

May 5, 1964

B. S. WILDI

3,132,039

HEAT RESPONSIVE RECORDING SHEET

Filed Dec. 22, 1960

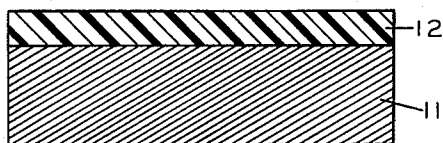


FIG. 1

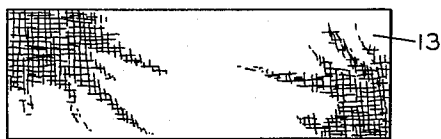


FIG. 2

INVENTOR.

BERNARD S. WILDI

BY *Lloyd B. Stevens, Jr.*

ATTORNEY

1

3,132,039

## HEAT RESPONSIVE RECORDING SHEET

Bernard S. Wildi, Dayton, Ohio, assignor to Monsanto Chemical Company, St. Louis, Mo., a corporation of Delaware

Filed Dec. 22, 1960, Ser. No. 77,512

7 Claims. (Cl. 117—36.8)

The invention relates to material or web (cloth, paper, and the like) which changes color upon being heated. This application is a continuation-in-part of copending application Serial No. 11,897, filed February 29, 1960.

Processes such as the "Thermo-Fax" process use treated paper which changes color on exposure to heat to allow the duplication of written matter, especially typing or penciled notes. Treated paper of the invention is suitable for this use. Normally, it is preferred to coat rather than impregnate the paper since then only the coating and not the paper itself need be heated to obtain the color change. To coat rather than impregnate paper, a conventional starch surface-sized paper is used. This paper is coated by treating with a methyl ethyl ketone solution of ethyl or nitrocellulose containing a coloring matter of the invention. Upon evaporation of the solvent, the cellulose and coloring matter is deposited on the paper as a coating. Also, designs, printing, and writing can be permanently inscribed on treated material of the invention by the use of a heated stylus, heated type, or the like. In addition, an entire treated material of the invention can be permanently colored or dyed by heating the material to a sufficiently high temperature to cause the color change. Alternatively, a design can be inscribed on cloth or paper by impregnating only a portion of the material in the form of a design, then when the material is heated, the colored design appears. Yet another way of inscribing a design, recording data, and the like on material of the invention is to use an electrical conduction recorder. The coloring material of the invention is semi-conductive and will be heated sufficiently to bring out the color by an electrical stylus as a result of passing current through the material.

It is an object of the invention to provide material which can be colored by the application of heat.

This and other objects of the invention will become apparent as the detailed description of the invention proceeds.

For the purposes of the invention, material or web is defined as paper, cloth, plastic film, or the like. The cloth or textile material can be natural or synthetic fibers of any type and can be specially treated to make it non-porous or not treated, depending on the use to which the material is to be put. Cotton, wool, paper, rayon, "nylon," or any other types of paper, cloth, or films such as "Mylar," "nylon 6 or 66," polyvinyl alcohol, etc., can be impregnated or coated with the coloring matter of the invention since this is merely a physical treatment and doesn't depend on the characteristics of the material. Normally, the coloring matter will be applied in a volatile solvent such as methanol or ethanol which, when it evaporates from the material, leaves the coloring matter evenly deposited on the material.

The articles of manufacture of the invention are materials treated with a heat-responsive coloring matter of the invention. This coloring matter is a reaction product of about 2 moles of ammonia or a lower (1-6 carbon atoms) alkyl monohydroxy alcohol with 1 mole of a nitrile such as pyromellitonitrile, or about a 1:1 reaction product of ammonia or a lower alkyl monohydroxy alcohol with a nitrile such as succinonitrile or phthalonitrile. The characteristic that is required in the nitrile molecule is that it must have at least one pair of nitrile groups on adjacent carbon atoms.

2

The heat responsive coloring material is normally produced by contacting the nitrile with the alcohol or ammonia at slightly elevated temperatures normally less than 100° C. In any event, heating must be kept below the temperature at which the particular reaction product changes color and this temperature varies with the particular reaction product. Actually, some reactants, especially the ammonia products, could probably be formed in good yield in a reasonable amount of time by contacting the reactants without heating or even at temperatures below room temperature (about 25° C.). Ammonia is more reactive than the alcohols, so the alcohols can be used as solvents for the nitriles while the ammonia reaction product is being formed; however, the ammonia reaction product can be made in the absence of an alcohol or other solvent medium if liquid ammonia is used as the solvent medium. A small amount of catalyst, such as sodium, to speed the reaction can be used but is not necessary. Although the reaction product can be produced using a 2:1 or 1:1 molar ratio of alcohol or ammonia to nitrile depending on the nitrile used, it is preferred to use a large excess of alcohol or ammonia over that required, to more quickly drive the reaction to completion.

