

1

2,695,245

PROCESS OF RECORDING BY DECOLORING

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1 Claim. (Cl. 117—15)

This invention relates to a process of recording by decoloring, and more particularly pertains to such a process in which, in a first step, the whole recording area of a base record material is colored by bringing together thereon two substances reactant on contact to produce a distinctive color and, in a second step, recordings are made on said area with a decoloring fluid. The data so recorded stands out as light areas against a dark colored background.

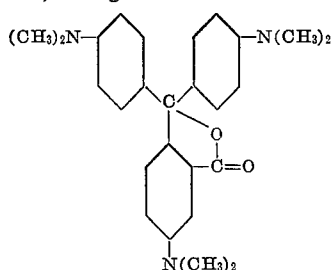
The process uses the phenomenon of adsorption and desorption of two reactive materials which normally are colorless in the unadsorbed state, but which produce a color on adsorption, one upon the other. The color is produced through an electron donor-acceptor chemical reaction, without any ion exchange. Thus, if there is applied to the adsorbed color reactants a non-color reactant adsorbate, which is preferentially adsorbed on the adsorbent, the color-producing adsorbate is desorbed with loss of color.

Preferably the base record material is white paper so the data recorded thereon appears in white against a colored background. In a modified form of the invention the base color of the record material includes coloring matter which is not decolorized by the decoloring fluid and coloring matter which is decolorized by the decoloring fluid, so the recorded data appears as a color lighter than the background color. This modified form of the invention includes the step of using a base record material which has a fixed color or applying a fixed color together with the decolorable color, as will be explained.

The invention is not deemed to be limited to the particular coloring and decoloring agents to be described in the preferred and modified forms of the invention as the principle is capable of being carried out with other coloring agents and decoloring agents of which persons skilled in the art will be fully aware.

The means of applying the decoloring fluid in a recording operation also is a matter of choice, whether it be done by letterpress type, planographic printing plates, porous type, writing stylus, or pen.

In the preferred embodiment of the invention the base record material, white paper, has the recording area thereof coated with a binder film containing solid particles of adsorbent material which acts as an acid and thereby causes a distinctive color in a coloring material which is applied thereto as the first step of the process. The color is produced by an electron donor-acceptor adsorption color reaction, which is reversible by desorption. The preferred coloring material is crystal violet lactone, which is 3,3 bis (p-dimethylaminophenyl) 6-dimethylamino phthalide, having the structure

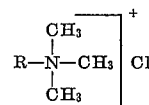


and which may be prepared in the manner disclosed in United States Patent No. Re. 23,024, which was granted

2

originally on the application of Clyde S. Adams. This compound, which normally exists as white crystals, is changed to a deep violet-blue when in adsorption contact with solid particles of an adsorbent solid compound which acts as an acid relative thereto. The adsorbent material preferred for use in the base paper sheet with crystal violet lactone is the natural clay-like material attapulgite. The attapulgite is applied to the paper by means of a starch binder or equivalent as commonly practiced in the paper coating art. The needle-shaped particles of attapulgite insure that parts of some are exposed without coverage by the starch so the applied fluid coloring material may be adsorbed thereon. One method of applying attapulgite to paper is to cook twenty per cent, by weight, of paper coating starch in water for fifteen minutes at 200° Fahrenheit and, after cooling, adding to one part, by weight, of the cooked starch four parts, by weight, of a dispersion of one part, by weight, of attapulgite in three parts, by weight, of water. The mixture is applied to paper at room temperature so as to leave a dried coating .0005 of an inch in thickness.

To facilitate the application of the crystal violet lactone to the coated paper, it is dissolved in toluene, a 3% solution, being sufficient. The toluene solution is applied to the attapulgite coated paper which immediately turns dark violet-blue due to the adsorption of the crystal violet lactone on the attapulgite particles. The colored paper is then dried and is ready for the second step of the process. The decoloring fluid contains a compound which displaces the crystal violet lactone adsorbed on the clay whereupon the crystal violet lactone resumes its natural white or colorless state. The decoloring agent is chosen so the displacement of the crystal violet lactone is permanent. It may be mentioned that water and ethyl alcohol are temporary-decoloring agents, through preferential adsorption, but their action is fleeting because, as evaporation occurs, the crystal violet lactone resumes its adsorption contact with the clay and again becomes colored. The preferred decoloring agent is stearyl trimethylammonium chloride which may be dissolved in ethyl alcohol for application to the colored paper. This decoloring agent has the general formula



R being the group $C_{18}H_{37}$. Many other compounds of the same general structure may be used, among which may be mentioned di-coco-dimethylammonium chloride, which is a mixture of di-lauryl-dimethylammonium chloride and di-myristyl-dimethylammonium chloride.

