3. Polymer having OH radical;

For example,

A. Particularly, cellulose ethers,

For example, ethyl cellulose, benzyl cellulose, hydroxyethyl cellulose, hydroxyethyl / ethyl cellulose, hydroxyethyl / benzyl cellulose and the like.

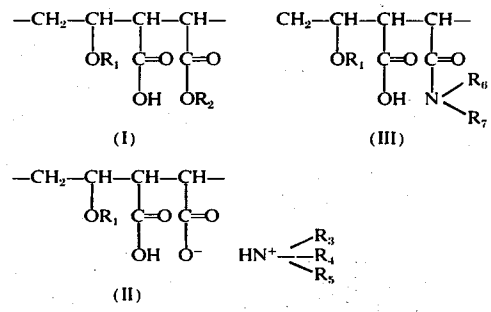
B. Phenolic resin;

Particularly, resol-type solvent-soluble phenol or cresol-formaldehyde resin and phenoxyacetic acid-formaldehyde resin.

Polymer (A) and polymer (B) as mentioned above are properly selected and combined in accordance with the aforementioned conditions. That is, at least a high polymer selected from the polymer (A) group and at least a high polymer selected from the polymer (B) group are mixed in a solution form and the complex thus formed is separated (when the solvent is water, alcohol, ketones and the like, the complex may be normally separated as gel), dissolved in a solvent for the complex, thereafter coated on a support and dried to form a thin layer. Alternatively, from the first each high polymer is dissolved and mixed in a solvent for the complex, coated on a support and dried to form a thin layer. In order to improve various responses to heat or a physical property of the film of the thermal recording layer, a third inert polymer or plasticizers may be added. These substances are selected from known materials.

For the purpose of facilitating the selection of the high polymers, combinations of high polymers and various embodiments of heat sensitive sheets made therefrom are shown in Example 7. An example of polymer (B) giving a preferable result when combined with a polymer (A) is α,β-unsaturated acid polymer, particularly, a copolymer of an alkyl vinyl ether and maleic anhydride. Thee combination of the above-mentioned polymer (B) and the polymer (A) provides a thermal recording sheet having excellent film physical properties such as flexibility, mechanical strength and the like and satisfying required characteristics such as heat sensitive temperature, image density, contrast, clearness of background and the like without adding any other third component.

Examples of appropriate copolymers of alkyl vinyl ether and maleic anhydride are mono esters [I], mono ammonium salts [II] and mono amides [III] of vinyl ethers having alkyl radical of C_1–C_{18} / maleic anhydride copolymer (copolymerization ratio being about 1:1). When copolymerization ratio is 1:1, the unit structure is represented as follows:

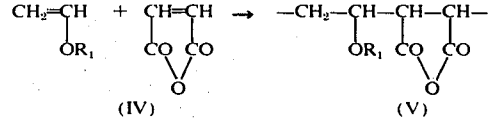


(I) (III)

(II)

wherein R_1 and R_2 are alkyl radicals having C_1–C_{13}, R_3–R_6 is hydrogen or an alkyl radical having C_1–C_{13}, and the total carbon atoms of R_3, R_4 and R_5, and R_6, R_7 is not more than 19.

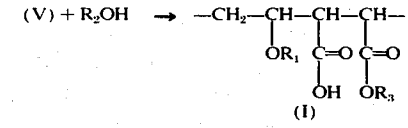
and maleic anhydride are polymerized in the presence of a peroxide by the process, for example, M. Imoto, K. Satomi, J. Polymer Sci., 31 208 (1960), to produce an alkyl vinyl ether / maleic anhydride copolymer [V]. Though the copolymerization ratio is somewhat different depending upon the type of vinyl ether or polymerization conditions, this is about 1:1.



(IV) (V)

Examples of suitable alkyl vinyl ethers are shown below. Only the alkyl radical R_1 is illustrated. The number in the parentheses is the boiling point: methyl (6.0°), ethyl (35.5°), n-propyl (65.5°), i-propyl (55°), n-butyl (94°), i-butyl (83°), t-butyl (75°), i-amyl (109°), n-hexyl (143°), n-octyl (58°, 44 mmHg), 2-ethyl hexyl (177°), n-decyl (101°, 11 mmHg), n-dodecyl (126°, 3 mmHg), n-octadecyl (182°, 3 mmHg). Some of them are already commercially available.

Alkyl vinyl ether / maleic anhydride copolymer [V] is reacted with an alcohol under moderate conditions to produce a monoester.



(I)

Usually the copolymer [V] and an excess of a corresponding alcohol are heated, and after the reaction is finished, [I] is obtained by removing the alcohol. In order to accelerate the reaction, if necessary, a small amount of a mineral acid such as hydrochloric acid, sulfuric acid and the like may be added. As the alcohol chain and branching increase, the heating period is extended, for example, 2 hours (at refluxing temperature) for methyl alcohol and approximately 24 hours (at 100°C, adding hydrochloric acid) for n-octadecyl alcohol.

Further, some of the methyl vinyl ether / maleic acid mono ether copolymers are supplied by General Aniline and Film Corp., for example, Gantrez ES Resin.

Mono ammonium salts [II] are obtained by neutralizing with ammonia or the corresponding alkyl amine after hydrolyzing the copolymer [V] and mono amides [III] are obtained by reacting ammonia or the corresponding primary or secondary alkyl amine with the copolymer [V].

The process for producing alkyl vinyl ether / maleic anhydride copolymer and the derivatives thereof is shown below.

1. An example of a process for producing n-butyl vinyl ether / maleic anhydride copolymer [VI]

Desiccated refined benzene (1000 ml.) is poured in a three-necked flask equipped with an agitator and a tube introducing nitrogen, and maleic anhydride (134 g.) and 135 g. of n-butyl vinyl ether (a reagent manufactured by Tokyo Kasei Kogyo K.K.) are dissolved therein, thereafter the substitution of nitrogen is carried out. Benzoyl peroxide (1.7 g.) is added thereto, agitated for 4 hours at 50°C – 60°C, then for 10 hours at 70°C.

A gelatinous polymer is obtained and benzene is removed therefrom. The resulting matter is washed sufficiently with ethylene dichloride and dried by removing water to produce 260 g. of a flocculent product.

The result of elementary analysis is C:61.5%, H:7.20%. These data agree well with the calculated values as 1/1 alternate copolymer of n-butyl vinyl ether / maleic anhydride, that is, C:60.6%, H:7.06%. η_{sp} in methyl ethyl ketone is approximately 1.2.

In the same manner, copolymers of approximately 1/1 ratio are obtained from i-butyl vinyl ether, i-octyl vinyl ether or n-octadecyl ether and maleic anhydride.

2. An example of a process for producing n-butyl vinyl ether / maleic acid mono ethyl ester copolymer [VII].

The 10 g. of compound (VI) obtained in the above example is dissolved in 100 ml. of ethyl alcohol containing a drop of concentrated hydrochloric acid, and boiled for 5 hours with removing water. Almost all of the alcohol is distilled at a reduced pressure, washed with a mixture of ether/hexane and dried to give 10g. of a white flocculent product. The product is n-butyl vinyl ether / maleic acid mono ethyl ester copolymer [VII]. Elementary analysis: C:60.2% (59.0%), H:8.32% (8.20%), wherein the values in parentheses are the theoretical values.

3. An example of the process for producing methyl vinyl ether / maleic acid mono-n-octyl ester copolymer [VIII].

Methyl vinyl ether / maleic anhydride copolymer (10 g.) (trade name, Gantrez A N 139, manufactured by General Aniline and Film Corp.) is dissolved in a solution of pyridine (100 ml.) in n-octyl alcohol (8.5 g.), agitated for 5 hours at 100°C, poured into water, and then the pH value is reduced with dilute hydrochloric acid. The resulting precipitate is filtered, washed and dried to produce a white flocculent product (9.5 g). The product is methyl vinyl ether / maleic acid mono-n-octyl ester.

Elementary analysis: C:61.9% (62.90%), H:8.5% (9.1%).

In the same manner, mono-n-octadecyl ester [IX] is obtained by using n-octadecyl alcohol as a substitute for n-octyl alcohol. Elementary analysis: C:68.8% (70.4%), H:9.9% (10.8%), wherein the values in parentheses are the theoretical values.

4. An example of a process for producing n-butyl vinyl ether / maleic acid mono amide copolymer [X] – [XIV].

Compound [VII] (10 g.) obtained in the above example, i.e. item 1, is dissolved in 100 ml. of acetone with agitating, and added to 200 ml. of a cold 20% aqueous ammonia solution. Then, the temperature is raised to 50°C for 2 hours. After cooling and adjusting the pH value to 1.0 with 5% hydrochloric acid, the separated precipitate is filtered, washed and dried to obtain a white flocculent product (9.0 g.). The product is n-butyl vinyl ether / maleic acid mono amide copolymer [X]. Elementary analysis: N:6.30% (6.50%) wherein the value in the parentheses is the theoretical value.

In the same manner, mono-N-methyl amide copolymer [XI] is obtained by using methyl amine as a substitute for aqueous ammonia. The elementary analysis value is N:5.85% (6.12%).