The invention will be more clearly understood from the following detailed description of specific examples thereof read in conjunction with the accompanying drawings wherein:

FIGURE 1 is an elevation view in cross-section of an embodiment of the invention, and

FIGURE 2 is a top view of another embodiment of the invention.

## Example 1

This example describes the preparation of a pyromellitonitrile/methanol reaction product. A 30 g. sample of pyromellitonitrile and 500 ml. of absolute methanol was refluxed for 24 hours. Pyromellitonitrile or 1,2,4,5-tetracyanobenzene is an old compound and is described in British Patent No. 698,049, Example 41. When the reaction mixture was cooled and filtered, there were recovered 17 g. of a light greenish-blue solid material which melted with decomposition at 265° C. This is largely unreacted pyromellitonitrile. The filtrate was then concentrated and yielded 3.90 g. of yellow crystals. These yellow crystals turn dark blue to black at about 165° C. without melting. When the yellow crystals were recrystallized from methanol, a yield of 2.0 g. of solid material was recovered which did not melt but turned black at 160-170° C. More yellow crystalline material was recovered on further concentration and cooling of the filtrate and this material was purified by recrystallization from methanol. This recrystallized material is the desired reaction product.

A sample of this desired solid reaction product was submitted for analysis. Infrared analysis showed NH or OH, C≡N, and =C=N— radicals. An elemental analysis of the product yielded the following results:

| Percent | Found | Calc'd for C <sub>12</sub> H <sub>10</sub> O <sub>2</sub> N <sub>4</sub> |
|---------|-------|--------------------------------------------------------------------------|
| C       | 59.0  | 59.5                                                                     |
| H       | 4.3   | 4.12                                                                     |
| N       | 21.2  | 23.13                                                                    |

When paper or cloth, e.g., filter paper, is impregnated with a methanol solution of the solid reaction product and then dried, a blue imprint is made on the paper or cloth by contact with a heated spatula, soldering iron, or hot plate. The color appears to be fast.

## Example 2

This is another example of the making of a pyro-

3

mellitonitrile/methanol reaction product. A sample of 30 g. of pyromellitonitrile and 4 pints of absolute methanol were refluxed for 24 hours. The reaction mixture became dark blue in color. This solution was filtered hot and a small amount of solid was obtained. The filtrate which was greenish-yellow in color was cooled in an ice bath and refiltered to obtain 17.35 g. of a greenish-yellow solid substance. This greenish-yellow solid heated at 145–155° C. begins to change color, at 160–175° C. it turns black-greenish, and by 200° C. it has turned purplish-black. It does not melt to temperatures of 500° C.

#### Example 3

This example describes the preparation of an ethanol/pyromellitonitrile reaction product. A sample of 30 g. of pyromellitonitrile and 2500 ml. of ethanol was refluxed for 24 hours. The reaction mixture became dark blue and was filtered while hot. The filtrate was cooled and 16.4 g. of blue crystals, M.P. 264–266° C., were recovered from the filtrate. This material starts turning color at 230–255° C. It appears that no substantial amount of reaction has occurred between the pyromellitonitrile and the ethanol. The remaining blue crystals, largely unreacted pyromellitonitrile, were put back into 2500 ml. of ethanol and additional refluxing was carried out for a period of about 4 days. The reaction mixture was black colored and was filtered while hot, recovering a few milligrams of black powder. The filtrate was then treated with the decolorizing substance and concentrated. The solid product recovered was light blue and does not melt at 300° C. At pyrolysis temperatures of about 450° C., this ethanol reaction product is converted to a purplish-black material closely resembling the heated methanol reaction product in appearance. Unlike the methanol reaction product, the ethanol product required appreciably higher temperatures to cause the color change.

#### Example 4

This example describes the preparation of a pyromellitonitrile/ammonia reaction product. A 20 g. sample of pyromellitonitrile and 2000 ml. of absolute ethanol were heated to reflux. Then for a period of 1½ hours, ammonia gas was passed into this reaction mixture. The reaction mixture became dark brown in color and was cooled while still passing ammonia into the mixture. The reaction mixture was let stand overnight and filtered. A green colored residue was recovered. After drying this residue, 21 g. of dried material were recovered. When this material is heated to 280° C., it begins to turn green without melting. At 360° C., it turns dark green.