The alcohol solution of stearyl trimethylammonium chloride when applied to the colored paper by a type-member, for instance a porous rubber printing stamp, immediately turns the paper white at points of fluid contact. The alcohol rapidly evaporates leaving the printed characters permanently white as the decoloring agent does not evaporate. An oily solvent may be used as the vehicle in which the decoloring agent is applied, if desired. The use of an oily vehicle is indicated in the event the decoloring fluid is subjected to an evaporating environment for long periods prior to application to the record material, such precluding the use of a volatile vehicle such as ethyl alcohol. The fluid vehicle is a matter of choice, as it plays no permanent part in the decoloring process.

In the modified process where it is desired to have the recorded data appear in color, the paper may be originally colored by a contrasting dye not affected by the decoloring agent used. With crystal violet lactone a suitable contrasting dye is Sudan Red and may be mixed directly with the toluene solution of crystal violet lactone. The paper so prepared is very dark purplish-blue and when recorded upon by the decoloring agent the recorded data appears red against the dark-blue background. Other contrasting dyes may be used in place of Sudan Red.

There are a number of compounds of the triphenyl methane type, of which crystal violet lactone is a mem-

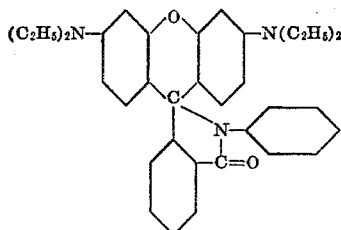
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ber, which may be used in place thereof and which will give a distinctive color when in adsorption contact with an acid adsorbent.

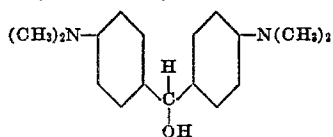
Malachite green lactone, which is 3,3 bis (p-dimethylaminophenyl) phthalide, and normally white or colorless, will give a green background color to the attapulgite coated paper.

A blue-green color is given by the normally white or colorless 3,3 bis (p-diethylaminophenyl) phthalide.

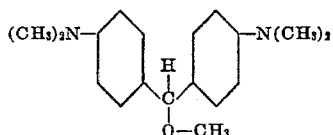
A red color is given by the normally white or colorless N-phenyl rhodamine B lactam which has the structure



A blue color is given by the normally white or colorless Michler's hydrol, having the structure



and the normally white or colorless methyl ether of Michler's hydrol, having the structure



And a bright blue color is produced by the normally white or colorless 3,3 bis (p-methylaminophenyl) phthalide.

All of these color producing compounds assume the colored form when in adsorption contact with attapul-

4

gite or such substitutes therefore as Halloysite, magnesium trisilicate and sodium aluminum silicate zeolite materials, and may be used in place of the crystal violet lactone in like amounts.

The decoloring of compounds adsorbed on clay by using a displacing adsorbate as provided by this process, is preferred over bleaching by reducing or oxidizing agents as such are often harmful to the record material, slow acting or malodorous, whereas displacing adsorbate compounds, such as those mentioned, are available that do not have such drawbacks.

The invention is not limited to a base web of paper as any base material that may be colored and printed or written upon may be used.

What is claimed is:

A process of recording data including the steps of providing a base web sheet; sensitizing the sheet by applying to it particles of attapulgite, the particles being applied so as to be held by the sheet so as to be substantially exposed to contact by an applied liquid; applying to the intended record area of the sheet 3,3 bis(p-dimethylaminophenyl)-6-dimethylamino phthalide carried in a liquid, which will turn the intended record area to a distinctive color; drying the sheet; and lastly applying to the colored portion of the sheet, as by printing type, stearyl trimethylammonium chloride carried in a liquid to decolor the printed area.

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