In the same manner, mono-N-i-propyl amide copolymer [XII] is obtained by using i-propyl amine. The elementary analysis value is N:4.95% (5.45%).

In the same manner, mono-N,N-diethyl amide copolymer [XIII] is obtained by using diethyl amine. The elementary analysis value is N:4.80% (5.15%) wherein the value in the parentheses is the theoretical value.

In the case of higher amines, the reaction is carried out in a solution of the amine in pyridine. Pyridine solution of n-hexyl amine (6.5 g.) is added to a solution of methyl vinyl ether / maleic anhydride copolymer (10 g.) (trade name, Gantrez AN-139, manufactured by General Aniline and Film Corp.) in 100 ml. of methyl ethyl ketone. After reacting for 2 hours at 40°C, most of the methyl ethyl ketone is distilled under reduced pressure and then dilute hydrochloric acid is added thereto. The resulting matter is washed with water and dried sufficiently to obtain 14.0g. of a white flocculent product. The elementary analysis value is N:5.1% (5.45%) wherein the value in the parentheses is the theoretical value. This product is methyl vinyl ether / maleic acid mono-N-n-hexyl amide copolymer [XIV].

In the same manner, by reacting Gantrez AN-119 (trade name) with N-methyl-N-n-octadecyl amine, there is obtained methyl vinyl ether / maleic acid mono N-methyl-N-n-octadecyl amide copolymer [XV]. The elementary analysis value is N:2.7% (3.20%).

The aforementioned layer comprising the complex of polymer (A) and polymer (B) is manufactured by coating the solvent solution on a suitable support and drying. The complex may be produced by mixing the polymer (A) solution with the polymer (B) solution and recovering the separated complex. It is economical, however, that the polymer (A) and the polymer (B) are mixed, dissolved in a solvent capable of dissolving the complex, and directly used as a coating solution.

In the complex thin layer thermal recording sheet according to this invention, various kinds of additives

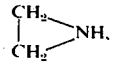
other than the complex of polymer (A) and polymer (B) may be added. As the additives, there may be mentioned a flattening agent of the coating such as silica aerogel (finely divided powder of SiO_2), titanium oxide powder and the like, and an image property controlling agent. It has been now found that some compounds have a powerful effect on the image property of this recording complex. In general, certain kinds of proton donors and proton acceptors may contribute to (1) reducing the back ground density, (2) decreasing the image density and contrast, and (3) decreasing the developing speed. Further, as these contribute to improvement in regeneration of the image and sharpness thereof, controlling the vanishing speed of the latent image, and reducing the aging period after coating and drying the recording sheet, and therefore the recording properties are improved.

The examples of proton donors and proton acceptors are shown as follows.

Proton donative capacity: (arranged in order of intensity)

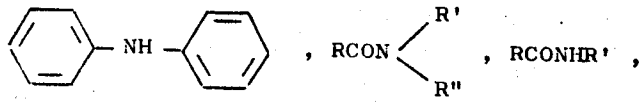
FH, HCl, RCOOH, C_6H_5OH, $C_6H_5NHCOCH_3$, RCONHR', ROH, $C_2H_5NHC_2H_5$, $RCONH_2$, H_2O, Cl_3CH,

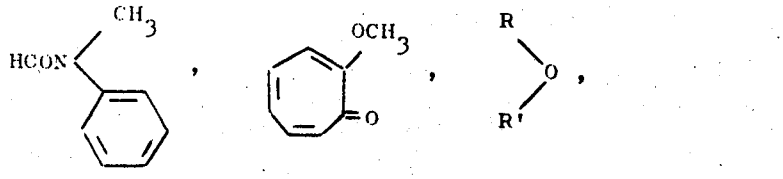
$C_6H_5—NH—C_6H_5$,

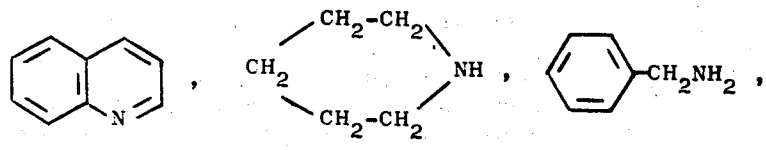


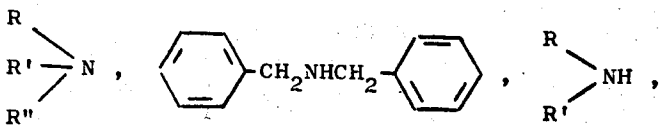
$C_6H_5NH_2$, $C_6H_5CH_2NH_2$.

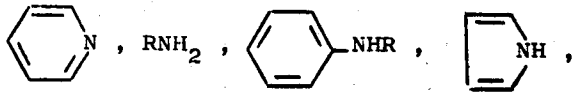
Proton accepting capacity: (arranged in order of intensity)

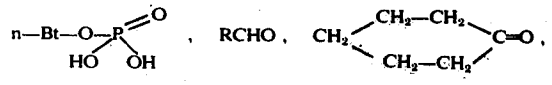


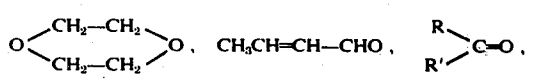


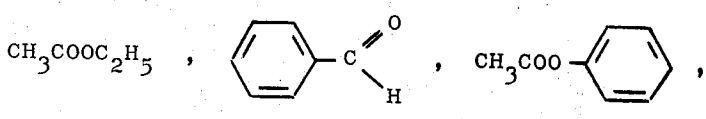


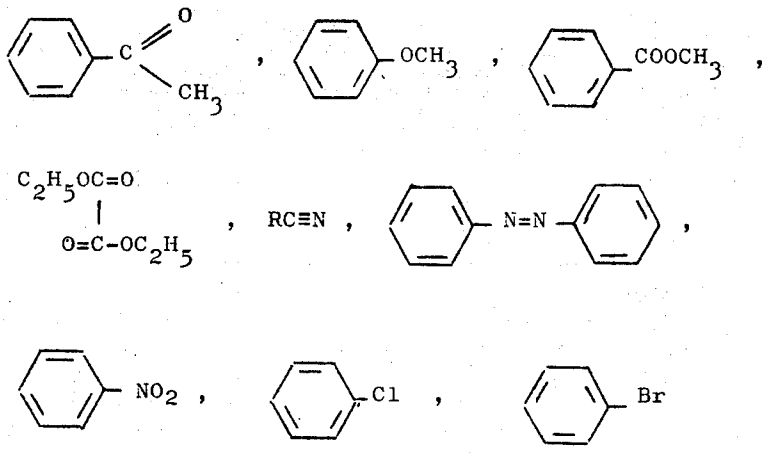












wherein R, R',R'' and the like are alkyl or aryl.

These effects of the proton donor and proton acceptor seem to be based on a certain interaction of hydrogen bond affecting the bond between polymer (A) and polymer (B) or space configuration.

The above explained effect of image property controlling agent is shown in the Examples (infra).

In the foregoing there are explained in detail proton donative polymers (A), proton acceptive polymers (B) and complexes thereof. The complex used for the present invention may be produced by combining one of the polymers (A) and the polymers (B) with a low molecular weight compound capable of forming a complex by combining with such polymers. The low molecular weight compound may be selected from compounds having a structure similar to the structure of the proton donative or proton acceptive monomer of the polymer (A) or (B).

When the complex of the polymer with the low molecular weight compound is used for visualizing by using a dye liquid developer, the dyeability of the polymer is a very important factor so that the polymer should be selected from polymers having dyeability. When a polymer (A) and a polymer (B) can form a complex, there may be often used a copolymer having monomer structures which constitute the polymer (A) and the polymer (B).

Explaining now about the dye liquid developer suitable for this invention, the latent image of the thermal recording sheet according to this invention is dyed by accepting selectively the dye from the dye liquid developer. There are many kinds of dye capable of being accepted. Whether a dye can be accepted is not always determined by its chemical structure. For example, whether there exists an anionic group or a cationic group is not a standard of selecting the dye, but whether the dye can dye one of the polymer components for the high polymer complex composing the recording sheet seems to be an important standard. It is practically preferred that the dye is relatively water-soluble.

The expression "relatively water-soluble" as used herein means to be soluble in water alone or a mixture of water and an organic solvent miscible with water such as alcohol, lower ketone, dioxane, benzyl alcohol and the like.

The following are representative dyes suitable for this invention.

Triphenylmethane dye such as Rhoduline Blue 6GA, Brilliant Green, Malachite Green, Para Rosaniline, Fuchsine, Methyl Violet 2B, Methyl Green, Crystal Violet, Ethyl Violet, Victoria Blue B, Victoria Blue R and the like; Xanthene dye such as Rhodamine B, Rhodamine 6G, Rhodamine 3B, Rhodamine S, Erythrasine, Eosine, Phloxine, Rose Bengal and the like; Mono azo dye such as Orenge I, Orenge RO, Orenge GG, Fast Red A, Amide Naphthol Red G, Sorbine Red BB, Brilliant Carmoisine O, Naphthol Red O, Fast Light Orenge GX, Orenge IV, Mentanil Yellow and the like; anthraquinone dye such as Alizarine Astrol B, Alizarine Pure Blue B, Alizarine Cyanine Green G, Anthraquinone Violet, Anthraquinone Blue and the like; ketoimine type dye such as Auramine O and Auramine G.