#### Example 5

This is another example describing the preparation of a pyromellitonitrile/ammonia reaction product. A sample of 10 g. of pyromellitonitrile and 500 ml. of methanol containing a trace of sodium was refluxed for 1 hour while passing ammonia gas through the reaction mixture. The reaction mixture was filtered hot, then the filtrate was concentrated, and on cooling yielded 2.80 g. of yellow material. This yellow material starts coloring at 180° C., turns dark, dull green-black at 280° C., and it does not melt at temperatures as high as 325° C. An elemental analysis of the yellow reaction product yielded the following results:

| Percent | Found | Calc'd for C <sub>22</sub> H <sub>18</sub> N <sub>10</sub> O |
|---------|-------|--------------------------------------------------------------|
| C-----  | 58.8  | 58.8                                                         |
| H-----  | 3.4   | 3.4                                                          |
| N-----  | 34.2  | 34.2                                                         |

#### Example 6

This example describes the preparation of a phthalonitrile/ammonia reaction product. A mixture of 6.5 g.

4

of phthalonitrile and 1500 ml. of methanol containing a small piece of sodium were mixed and warmed on a steam bath. Gaseous ammonia was passed through the reaction mixture for 2 hours. Then the reaction mixture was concentrated and yielded 46 g. of yellow crystals. These yellow crystals were recrystallized from methanol. These yellow crystals melt with decomposition and gas evolution at 207° C. Also, these yellow crystals, upon being heated to 200° C., turn green. An elemental analysis of these yellow crystals yielded the following results:

| Percent | Found | Calc'd for C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> |
|---------|-------|---------------------------------------------------------|
| C-----  | 55.1  | 66.1                                                    |
| H-----  | 4.9   | 4.9                                                     |
| N-----  | 28.5  | 28.9                                                    |

#### Example 7

This example describes the preparation of a succinonitrile/ammonia reaction product. A sample of 100 g. of succinonitrile, 600 ml. of methanol, and a small piece of sodium (half of a size 7 pea of sodium) in 20 ml. of methanol were added to a reaction flask having a reflux condenser. The mixture of reagents was heated on a steam bath to reflux and ammonia gas was passed into the reaction mixture for 3½ hours. Then the reaction mixture was concentrated to about 300 ml., cooled and crystals separated. 10.3 g. of crystalline material were obtained. This material colors at 130° C., is black at 150° C., and does not melt up to 250° C. The crystals tend to darken on standing. A piece of filter paper soaked with a solution of the crystalline product and dried is colorless, but gives a red-black color when touched with a hot spatula.

In FIGURE 7 of the drawing 11 represents a cross-section of a sheet of starch surface-sized paper. The starch surface-sized layer is on the top surface of 11 and separates 11 from 12, which is a coating on 11 of a mixture of ethyl cellulose and pyromellitonitrile/methanol reaction product of Example 1.

In FIGURE 2 of the drawing 13 represents a sheet of porous paper which has been impregnated with pyromellitonitrile/methanol reaction product of Example 1.

Although the invention has been described in terms of specified embodiments which are set forth in considerable detail, it should be understood that this is by way of illustration only and that the invention is not necessarily limited thereto, since alternative embodiments and operating techniques will become apparent to those skilled in the art in view of the disclosure. For example, the ammonia used to form reaction products of the invention could be replaced by primary or secondary amines and/or the nitriles could contain substituents that didn't interfere with or that even facilitate the formation of the reaction products or the coloring of these products upon being heated. Such modified reaction products would, to a degree, be the equivalent of the ammonia or alcohol and unsubstituted nitrile reaction products. Accordingly, modifications are contemplated which can be made without departing from the spirit of the described invention.

What is claimed is:

1. As an article of manufacture, web treated with a reaction product made by reacting a compound selected from the class consisting of ammonia and lower alkyl monohydroxy alcohols with a nitrile selected from the class consisting of succinonitrile, phthalonitrile and pyromellitonitrile at a temperature sufficiently high to cause said compound and said nitrile to react in molar ratio of about 2:1 of compound to nitrile when pyromellitonitrile is the nitrile and about 1:1 when another of said nitriles is the nitrile, but an insufficiently high temperature to cause substantial decomposition of said reaction product as indicated by a color change thereof.

## 5

2. An article of claim 1 wherein said web is paper.  
3. An article of claim 1 wherein said compound is methanol and said nitrile is pyromellitonitrile.  
4. An article of claim 1 wherein said compound is ethanol and said nitrile is pyromellitonitrile.  
5. An article of claim 1 wherein said compound is ammonia and said nitrile is pyromellitonitrile.  
6. An article of claim 1 wherein said compound is ammonia and said nitrile is phthalonitrile.  
7. An article of claim 1 wherein said compound is ammonia and said nitrile is succinonitrile.

2,967,785  
2,995,465  
2,995,468

5

698,049

## 6

## References Cited in the file of this patent

## UNITED STATES PATENTS

Allen et al. ----- Jan. 10, 1961  
Richey ----- Aug. 8, 1961  
Steiger ----- Aug. 8, 1961

## FOREIGN PATENTS

Great Britain ----- Oct. 7, 1953