An aqueous solution of these dyes or an aqueous solution containing alcohol, lower ketone, dioxane and benzyl alcohol of these dyes may be used as a dye liquid developer. Further, a buffer solution for adjusting pH, or an inorganic salt such as sodium sulfate, sodium chloride and the like for controlling the dyeing capacity, or an organic mordant such as poly-N-vinyl pyridinium quaternary salt and the like other than the dye may be added to the dye liquid developer. When the complex obtained from a N-vinly lactam polymer and the like has an anionic radical such as a carboxylic acid radical or a sulfonic acid radical and the like, it is desirable that the pH value is neutral or acid for the purpose of decreasing the background density as far as possible.

Further, if necessary, there may be used an oil type dye such as Oil Brown N, Oil Red O, Solvent Blue 16, Solvent Violet 17, Solvent Black 12 and the like. A negative image is generally obtained by using an oil type dye.

The above mentioned dyes are common dyes. However, the dye used for a dye liquid developer according to this invention is not limited only to a colored substance, but may include a substance such as a fluorescent substance, an ultraviolet ray absorber, an electron ray absorber and the like which produce an image by irradiation with ultraviolet rays and electron rays, and the like. Further, it should be understood that a liquid developer containing a substance capable of forming a colored substance by reaction with a third substance incorporated in the thermal recording layer is also within the scope of the dye liquid developer of the present invention. There may be mentioned, for example, a combination of a metal salt and a chelating agent and a combination of a diazo compound and an azo coupler (one of them is incorporated in either the thermal recording layer or the liquid developer). It is very easy to

select a substance which is inert and not heat sensitivity when incorporated in the thermal recording layer.

The following examples are given to illustrate embodiments of the invention as it is presently preferred to practice it. It will be understood that these examples are illustrative, and the invention is not to be considered as restricted thereto.

EXAMPLE 1

30 g. of methyl vinyl ether / maleic acid mono n-butyl ester copolymer [trade name: Gantrez ES-425 manufactured by GAF (General Aniline and Film Corp.); solid content: 50%] was added to a solution of 15 g. of poly-N-vinyl pyrrolidone (trade name: PVP, K-90 manufactured by GAF) in 150 g. of alcohol and stirred to obtain a gel-like high polymer complex. 150 g. of dimethyl formamide was added to said gel-like complex to dissolve said gel-like matter and obtain a homogeneous and clear solution. A polyester film of 70 microns in thickness subjected to a treatment of imparting a hydrophilic property was coated with said solution and dried by hot air at 70° – 80°C (the thickness of said coating was 2 microns after drying). The properties of said film such as its heat sensitive temperature or contrast may be stabilized after standing at room temperature (about 20°C) for several days. Said produced thermal recording sheet was contacted with a thermal wedge composed of aluminum hot plates set at temperatures between 40°C and 150°C at intervals of 10°C for about 3 seconds, then dipped in a dye liquid developer D-1 (a solution of 0.5 g. of Crystal Violet in 100 ml. of distilled water) and washed with water. An image began to appear at 60°C and showed about maximum density at 70°C. In other words, the initial changing temperature of said thermal recording sheet was 60°C and the total changing temperature was 70°C.

The process for preparing said high polymer complex solution is fairly optional. The polyester film coated with a solution of a copolymer of poly-N-vinyl pyrrolidone and mono-n-butyl ester in a mixture of 150 g. of alcohol and 150 g. of dimethyl formamide was a thermal recording sheet having the same properties as that of the above mentioned one.

The film surface of said thermal recording sheet was closely contacted with one side of a manuscript printed on both sides and passed through a Thermofax copying machine (Secretary type, manufactured by Minesota Mining and Manufacturing Co.). A visible change was scarcely found on said surface at this stage. A clear violet image appeared on the portion corresponding to letter portions of the manuscript when the thermal recording sheet was dipped in a dye liquid developer D-1 (liquid temperature: 20°C) and pulled up, and said image was fixed firmly on the sheet without any further treatment. Said image density was 1.54 (measured by a red filter) and the background density was 0.02. A transparent image having high contrast was formed by projecting said sheet using an overhead projector.

Table 6 shows the relation between standing time and image density when the thermal recording sheet of this Example was passed through a Thermofax copying machine with a black colored manuscript, allowed to stand at 20°C (room temperature) for a predetermined time and then developed with said dye liquid developer D-1.

Table 6

Relation between an image density and a standing time up to developing after giving a thermal pattern

Standing Time	Image density (red filter)
directly after	1.50
after 10 minutes	1.50
30 minutes	1.40
1 hour	1.20
12 hours	0.10
24 hours	0.02

Table 6 shows the reversibility of a latent image formed on the recording sheet of this invention. It is found in Table 6 that the recording sheet of this invention can be used once more and add-on of other images is possible after standing for about 24 hours since the latent image disappears almost completely after standing for about 24 hours, and that it is possible to stock copies since the image density hardly changes at standing times of 10 – 30 minutes.

Table 7 shows the image characteristic when the solution of the high polymer complex of this Example was applied to a polyester sheet under the above conditions, dried and then allowed to stand at 20°C (room temperature). The background density after standing at various times and developing in a dye liquid developer D-1 was measured (developed without passing through Thermofax copying machine).

Table 7

Relation between standing time and background density

Standing Time	Background Density (red filter)
directly after	1.45
after 12 hours	0.50
24 hours	0.25
3 days	0.05
7 days	0.02
10 days	0.02

Table 8 shows that various dye liquid developers may be used for the sheet of this Example.

Table 8

Results developed in various dye developing solutions

Liquid Developer Number	Composition of Liquid Developer	Density: Image	Density: Back Ground	Density: Filter
D-II	0.5% aqueous solution of p-rose aniline hydrochloride	0.87	0.02	Green
D-III	0.5% aqueous solution of Kayacryl Red	0.20	0.00	"
D-IV	Solution of 0.5 g. Diamond Green in 100 ml. of a mixture of alcohol and water (1:1)	0.51	0.08	Red
D-V	Solution of 0.5 g. Methyl Violet in 100 ml. of a mixture of acetone and water (1:1)	1.20	0.07	"

Note: Dipping in a liquid developer at 20°C for 5 seconds

There is an optimum range in composition ratio of the poly-N-vinyl pyrrolidone / mono-n-butyl ester copolymer. Said range changes depending upon the formulation of the liquid developer and the temperature of the liquid developer. Table 9 shows the relation between the composition ratio of poly-N-vinyl pyrrolidone / mono-n-butyl ester copolymer and the image

property when developed with a dye liquid developer D-1 at 18°C for 8 seconds.

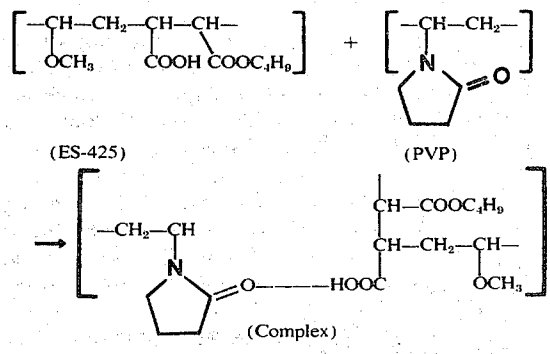
Table 9

Relation between the composition ratio of poly-N-vinyl pyrrolidone and methyl vinyl ether / maleic acid mono-n-butyl ester copolymer and the image property

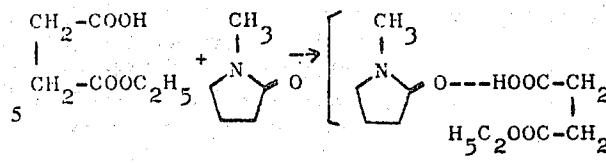
Sample Number	PVP K-90	Amount (g.) Gantrez ES-425 (Solid Content; g.)	Composition Ratio	Density Image	Density Back Ground
1	20	0	10 / 10	film was dissolved	—
2	18	2	9 / 1	1.50	1.45
3	14	6	7 / 3	1.40	0.60
4	11	9	5.5 / 4.4	1.30	0.05
5	10	10	5 / 5	1.30	0.02
6	9	11	4.5 / 5.5	1.20	0.02
7	6	14	3 / 7	0.50	0.01
8	2	18	1 / 9	0.20	0.00
9	0	20	0 / 10	0.0	0.00

Some spectroscopic data of a specific polymer complex is shown. In FIG. 1, the infrared absorption spectrum of the complex of polyvinyl pyrrolidone (PVP) and methy vinyl ether / maleic acid mono-n-butyl ester copolymer (ES-425) is shown.

A gel-like product is precipitated by mixing PVP and ES-425 in alcohol, washed with alcohol several times and dried to produce a white powdered complex. The complex always shows a constant elementary analysis regardless of the molar ratio of PVP to ES-425. The elementary analysis is as follows: C 58.02%, H 7.64%, N 4.71%. The molar ratio of PVP in said complex calculated value of the elementary analysis is 55%. In FIG. 2, absorption of carbonyl radical of pvp, 1680 cm^{-1} and absorption of carboxylic acid of ES-425, 1715 cm^{-1}, as illustrated in FIG. 1 disappear, and a new broad absorption having the peak at 1660 cm^{-1} appears. Said new adsorption is considered to be the adsorption due to the shifting of the proton of carboxylic acid and carbonyl radical to the side of low wave member as the result of hydrogen bonding of proton of carboxylic acid and carbonyl radical. Hydrogen bonding is considered to contribute to the formation of said complex as shown in the following scheme.



Next, the infrared absorption spectrum of the complex of N-methyl pyrolidone and mono ethyl succinate ester is considered. Absorption of the carboxylic acid of the succinic acid mono ethyl ester is present at 1715 cm^{-1} and that of the carbonyl radical of N-methyl pyrrolidone is present at 1685 cm^{-1}, but absorption of the complex appears at 1648 cm^{-1} as a result of shifting to the low wave number by hydrogen bonding of the carboxylic acid and carbonyl radicals, and both absorptions of 1715 cm^{-1} and 1685 cm^{-1} disappear.



The formation of a latent image on a heat sensitive layer of this invention is explained by the infrared absorption spectrum as described above.

when a complex is partly heated, the physical and/or chemical properties of the heated portion are different from those of the portions which are not heated.

Changes in the physical and chemical properties in the heated portion are due to the change of bonding state between molecules constituting the complex, and this has been confirmed by infrared absorption spectra. For example, the complex produced from PVP and ES-425 is formed by hydrogen bonding of the carbonyl radical of PVP and the carboxylic acid of ES-425, and thereby an absorption appears at 1660 cm^{-1} in an infrared absorption spectrum. FIG. 3 shows an infrared absorption spectrum directly after heating the complex. When the complex is heated, the absorption at 1660 cm^{-1} changes to two sbsorptions at 1680 cm^{-1} and 1640 cm^{-1}, and a shoulder of absorption appears at 1715 cm^{-1}. Since the absorption at 1680 cm^{-1} corresponds to the position of the carbonyl radical of PVP which is not hydrogen bonded and the absorption at 1715 cm^{-1} corresponds to the position of the carboxylic acid of ES-425, it is confirmed that the hydrogen bond is partially dissociated by heating.

When said changed complex stands for a long time at room temperature, the bond of said complex by hydrogen bond recovers to provide the same infrared absorption spectrum as that of the initial complex. This phenomenon corresponds to disappearance of difference of physical and chemical properties of the complex.

In the foregoing, the spectroscopic properties and the mechanism of forming the latent image are explained with respect to only a specific example, but such specific example is used for the purpose of aiding in understanding of this invention and should not be construed as a limitation to the scope of the invention.

EXAMPLE 2

15g. of poly-N-vinyl pyrrolidone (trade name: PVP K-90) and 14g. of methyl vinyl ether/maleic acid mono-N-n-hexylamide [XIV] were dissolved in a mixture of 150g. of alcohol and 150g. of dimethyl formamide. The resulting solution was applied to a semi-transparent tracing paper (of a thickness of about 30 microns) in a thickness of about 2 microns and dried. Since the heat sensitivity of said product is stabilized after about 10 days, the said product was allowed to stand for said period, cut into a tape for contact with a heated printing head(a small computer manufactured by Canon Co., trade name: pocketronic) and the latter operated.

The surface of said tape was moistened with a felt absorbing the dye liquid developer D-IV used in Example 1 to print red clear figures.

EXAMPLE 3

This Example relates to a sheet for stylus recording used in oscillograph recording. N-vinyl pyrrolidone polymer and vinyl ether/maleic acid copolymer at com-

pounding amounts as shown in Table 10 were dissolved in 300g. of a mixture of alcohol and dimethyl formamide of the same amount as that of alcohol. Said solution was applied to an opaque tracing paper and dried in hot air at 90° – 100°C (thickness of film after drying: 2 microns).

Table 10

Treatment No.	N-Vinyl pyrrolidone polymer (g.)	Vinyl ether/maleic acid copolymer (g.)
1	PVPK-90 (15 g.)	Methyl vinyl ether/maleic acid mono-n-octyl ester copolymer [VIII] (15 g.)
2	PVPK-90 (12 g.)	Methyl vinyl ether/maleic acid mono-n-octadecyl ester copolymer [IX] (15 g.)
3	PVP/VAE-735* (15 g.)	n-butyl vinyl ether/maleic acid mono amide copolymer [X] (15 g.)
4	PVPK-90 (14 g.)	n-butyl vinyl ether/maleic acid mono-N-1-propyl amide compolymer [XII] (15 g.)
5	PVPK-90 (12 g.)	Methyl vinyl ether/maleic acid mono N-methyl-N-octadecyl amide copolymer [XV] (15 g.)
6	PVP/VAE-535** (15 g.)	n-butyl vinyl ether/maleic acid mono N-methyl amide copolymer [XI] (15 g.)

Note:
*PVP/VAE-735: N-vinyl pyrrolidone/vinyl acetate 70/30 copolymer (G A F co)
**PVP/VAE-535: N-vinyl pyrrolidone/vinyl acetate 50/50 copolymer (G A F co)

(g.: weight of solid content)

The sheet thus produced was cut to form a tape and was permitted to stand at room temperature for 10 days. Said tape was charged into an oscillograph of an electrocardiograph, was traced by a heated stylus (head temperature:120°C) and then developed by moistening the surface of film by a felt impregnating a dye liquid developer to obtain the following results.

Treatment No.	Dye liquid developer	Developing time	Image density	Back ground density	Remarks
		(seconds)			
1	D-I	3	middle	0.02	
	D-VI	3	large	0.03	
2	D-I	3	small	0.01	
	D-VII	3	large	0.02	
3	D-I	3	middle	0.02	line is
	D-VII	3	large	0.1	blurred
4	D-I	3	small	0.01	
	D-VI	3	large	0.04	
5	D-VII	5	large	0.02	
6	D-VIII	5	large	0.03	

Note: Composition of dye liquid developer

D-VI	Anthraquinone Blue AB	0.3 g.
	Alcohol	30 ml.
	Water	70 ml.
D-VII	Anthraquinone Blue AB	0.3 g.
	Alcohol	70 ml.
	Water	30 ml.
D-VIII	Anthraquinone Blue AB	0.3 g.
	i-propyl alcohol	50 ml.
	Water	50 ml.

EXAMPLE 4

This exmaple shows that the thermal recording sheet may be used as a master for dye transfer process.

35g. (solid content: about 17g.) of N-vinyl pyrrolidone/vinyl acetate copolymer (trade name: PVP/VAE-735 manufactured by GAF Co) and 15g. of n-butyl vinyl ether/maleic acid mono ethyl ester copolymer [VII] were dissolved in 300g. of a mixture of alcohol and dimethyl formaldehyde (1 : 1). The resulting solution was applied to a polyester sheet at the thickness of about 3 microns (after drying) and dried to obtain a master. The master after standing for 10 days at room temperature can be used stably. The master was cut in the dimension of a cabinet and a small hole was provided in said master for registration.

On the other hand, black-white originals corresponding to each of three colors for regeneration of said three colors were prepared, and each original was passed through a Thermofax copying machine with said master for exposure. The master was developed by the following liquid developer corresponding to each color, and lightly washed with water to obtain masters of cyan, magenta and yellow.

Composition of Cyan liquid developer:

D-IX	Anthraquinone Blue AB	1.1 g.
	Sodium primary phosphate-monohydrate	10 g.
	Water	1000 ml.

Composition of Magenta liquid developer:

D-X	Anthraquinone lupinol R conc	4.0 g.
	Sodium primary phosphate-mono hydrate	13 g.
	Borax	1.0 g.
	Water	1000 ml.

Yellow liquid developer:

D-XI	Tartrazine	2.0 g.
	Sodium primary phosphate-monohydrate	20 g.
	Borax	10 g.
	Water	1000 ml.

A baryta paper coated with gelatine was mordanted as follows:

Solution No. 1:	Aluminium sulfate	100 g.
	Water	500 ml.
Solution No.2:	Sodium carbonate	20 g.
	Water	250 ml.

A baryta paper was dipped in the mordanting solution produced by adding solution No.2 to solution No.1 for 5 minutes, then dipped in 5% solution of sodium acetate for 5 minutes, and washed with water for 5 minutes.

The coloring matters were transferred to said baryta paper by laying one color master upon the others in predetermined positions respectively on said baryta paper and squeezing to obtain color prints of cyan, magenta and yellow.

Said master may be used repeatedly at least 20 times. The black-white original for printing of a master may be produced easily by a known method. For example the black-white intermediate original for regenerating yellow, magenta and cyan may be obtained by laying each filter of blue, green and red on a colored original respectively and copying by an electrophotographic copying machine on a panchromatically-sensitized ZnO electrophotographic paper. Since the toner developer used for electrophotographic copying paper absorbs effectively the light from the light souce of a Thermofax copying machine, the intermediate original thus obtained may be utilized to produce a master.

Colouring matters except the described above which are suitable for development and transferring are as follows:

1. Cyans:
   Patent Blue conc.
   Brilliant Blue
   Alizarine Blue (AB)
   Fast And Green B
2. Magentas:
   Acid Magenta 2B conc.
   Fast Fuchsine
   Fast Crimson 6 BL
   Violamine RR
3. Yellow:
   Quinorine Yellow
   Pontamine Yellow CH (conc.)
   Pontamine Fast yellow NN

EXAMPLE 5

15g. of poly-N-vinyl pyrrolidone (trade mane: PVP K-90and 15g. of a methyl vinyl ether/maleic acid mono ester copolymer having various lengths of ester radical chains were combined to produce a thermal recording sheet by the same procedure as that of Example 1. Said sheet was passed through a Thermoflex copying machine with an original and developed by the dye developing solution D-1. Table 11 shows that the longer the length of chain of the alkyl radical, the longer the developing time, that is, the developing speed decreases. When the developing speed is too high, a rapid treatment may be possible, but the background density tends to increase if the developing time and temperature are not controlled. When the alkyl chain is not less than C_5, the developing speed is low, but an image having a continuous tone and a clear background is obtained. It is preferred to add an organic solvent miscible with water such as alcohol, acetone, methyl ethyl ketone, dioxane and the like to a dye liquid developer to increase the image density.

Table 11

Sample No.	Ester radicals of methyl vinyl ester/maleic acid mono ester copolymer	Developing Speed	Back ground density
1	Methyl	very high	high
2	Methyl[1]	high	high
3	1-propyl[2]	high	middle
4	n-butyl[3]	middle	low
5	2-ethylhexyl	low	low
6	n-decyl	low	low
7	benzyl	middle	low

Note:
[1]Gantrez ES-225 (manufactured by GAF)
[2]Gantrez ES-335-I (manufactured by GAF)
[3]Gantrez ES-425 (manufactured by GAF)

EXAMPLE 6

15g. of poly-N-vinyl-5-methyl-2-oxazolidone (K value is 32; $\log\eta rel = [7.5Ko^2/(1+1.5Ko)] + Ko$, $K=10^3Ko$, η rel. is specific viscosity) and 30g. of methyl vinyl ether/maleic acid mono-n-butyl ester (trade name:Gantrez ES-425) were dissolved in 300g. of dimethyl formaldehyde. Said solution was applied to a polyester film subjected to a treatment imparting hydrophilic property at the thickness of 2.5 microns (after drying) and dried at 80°C. After 7 days, said film was laid on an original and printed by a Thermalfax copying machine and immediately developed in the dye liquid developer D-1 for 5 seconds to obtain about 1.3 of maximum density (red filter was used) and 0.03 of background density. Furthermore, 18g of N-vinyl-5-methyl-2-oxazolidone/vinyl acetate copolymer (mixing ratio 50/50) was used in place of poly-N-vinyl-5-methyl-2-oxazolidone to produce the same thermal recording sheet. Said thermal recording sheet was developed by the dye liquid developer D-VII disclosed in Example 3 to obtain the same clear image as that in Example 3.

EXAMPLE 7

Solutions of various compounds were prepared, and two solutions selected therefrom were mixed with each other for a gel time test.

A mixture of two compounds in the same amount was dissolved in a suitable solvent for coating, and said solution was applied to a polyester film at the thickness of 2 – 4 microns (after drying) and dried to prepare a sample. The heat sensitivity was tested with respect to said sample. The heat sensitivity was determined by judging whether an image having contrast was formed or not when said sample was pressed by a heat wedge and developed by a dye liquid developer. The results are shown in Table 12.

Table 12

Experiment No.	Compound (A)	Compound (B)	Solvent[1]	Gelation[2]	Solvent for Coating	Homogeneity of layer	Heat Sensitivity	Remarks
1	PVP K-90	Vinyl acetate/maleic acid mono ethyl ester copolymer (1/1)	alcohol	+	alcohol DMF (1/1)	a little opaque	+	
2	"	Styrene/maleic acid mono ethyl ester copolymer (1/1)	alcohol	+	alcohol/ DMF (1/1)	opaque	–	
3	"	Polystyrene	chloroform	–	chloroform	opaque	–	Phase separate
4	"	Polyvinyl alcohol	water	–	water	transparent	–	
5	"	Polymethyl vinyl ether	water	–	water	transparent	–	
6	"	Polyvinyl hydrogen phthalate	alcohol	+	DMF		–	Phase separate
7	"	Cellulose hydrogen phthalate	alcohol	+	DMF	a little opaque	–	Phase separate

Table 12-continued

Experiment No.	Compound (A)	Compound (B)	Solvent[1]	Gelation[2]	Solvent for Coating	Homogeneity of layer	Heat Sensitivity	Remarks
8	"	Methyl cellulose hydrogen succinate	alcohol	+	DMF	transparent	+	
9		Benzyl cellulose hydrogen succinate	alcohol	+	DMF	transparent	+	
10	"	P-sulfobenzene cellulose acetate	water	+	DMF	a little opaque	+	
11	"	Ethyl cellulose	alcohol	−	alcohol	transparent	−	
12	"	Ethyl/hydroxy ethyl cellulose	alcohol	+	alcohol DMF (1/1)	transparent	++	
13	"	Mono ammonium salt of methyl vinyl ether/ maleic acid copolymer	alcohol	+	alcohol/ DMF (1/1)	transparent	++	Back Ground density: a little high
14	N-vinyl pirrolidone/ vinyl acetate copolymer 70/30	Mono-N-methyl ammonium salt of methyl vinyl ether/maleic acid copolymer	alcohol	+	alcohol/ DMF (1/1)	transparent	++	
15	"	Hydroxy ethyl cellulose	alcohol	+	"	a little opaque	+	
16	Poly-N-vinyl piperidone	Methyl vinyl ether/maleic acid mono ethyl ester	alcohol	+	"	transparent	++	
17	Poly-N-vinyl caprolactam	"	alcohol	+	"	"	++	
18	Poly-N-vinyl morpholinone	"	alcohol	+	"	"	++	
19	Poly-N-vinyl-2-Oxazolidone	"	alcohol/ water (1/1)	+	"	"	++	
20	Poly-N-vinyl imidazole	"	"	+	"	"	++	
21	Poly-4-vinyl pyridine	"	alcohol	+	"	"	+	
22	Poly-N-vinyl-5-methyl-2-oxazolidone	Hydroxy ethyl cellulose	"	+	"	"	+	
23	"	Methyl vinyl ether/maleic acid mono-N-i-propyl amide	"	+	"	"	++	
24	N-vinyl-5-methyl-2-oxazolidone/ vinyl acetate copolymer (1/1)	"	"	+	"	"	++	
25	"	Polyvinyl methyl ether	"	−	alcohol	"	−	
26	Polyvinyl methyl ether	Polyvinyl methyl ether	"	−	"	"	−	
27	Polyvinyl acetate	Methyl vinyl ether/maleic acid mono ethyl ester	"	−	"	"	−	
28	Polyethylene oxide	Resol type phenol formaldehyde resin	—	−	MEK	"	+	
29	PVP K-90	Succinic acid monobennzyl ester	alcohol	−	alcohol	"	+	
30	N-octyl pyrrolidone	methyl vinyl ether/ maleic acid monobutyl ester	alcohol	−	"	"	+	
31	N-vinyl pyrrolidone/metacrylic acid/ methyl methacrylate copolymer (1:1:1)				DMF	"	+	

Note:
[1]Solvent for testing of gelation
[2]Gelation: + No gelation: −
[3]The higher a contrast of an image is, the more number of + is.

EXAMPLE 8

The thermal recording sheet composed of the mixture of PVP K-90 and Gantrez ES-425 (1 : 1) as prepared in Example 1 was developed in a liquid developer of p-rose aniline hydrochloride to obtain a pure rose colored image. After said film stood for about 24 hours, an original picture different from the first original picture was printed onto said film and then said printed film was developed in the liquid developer of Crystal Violet disclosed in Example 1 to form a violet image upon a pure rose image. Furthermore, said film recovered, and then was developed in the developing solution of Acridine Orange to form an orange image on the above mentioned two images.

EXAMPLE 9

This example relates to a method for preparing and for using the thermal recording sheet suitable for regenerating the negative-positive image.

10g. of poly-N-vinyl pyrrolidone (trade name: PVP

K-90) was dissolved in 100 ml. of water, and 15 ml. of a 10% aqueous solution of silver nitrate and a 5% aqueous solution of common salt were added by a Double jet method with vigorous stirring. After stirring for 30 minutes, 5g. of hydroquinone, 20g. of sodium sulfite and 10g. of sodium carbonate were dissolved in 100 ml. of water and 50 ml. of the solution thus obtained was added little by little and stirred for one hour at 40°C. The above mentioned procedure was conducted in a light room.

After lowering from 40°C to room temperature, the pH was lowered to 4.0 – 5.0 with 10% HNO_3 and there was added immediately a solution of 30g. (solid content: 50%) of vinyl methyl ether/maleic acid mono ethyl ester copolymer (trade name: Gantrez ES-425 manufactured by GAF Co) in 100 ml. of alcohol. The gel thus formed was separated, washed with water and then washed with alcohol.

Said gel was dissolved in a mixture of alcohol and dimethyl formamide (1 : 1) and 10g. (solid content: 5g.) of N-vinyl pyridine/vinyl acetate copolymer (trade name: PVP/VAE-735) was added. The resulting solution was applied to a polyester sheet at the thickness of 3 microns (after drying) and dried. The resulting film contained silver colloid and was light brown and had infrared absorbing properties. After stabilizing by standing at room temperature, said sheet was contacted with a negative photography image and exposed to a Xenon flashing discharge lamp (trade mark: Press-150 manufactured by Minicham) at a short distance and immediately developed in the dye liquid developer D-II to obtain a clear positive image. Said sheet was printed by a step wedge having $\sqrt{2}$ step and was developed. The maximum density was 1.5 (green filter) and the back ground density was 0.25. Eight steps are observed between the maximum density and the background density.

Said thermal recording sheet may be used for recording by laser scanning. When the laser ray (having a wave length of 6328 Å, spot diameter of 2 microns on the sheet and an intensity of 10 milliwatt) scans the thermal recording sheet at 2 m./sec. and said thermal recording sheet was developed with the dye liquid developer D-II, the record of sharp locus was obtained.

It is effective to use various infrared absorbers such as phenyl fluorene derivative. Manganese complex of azo dyes or commercially organic infrared absorbers containing antimony may be used in place of silver coloid in the thermal recording layer.

EXAMPLE 10

This example relates to the effect of an agent used to control the properties of the image.

1. When PVP/ES-425 is 6/4 (molar ratio)

A solution of 12g. of poly-N-vinyl pyrrolidone (trade name: PVP K-90, manufactured by GAF), 16g. of methyl vinyl ether/maleic acid mono-n-butyl ester copolymer (50% solution) (trade name: Gantrez ES-425, manufactured by GAF), 150g. of ethanol, 50g. of dimethyl formamide and 10g. of an additive was applied to a polyester film, dried and allowed to stand for 10 days at room temperature. The prepared thermal recording sheet was passed through a Thermofax copying machine with an original and developed by a machine under the following condition.

Developing solution: 10% water solution on Malachite Green oxalate.

Developing time: 3 sec.

Developing temperature: 30°C

The results are shown in Table 13.

Table 13

Addition Agents	Image Density	Background Density	D_I-D_{II}
None	1.41	1.08	0.33
α-Chloroanthraquinone	1.27	0.68	0.59
Benzophenone	1.46	1.10	0.36
p-dimethylamino benzaldehyde	1.46	1.11	0.35
9-fluorene carboxylic acid	1.33	0.31	1.02
p-nitro phenal	1.57	0.97	0.60
Michler's ketone	1.41	0.84	0.57
p-nitro phenyl acetate	1.52	1.22	0.30
p-benzoquinone	1.42	0.90	0.52
Benzhydrol	1.41	0.81	0.60
Benzoin	1.45	1.07	0.38

$D_I D_{II}$: Image Density-Background Density

2. When PVP/ES-425 is 4/6 (molar ratio)

A solution comprised of 8.0g. of poly-N-vinyl pyrrolidone (trade name: PVP K-90 manufactured by GAF Co), 24g. of methyl vinyl ether/maleic acid mono-n-butyl ester copolymer (50% solution) (trade name: Gantrez ES-425 manufactured by GAF Co), 150g. of ethanol, 50g. of dimethylformaldehyde and 10g. of an addition agent was applied on a polyester film and dried. After standing for 7 days at room temperature, said thermal recording sheet was passed through a Tharmafax copying machine with a manuscript and developed by machine under the following conditions.

Developing solution: 1.0% water solution of Malachite Green oxalate

Developing time: 10 sec.

Developing temperature: 30°C

The results are shown in Table 14 below.

Table 14

Addition Agents	Image Density	Background Density	D_I-D_{II}
None	0.75	0.09	0.66
α-chloranthraquinone	0.85	0.20	0.65
Benzophenone	1.09	0.08	1.01
p-dimethylamine benzaldehyde	0.78	0.07	0.71
9-fluorene carboxylic acid	0.83	0.34	0.49
p-nitrophenol	0.58	0.34	0.24
Michler's ketone	0.95	0.11	0.84
p-nitrophenyl acetate	0.95	0.42	0.53
p-benzoquinone	0.81	0.17	0.64
Benzhydrol	0.95	0.47	0.48
Benzoin	0.90	0.07	0.83

D_I-D_{II}: Image Density-Background Density

Developing by the machine disclosed above is the developing method using the following developing machine. The developing is conducted in such a way that a film transferred by a field roller provides aberration of position to an actuator, a photoswitch connects by said aberration of position, said film is put between crip plates connecting to the comfollower on the film conveyer to be fixed, said film is treated by fountain development, and excess liquid developer scraped off with a blade.

Tables 13 and 14 show that the most effective additive is 9-fluorene carboxylic acid in (1) and benzophenone in (2). The results show that weak mutual action among high polymer (A), high polymer (B) and the additive provides an influence on the image property.

EXAMPLE 11

15g. of polyvinyl pyrrolidone (trade name: PVP K-90, manufactured by GAF) was dissolved in 150 g. of alcohol and 30g. of methyl vinyl ether/maleic acid mono-n-butyl ester copolymer (trade name: Gantrez ES-425, manufactured by GAF) (solid content: 50%) was added to said solution and permitted to stand to obtain a gel-like high polymer complex. 150g. of dimethyl formamide was added to said gel-like complex to obtain a homogeneous and clear solution. Said solution was applied to a polyester film at a thickness of 70 microns (the film having been subjected to a treatment imparting a hydrophilic property) dried by hot air at 70° – 80°C. (The thickness of said film was 2 microns after drying). After standing for several days at room temperature (about 20°C), the properties of said sheet such as heat sensitive temperature, contrast and the like are stabilized. Said thermal recording sheet is passed through a Thermofax copying machine (Secretary type manufactured by Minesota Mining and Manufacturing Co.) with an original.

Visible changes on said sheet were not seen in the above mentioned step. Said thermal recording sheet having a latent image was washed off with a 1% aqueous solution of Rose Bengal for 5 minutes to dissolve the portion of the latent image and obtain a relief image.

EXAMPLE 12

When a latent image formed on a thermal recording sheet prepared by the method of Example 11 except adding a small amount of phenolphthalein to the composition of Example 11 was exposed to ammonia vapor for 10 minutes, a reddish rose color was formed at the portion of the latent image. Thus a visible image was obtained.

EXAMPLE 13

Silver behenate (25g.) and hydroquinone (1g.) were added to and dispersed in a solution of the complex obtained in Example 1 in dimethylformamide, coated on a polyester film of 70 microns in thickness and dried at room temperature. The resulting thermal recording sheet was contacted with a first original and passed through a copier which was adjusted to give a thermal pattern of 120°– 150°C. to produce a dark brown image due to the reduction of the silver behenate. Then a portion of the thermal recording member having no image was contacted with a second original and passed through a copier adjusted to give a thermal pattern of 60°–80°. The silver behenate did not react with the complex under such temperature conditions and failed to produce any image of the second original.

The resulting sheet was developed with the dye liquid developer D-1 in Example 1 and there was obtained an image of the second original.

We claim:

1. A thermal recording member useful for forming a reversible latent image by heating which is capable of being developed into a permanent visible image, said recording member comprising a support having thereon a uniform and transparent recording layer composed of a heat-sensitive composition which comprises a polymer complex including a polymer moiety which is normally dyeable at room temperature but which, in the polymer complex, is dyeable only after heating the complex to an elevated temperature, wherein said polymer complex is a complex of a polymer (A) and a polymer (B); and wherein said polymer (A) is a dyeable polymer selected from the group consisting of homopolymers and copolymers of N-vinyl lactams, N-vinyl cyclic carbamates, N-vinyl imidazoles, vinyl pyridines, alkylene oxides and acrylamides; and wherein said polymer (B) is selected from the group consisting of polymers having a carboxylic acid radical, a sulfonic acid radical or an OH radical.

2. A thermal recording member according to claim **1** wherein said polymer (A) is a homopolymer of one of said group, a copolymer of more than one of said group or a copolymer of one of said group with a different vinyl monomer.

3. A thermal recording member according to claim **2** wherein said different vinyl monomer is selected from the group consisting of methacrylates, acrylates, acrylamides, acrylonitrile, vinyl ethers, vinyl acetate, vinyl imidazoles and ethylene.

4. A thermal recording member accroding to claim **1** in which said polymer (A) is selected from the group consisting of homopolymers and copolymers of N-vinyl pyrrolidone, N-vinyl-3-methyl pyrrolidone, N-vinyl-5-methyl pyrrolidone, N-vinyl-3,3,5-trimethyl pyrrolidone, N-vinyl-3-benzylpyrrolidone, N-vinyl piperidone, N-vinyl-4-methyl piperidone, N-vinyl caprolactam, N-vinyl capryllactam, N-vinyl-3-morpholinone, N-vinyl thiopyrrolidone, N-vinyl-2 pyriodone, N-vinyl-2-oxazolidone, N-vinyl-5-methyl-2-oxazolidone, N-vinyl-5-ethyl-2-oxazolidone, N-vinyl-4-methyl-2-oxazolidone, N-vinyl-2-thio-oxazolidone, N-vinyl-2-mercaptobenzothiazole, N-vinyl imidazole, N-vinyl-2-methyl imidazole, N-vinyl-4-methyl imidazole, ethylene oxide, propylene oxide, methacrylamide, acrylamide, N-methyl acrylamide, N-n-butyl acrylamide, N-benzyl acrylamide, 2-vinylpyridine and 4-vinyl pyridine.

5. A thermal recording member according to claim **1** in which said polymer (B) is selected from the group consisting of polyesters obtained by reacting an aliphatic polyhydric carboxylic acid and diols, acid cellulose derivatives, an acid polyvinyl polymer, an acrylic acid polymer, a methacrylic acid polymer, an α, β-unsaturated acid polymer, acid polyvinyl alcohol derivatives, cellulose ethers, a phenolic resin, a cresol-formaldehyde resin and a phenoxyacetic acidformaldehyde resin.

6. A thermal recording member according to claim **1,** in which said polymer (B) is selected from the group consisting of homopolymers and copolymers of maleic anhydride, maleic anhydride mono-esters and maleic anhydride mono-amides.

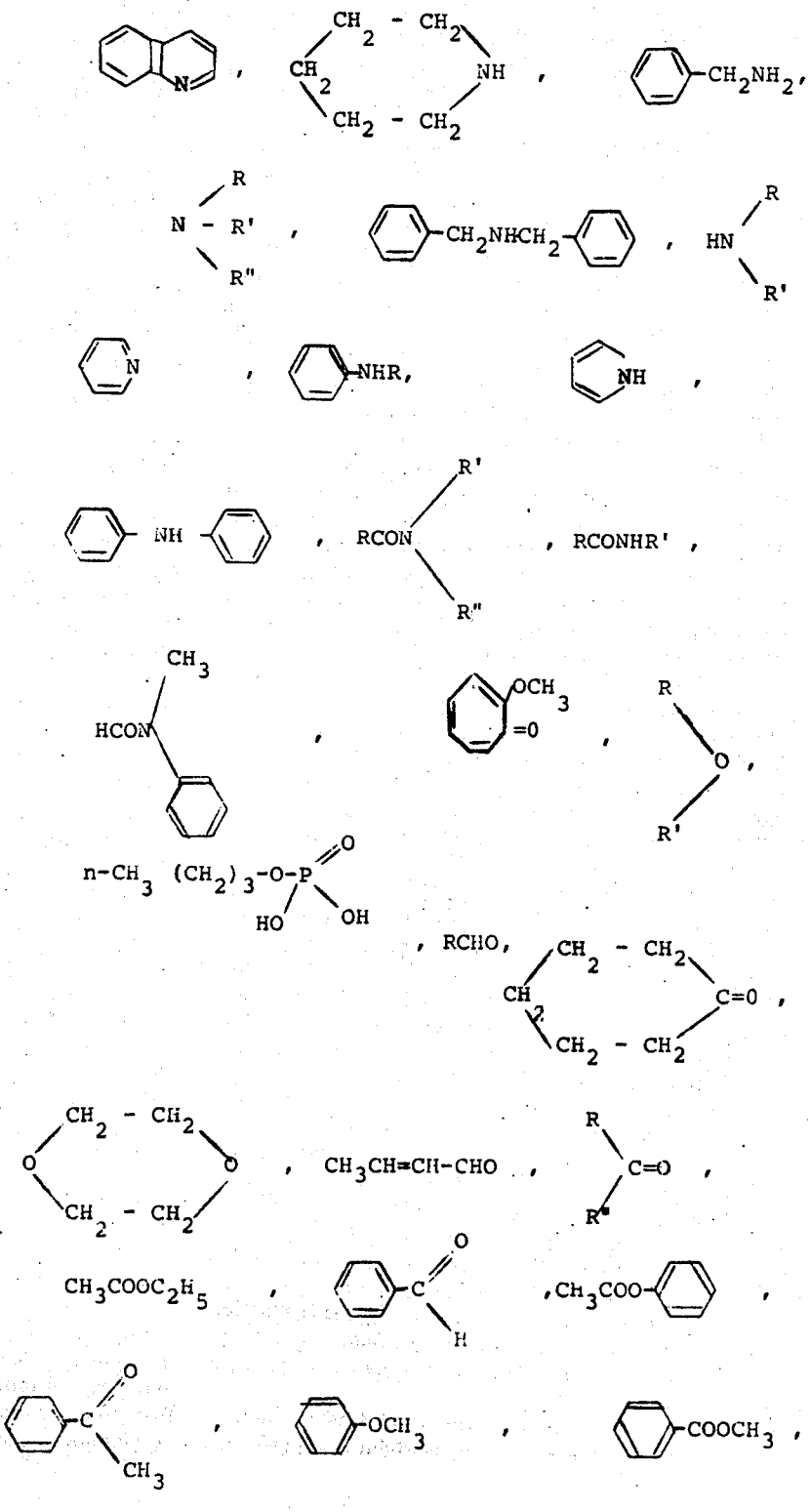
7. A thermal recording member according to claim **1** in which said polymer (B) is selected from the group consisting of copolymers of (1) and α, β-unsaturated acid selected from the group consisting of maleic anhydride, maleic anhydride mon-esters, maleic anhydride mono-amides, itaconic anhydride, citraconic anhydride and diester fumarate, and (2) a vinyl monomer selected from the group consisting of vinyl acetate, vinyl ethers, acrylamide, vinyl esters, ethylene and acrylic esters.

8. A thermal recording member according to claim **1** in which said polymer (B) is selected from the group consisting of methyl vinyl ether/maleic acid copolymers, methyl vinyl ether/maleic acid mono n-butyl ester copolymers, methyl vinyl ether/maleic acid mono-N-n-hexylamide copolymers, methyl vinyl ether/maleic acid mono-n-octyl ester copolymers,

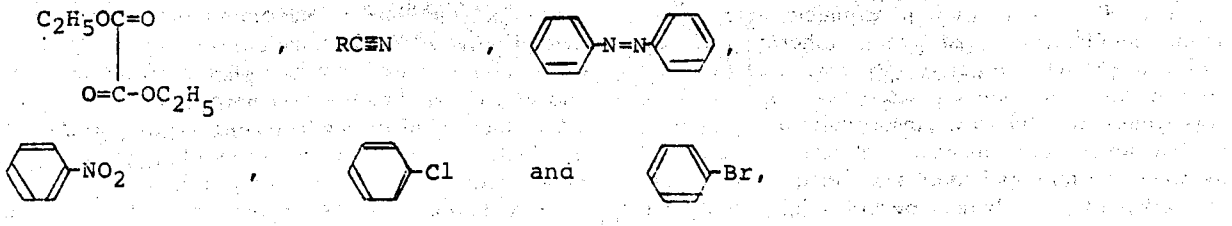
methyl vinyl ether/maleic acid mono-n-octadecyl ester copolymers, n-butyl vinyl ether/maleic acid mono-amide copolymers, n-butyl vinyl ether/maleic acid mono-N-i-propyl amide copolymers, methyl vinyl ether/maleic acid mono-N-methyl-N-octadecyl amide copolymers, n-butyl vinyl ether/maleic acid mono-N-methyl amide copolymers, n-butyl ether/maleic acid mono ethyl ester copolymers, vinyl acetate/maleic acid mon-ethyl ester copolymers, methyl cellulose hydrogen succinate, benzyl cellulose hydrogen succinate, p-sulfobenzene cellulose acetate, ethyl hydroxyethyl cellulose, mono-ammonium salts of methyl vinyl ether/maleic acid copolymers, mono-N-methyl ammonium salts of methyl vinyl ether/maleic acid copolymers, hydroxyethyl cellulose, resol-type phenol formaldehyde resins and succinic acid monobenzyl esters.

9. A thermal recording member according to claim **1** in which the heat-sensitive composition further contains a proton acceptor or a proton donor.

10. A thermal recording member according to claim **9**, in which the proton acceptor is selected from the group consisting of:



-Continued



wherein R, R′ and R″ each represents alkyl or aryl.

11. A thermal recording member according to claim **9** in which the proton donor is selected from the group consisting of FH, HCl, R—COOH, C_6H_5OH, $C_6H_5NHCOCH_3$, RCONHR′, $C_2H_5NHC_2H_5$, $RCONH_2$, H_2O, Cl_3CH, C_6H_5—NH—C_6H_5, $(CH_2)_2NH$, $C_6H_5NH_2$ and $C_6H_5CH_2NH_2$, wherein R and R′ are each alkyl or aryl.

12. A thermal recording member according to claim **1** in which the heat-sensitive composition further contains an aliphatic or aromatic ketone which is non-volatile at room temperature.

13. A thermal recording member according to claim **1** in which the heat-sensitive composition further contains a member selected from the group consisting of α-chloroanthraquinone, benzophenone, p-dimethylaminobenzaldehyde, 9-fluorene carboxylic acid, p-nitro phenol, Michler's ketone, p-nitro phenyl acetate, p-benzoquinone, benzhydrol and benzoin.

14. A thermal recording member useful for forming a reversible latent image by heating which is capable of being developed into a permanent visible image, said recording member having a uniform and transparent heat-sensitive recording layer which comprises a polymer complex of a polymer (A) and a polymer (B); wherein said polymer (A) is selected from the group consisting of poly-N-vinyl pyrrolidone, N-vinyl pyrrolidone/vinyl acetate copolymers, poly-N-vinyl-5-methyl-2-oxazolidone, N-vinyl-5-methyl-2-oxazolidone/vinyl acetate copolymers, poly-N-vinyl piperidone, poly-N-vinyl caprolactam, poly-N-vinyl morpholinone, poly-N-vinyl-2-oxazolidone, polyn-N-vinyl imidazole, poly-4-vinyl pyridine, polyethylene oxide and poly-N-octyl pyrrolidone, and wherein said polymer (B) is selected from the group consisting of methyl vinyl ether/maleic acid copolymers, methyl vinyl ether/maleic acid mono-n-butyl ester copolymers, methyl vinyl ether/maleic acid mono-N-n-hexylamide copolymers, methyl vinyl ether/maleic acid mono-n-octyl ester copolymers, methyl vinyl ether/maleic acid mono-n-octadecyl ester copolymers, n-butyl vinyl ether/maleic acid mono-amide copolymers, n-butyl vinyl ether/maleic acid mono-N-i-propyl amide copolymers, methyl vinyl ether/maleic acid mono-N-methyl-N-octadecyl amide copolymers, n-butyl vinyl ether/maleic acid mono-N-methyl amide copolymers, n-butyl vinyl ether/maleic acid mono ethyl ester copolymers, vinyl acetate/maleic acid mono ethyl ester copolymers, methyl cellulose hydrogen succinate, benzyl cellulose hydrogen succinate, p-sulfobenzene cellulose acetate, ethyl hydroxy ethyl cellulose, mono-ammonium salts of methyl vinyl ether/maleic acid copolymers, mono-N-methyl ammonium salts of methyl vinyl ether/maleic acid copolymers, hydroxy ethyl cellulose, resol-type phenol formaldehyde resins and succinic acid monobenzyl ester.

15. A thermal recording member useful for forming a reversible latent image by heating which is capable of being developed into a permanent visible image, said recording member having a uniform heat-sensitive recording layer which comprises a polymer complex of poly-N-vinyl pyrrolidone and a methyl vinyl ether/maleic acid mono-n-butyl ester copolymer.

16. A thermal recording method which comprises forming a reversible latent image by applying a thermal pattern to a recording member having a uniform and transparent heat-sensitive layer which contains a polymer complex of a polymer (A) and a polymer (B), said polymer (A) being selected from the group consisting of homopolymers and copolymers of N-vinyl lactams, N-vinyl cyclic carbamates, N-vinyl imidazoles, vinyl pyridines, alkylene oxides and acrylamides, and said polymer (B) being selected from the group consisting of polymers having a carboxylic acid radical, a sulfonic acid radical or an OH radical, and then contacting said heat-sensitive layer with a dye solution to convert said reversible latent image into a permanent visible image.

17. A thermal recording method according to claim **16** in which said dye solution is an aqueous dye solution.

18. A thermal recording method according to claim **16** in which said dye is selected from the group consisting of triphenylmethane dyes, xanthene dyes, mono azo dyes, anthraquinone dyes and ketoimine type dyes.

19. A thermal recording method according to claim **16** in which said polymer (A) is selected from the group consisting of homopolymers and copolymers of N-vinyl pyrrolidone, N-vinyl-3-methyl pyrrolidone, N-vinyl-5-methyl pyrrolidone, N-vinyl-3,3,5-trimethyl pyrrolidone, N-vinyl-3-benzyl-pyrrolidone, N-vinyl piperidone, N-vinyl-4-methyl piperidone, N-vinyl caprolactam, N-vinyl capryllactam, N-vinyl-3-morpholinone, N-vinyl thiopyrrolidone, N-vinyl-2-pyridone, N-vinyl-2-oxazolidone, N-vinyl-5-methyl-2-oxazolidone, N-vinyl-5-ethyl-2-oxazolidone, N-vinyl-4-methyl-2-oxazolidone, N-vinyl-2-thiooxazolidone, N-vinyl-2-mercaptobenzothiazole, N-vinyl imidazole, N-vinyl-2-methyl imidazole, N-vinyl-4-methyl imidazole, ethylene oxide, propylene oxide, methacrylamide, acrylamide, N-methyl acrylamide, N-n-butyl acrylamide, N-benzyl acrylamide, 2-vinylpyridone and 4-vinyl pyridine.

20. A thermal recording method according to claim **16** in which said polymer (B) is selected from the group consisting of homopolymers and copolymers of maleic anhydride, maleic anhydride mono-esters and maleic anhydride mono-amides.

21. A thermal recording method according to claim **16** in which said polymer (B) is selected from the group consisting of copolymers of (1) an α,β-unsaturated acid selected from the group consisting of maleic anhydride, maleic anhydride mono-esters, maleic anhydride mono-amides, itaconic anhydride, citraconic anhydride and diester fumarate, and (2) a vinyl monomer selected from the group consisting of vinyl acetate, vinyl ethers, acrylamide, vinyl esters, ethylene and acrylic esters.

22. A thermal recording method according to claim 16 in which said polymer (B) is selected from the group consisting of methyl vinyl ether/maleic acid copolymers, methyl vinyl ether/maleic acid mono-n-butyl ester copolymers, methyl vinyl ether/maleic acid mono-N-n-hexylamide copolymers, methyl vinyl ether/maleic acid mono-n-octyl ester copolymers, methyl vinyl ether/maleic acid mono-n-octadecyl ester copolymers, n-butyl vinyl ether/maleic acid mon-amide copolymers, n-butyl vinyl ether/maleic acid mono-N-i-propyl amide copolymers, methyl vinyl ether/maleic acid mono-N-methyl-N-octadecyl amide copolymers, n-butyl vinyl ether/maleic acid mono-N-methyl amide copolymers, n-butyl vinyl ether/maleic acid mono ethyl ester copolymers, vinyl acetate/maleic acid mono ethyl ester copolymers, methyl cellulose hydrogen succinate, benzyl cellulose hydrogen succinate, p-sulfobenzene cellulose acetate, ethyl hydroxy ethyl cellulose, mono-ammonium salts of methyl vinyl ether/maleic acid copolymers, mono-N-methyl ammonium salts of methyl vinyl ether/maleic acid copolymers, hydroxy ethyl cellulose, resol-type phenol formaldehyde resins and succinic acid monobenzyl ester.

23. A Thermal recording method which comprises applying a thermal pattern to a recording member having a uniform and transparent heat-sensitive layer which contains a polymer complex of poly-N-vinyl pyrrolidone and a vinyl ether/maleic acid mono ester copolymer.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,912,844 Dated October 14, 1975

Inventor(s) ICHIRO ENDO, ET AL

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, Line 50, "to form" should read --forms--

Column 2, Line 61, "behavier" should read --behavior--

Column 17, Line 29, "135" should read --136--

Column 22, Line 24 "Orenge" all three occurrences should read --Orange--; and at Line 27, "Orenge" both occurrences should read --Orange--

Column 25, Line 60, "pyrolidone" should read --pyrrolidone--

Column 26, Line 25, "sbsorptions" should read --absorptions--

Column 31, in Table 12, under the heading "Compound (A)" in experiment No. 14, "pirrolidone" should read --pyrrolidone--

Column 36, Line 37, and Column 37, Line 9 and at Column 41, Line 9, all three occurrences, "mon-" should read --mono- --

Column 39, Line 42, "polyn" should read --poly--

Signed and Sealed this

twenty-third Day of *March 1976*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,912,844 Dated October 14, 1975

Inventor(s) ICHIRO ENDO, ET AL

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, Lines 1-2, "Representative" should read --represen-tative--

Column 8, Line 49, "σ-electron" should read --π-electron--

Column 9, Line 25, "Has" should read --It has--

Column 11, Line 34, "methacryl" should read --poly-methacryl--

Column 12, Line 5, "enable" should read --enables--

Column 12, Line 37, "nptrate" should read --nitrate--

Column 14, Line 24, delete the word "is"

Column 14, Line 33, delete the word "the"

Column 15, Line 66, "Thee" should read --The--

Column 16, After Line 31, insert the following paragraph.

¶--Alkyl vinyl ethers having the formula:--

Column 17, Line 50, "The 10g." should read --10g.--

Column 23, Line 1, "sensitivity" should read --sensitive--

Column 24, Line 2, "an image" should read --image--, and "and a" should read --and--

Column 26, Line 11, "when" should read --When--

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,912,844 Dated October 14, 1975

Inventor(s) ICHIRO ENDO, ET AL

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 27, Line 19, "compolymer" should read --copolymer--

Column 29, Line 21, "mane" should read --name--

Column 29, Line 22, "K-90and" should read --K-90) and--

Column 31, in Table 12, under the heading "Compound (B)" in experiment No. 29, "monobennzyl" should read --monobenzyl--

Column 33, Line 28, "photography" should read --photographic--

Column 33, Line 49, "of" should read --of the--

Column 34, Line 31, "tharmafax" should read --Thermofax--

Column 34, Line 44, "p-dimethylamine" should read --p-dimethylamino--

Signed and Sealed this

twenty-third Day of *March 1976*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks