Dec. 3, 1968 S. S. FIERKE ET AL 3,414,423

PROCESS FOR ERASING AND REGENERATING THERMOGRAPHIC MATERIALS

Filed Nov. 4, 1965

FIG. 1

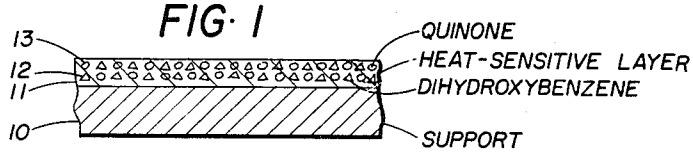


FIG. 2

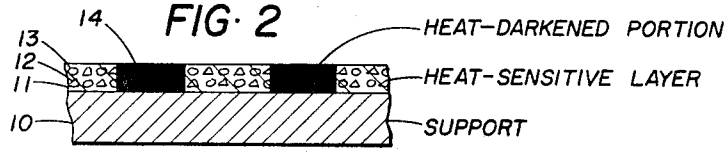
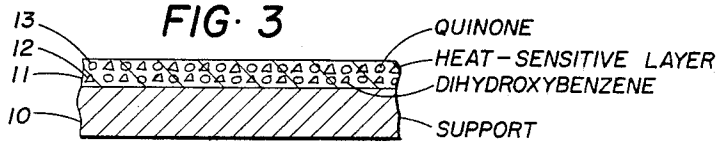


FIG. 3



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PROCESS FOR ERASING AND REGENERATING THERMOGRAPHIC MATERIALS

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This invention relates to a process for reversibly erasing heat-developed thermographic materials to render them reusable. In a particular aspect, this invention relates to a process for erasing images on a quinone-dihydroxybenzene thermographic material and regenerating such material through solvent action.

A number of thermographic copy materials an methods have been discussed in detail in numerous publications and patents. This rather widespread interest reflects the recognized attributes of thermographic reproduction as a means of producing facsimile copies on a commercial basis. However, prior discussions of thermography generaly recognize reversibility of image-formation, or fading thereof as a drawback. Such discussions have been prooccupied with fading or loss of image which would compromise the permanency of thermographically-formed images.

However, it is an object of this invention to provide a novel method for erasing thermographically-formed images from copying sheets.

Another object of this invention is to provide a method for regenerating heat-exposed thermographic copying materials.

Other objects of this invention will be apparent from the discussion, examples, drawings and claims.

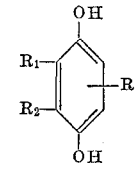
The instant invention provides a means whereby a conventional thermographic process (e.g. one that is considered "permanent") can be selectively treated to erase the image. Most surprisingly the erased sheet again becomes uniformly heat sensitive rather than, as might be expected, uniformly heat insensitive or heat exposed. Thus a facsmile copy is produced by imagewase exposure of the thermographic copying sheet to heat such as by projection exposure or reflex exposure of infrared radiation. The facsimile so formed may be stored indefinitely on a basis comparable to other conventional thermographic materials. However, the exposed copying sheet may be erased and returned to a condition substantially the same as that of an unexposed sheet by subjecting it to the process of the instant invention.

According to the present invention, images formed on heat-sensitive material containing quinone compound and dihydroxybenzene compounds can be erased and the material in the heat-exposed area returned to a heat-sensitive condition by subjecting material to the action of either one or a mixture of a large number of organic solvents. The quinone-dihydroxybenzene thermographic system becomes colored in areas exposed to heat as a result of rather complicated complexing by the quinone and dihydroxybenzene compounds. Such complexes are highly colored, normally stable and, in fact, form the basis for a convenient and advantageous thermographic process. Surprisingly, the action of many organic solvents upon the system is not to accelerate the formation of complexes but, instead, to reverse the formation of the complex and regenerate the quinone compound and dihydroxybenzene compound.

The two components forming the heat-sensitive areas of the copying sheets of the quinone-dihydroxybenzene compound system can be coated on any suitable support though supports having low conductivity are preferred for sharp images. Ordinary paper can be used as a support for the heat-sensitive composition and the paper can be

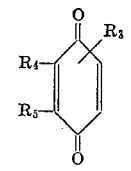
transparent, translucent or opaque. Either the original or copying sheet support should transmit the exposing radiation. Of course neither should char under copying conditions.

The dihydroxybenzene compounds useful in practicing the instant invention comprise the hydroquinones, pyrocatechols, pyrogallols, etc. These dihydroxybenzenes can contain one or more of the conventional substituents of the type common in organic chemistry. These substituents do not generally interfere with the color forming reaction or the erasing process. A particularly useful group of dihydroxybenzene compounds comprises those represented from the following formula:



wherein R and R_2 each represents a hydrogen atom, an alkyl group (e.g., methyl, ethyl, n-propyl, isopropyl, n-butyl isobutyl, tert.-butyl, n-amyl, isoamyl, tert.-amyl, n-hexyl, isohexyl, 2-ethylbutyl, n-octyl, isooctyl, tert.-octyl, n-nonyl, n-decyl, n-lauryl, n-hexadecyl, sec.-hexadecyl, n-octadecyl, etc.), an alkenyl group (e.g., allyl, crotyl, etc.), a halogen atom (e.g., chlorine, bromine, etc.), a hydroxyl group, an acyl group (e.g., acetyl, butyryl, caprylyl, palmitoyl, etc.), an acyloxyl group (e.g., acetoxyl, benzoxyl, etc.) a carbamyl group (e.g., carbamyl, N-ethylcarbamyl, N-methylcarbamyl, N-2-aminoethylcarbamyl, etc.), or an aryl group (e.g., phenyl, p-chlorophenyl, p-nitrophenyl, o-, n-, or p-tolyl, etc.), R_1 represents a hydrogen atom, or R_1 and R_2 together represent the groups necessary to complete a benzene ring (which can contain simple substituents, such as methyl, ethyl, hydroxyl, bromine, chlorine, etc.).

The quinone compounds specially useful in the practice of the instant invention, which will hereafter be referred to as quinone, include those represented by the following general formula:



wherein R_3 and R_5 each represents a hydrogen atom, an alkyl group (e.g., methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert.-butyl, n-amyl, isoamyl, tert.-amyl, n-hexyl, isohexyl, 2-ethylbutyl, n-octyl, isooctyl, tert.-octyl, n-nonyl, n-decyl, n-lauryl, n-hexadecyl, sec.-hexadecyl, n-octadecyl, etc.), an alkenyl group (e.g., allyl, crotyl, etc.), a halogen atom (e.g., chlorine, bromine, etc.), a hydroxyl group, an acyl group (e.g., acetyl, butyryl, caprylyl, palmitoyl, etc.), an acyloxyl group (e.g., acetoxyl, benzoyl, etc.), a carbamyl group (e.g., carbamyl, N-ethylcarbamyl, N-methylcarbamyl, N-2-aminoethylcarbamyl, etc.), or an aryl group (e.g. phenyl, p-chorophenyl, p-nitrophenyl, o-, n-, or p-tolyl, etc.), R_4 represents a hydrogen atom, or alternatively, R_4 and R_5 together represent the groups necessary to form a benzene ring (which can contain simple substituents, such as methyl, ethyl, hydroxyl, bromine, chlorine, etc.).

More detailed methods for preparing both the starting materials and the quinone-dihydroxybenzene compound copying sheets are to be found in Crevling et al. U.S. Patent No. 2,899,334 issued Aug. 11, 1959.

Images formed on the above discussed quinone-dihy-

droxybenzene compound thermographic system can be, as stated above, erased by an organic solvent treatment. However, merely flooding the copying sheet with solvents such as by dipping it into a liquid organic solvent would leach much of the thermographic material from the copying sheet and greatly curtail satisfactory reuse of the erased sheet. This drawback can be avoided by spraying the image-containing copying sheet with a mist or fog of the organic solvent and allowing the solvent to penetrate the thermographic coating. In this embodiment, the mist decomposes the color-forming quinone-dihydroxybenzene complex but does not carry away appreciable amounts of the thermographic material when removed from the erased copying sheet by evaporation. Such mists can be produced by conventional atomizers or spray means. The mist is preferably moderately warm.

A particularly preferred embodiment of the instant invention involves the use of solvent vapors to erase quinone-dihydroxybenzene compound thermographic copying sheets. According to this embodiment in the invention, the exposed copying sheet is exposed to vapors of the organic solvent. The image is quickly and cleanly erased and the copying sheet rendered ready for reuse in a matter of seconds. Of course it is preferable that the solvent vapors be at or near the saturation point to enhance the erasing process.

Also, it is desirable that the vapors be at a temperature lower than that used when forming thermographic images on the copying sheet. However, since many of the organic solvents used in the process of the instant invention are volatile, this consideration presents no practical problem.

Many organic solvents are operable in the process of the instant invention. Any solvent for the quinone-dihydroxybenzene complex usually permits the complex to re-equilibrate into its dihydroxybenzene compound and quinone compound components. It will of course be apparent that the preferred solvents are those which dissolve the complex but which are not solvents for the quinone compound or dihydroxybenzene compound products since this obviously will facilitate production of the quinone compound and dihydroxybenzene compound components through a precipitation process. However, even solvents which dissolve not only the colored complex but also dissolve either or both of its quinone compound and dihydroxybenzene compound components are operable in that the quinone compound and dihydroxybenzene compound components tend to recrystallize from such solvents upon evaporation rather than reforming the complex. Commonly available solvents which are operable with the process of the instant invention comprise methanol, ethanol, acetone, tetrahydrofuran, benzene, acetonitrile, ethyl acetate, methylene chloride, chloroform, carbon tetrachloride, hexane, cyclohexane, acetic acid, lower dialkyl ethers having less than about 7 total carbon atoms, and mixtures of two or more of these solvents.

It will be recognized that the process is operable with many of the well-known compositions commonly referred to as organic solvents.

Copying sheets erased and regenerated according to the instant invention can be re-exposed to produce a new image and again erased and regenerated many times. It is only necessary to subject the copying sheet to the solvent mist or solvent vapor atmosphere for a period of a few seconds or until the image disappears. When the image is erased, the copy sheet is regenerated for further use.

The quinone and dihydroxybenzene compounds forming the thermographic system with which the instant invention is useful are, in part, shown by the following tabulation. The compounds listed in the table are named as either hydroquinone compounds or p-quinone compounds, except in those cases bearing an asterisk. In the latter cases, the compounds are named as complete chemicals for purposes of convenience, i.e., they are not named as hydroquinone compounds having substituents in the positions indicated above.

Ex.	Hydroquinone	p-Quinone	Color of Image
1	2-methyl-5-n-hexadecyl	2-methyl-5-n-hexadecyl	Blue.
2	2,5-di-n-octyl	2,5-di-n-octyl	Do.
3	2,5-di-n-nonyl	2,5-di-n-nonyl	Do.
4	2-n-lauryl-5-n-amyl	2-n-lauryl-5-n-amyl	Do.
5	2,5-di-n-lauryl	2,5-di-n-lauryl	Do.
6	n-Octadecyl	2,5-di-n-octyl	Purple.
7	2,5-di-n-octyl	2-methyl-5-n-hexadecyl	Blue.
8	n-Octadecyl	2-methyl-5-n-hexadecyl	Purple.
9	2-n-lauryl-5-n-amyl	di-n-lauryl	Blue.
10	Methyl	2-methyl-5-n-hexadecyl	Do.
11	Isopropyl	do	Do.
12	Chloro	do	Purple.
13	2-methyl-5-palmitoyl	do	Yellow.
14	2-caprylyl-5-n-octyl	2,5-di-n-octyl	Do.
15	n-Octadecyl	n-Octadecyl	Purple.
16	n-Octyl	n-Octyl	Do.
17	2-methyl-5-n-hexadecyl	p-Chlorophenyl	Red Magenta.
18	2-methyl-5-n-hexadecyl	p-Nitrophenyl	Green.
19	2-chloro-6-tert.-butyl	2,5-diacetoxy	Blue.
20	2-chloro-6-tert.-butyl	2,3-dichloro	Do.
21	2,5-di-tert.-amyl	2-methyl-5-n-hexadecyl	Do.
22	2,5-di-tert.-octyl	do	Do.
23	1,2,4,5-tetrahydroxy-benzene.	do	Do.
24	Trimethyl	do	Do.
25	2-allyl-5-tert.-butyl	do	Do.
26	N-(2-aminoethyl)-gentisamide.*	do	Do.
27	1,2,4,5-tetrahydroxy-benzene.*	2,5-diacetoxy	Do.
28	Trimethyl	do	Do.
29	4,4'-dimethyl-2,2'-5,5'-tetrahydroxy-biphenyl.*	3,4-di-p-chlorophenyl	Do.
30	2-methyl-5-n-hexadecyl	1,4-naphthoquinone *	Red.
31	Phenyl	2-methyl-5-n-hexadecyl	Purple.
32	2,5-di-n-octyl	n-Octadecyl	Blue.
33	do	n-Octyl	Do.
34	do	2,5-di-tert.-amyl	Do.
35	do	2,5-di-n-lauryl	Do.
36	do	2-n-Lauryl-5-n-amyl	Do.
37	do	2,5-di-n-nonyl	Do.
38	do	n-Lauryl	Do.
39	n-Octyl	n-Octadecyl	Do.
40	do	2,5-di-n-octyl	Do.
41	do	2,5-di-n-lauryl	Do.
42	do	2-n-lauryl-5-n-amyl	Do.
43	do	2,5-di-n-nonyl	Do.
44	do	n-Lauryl	Do.
45	2,6-di-n-octyl	2,5-di-n-octyl	Do.
46	2,6-di-n-octyl	n-Octadecyl	Do.
47	do	n-Octyl	Do.
48	do	2,5-di-n-lauryl	Do.
49	do	2-n-lauryl-5-n-amyl	Do.
50	do	2,5-di-n-nonyl	Do.
51	2,5-di-n-lauryl	2,5-di-n-octyl	Do.
52	do	n-Octadecyl	Do.
53	do	n-Octyl	Do.
54	do	2,5-di-tert.-amyl	Do.
55	do	Tetramethyl	Do.
56	do	2-n-lauryl-5-n-amyl	Do.
57	do	2,5-di-n-nonyl	Do.
58	do	n-Lauryl	Do.
59	Sec.-hexadecyl	2,5-di-n-octyl	Do.
60	do	n-Octadecyl	Do.
61	do	2-n-lauryl-5-n-amyl	Do.
62	do	2,5-di-n-lauryl	Do.
63	2-n-lauryl-5-n-amyl	2,5-di-n-octyl	Do.
64	do	n-Octadecyl	Do.
65	do	n-Octyl	Do.
66	do	2,5-di-tert.-amyl	Do.
67	do	2,5-di-n-lauryl	Do.
68	do	Tetramethyl	Do.
69	do	2,5-di-n-nonyl	Do.
70	do	n-Lauryl	Do.
71	2,5-di-n-nonyl	2,5-di-n-octyl	Do.
72	do	n-Octadecyl	Do.
73	do	n-Octyl	Do.
74	do	2,5-di-n-lauryl	Do.
75	do	Tetramethyl	Do.
76	do	2-n-lauryl-5-n-amyl	Do.
77	do	n-Lauryl	Do.
78	Sec.-octadecyl	n-Octadecyl	Do.
79	do	n-Octyl	Do.
80	do	2,5-di-n-lauryl	Do.
81	2,5-di-n-butyl	2,5-di-n-octyl	Do.
82	do	n-Octadecyl	Do.
83	do	n-Octyl	Do.
84	do	2,5-di-n-lauryl	Do.
85	do	2-n-lauryl-5-n-amyl	Do.
86	do	2,5-di-n-nonyl	Do.
87	4-phenylcatechol*	2-methyl-5-n-hexadecyl	Do.
88	Pyrogallol*	do	Do.
89	2-methyl-5-n-hexadecyl plus 2-methyl-5-n-palmityl.	do	Black.

Example 90

Solution A.—7.0 grams of 2-methyl-5-n hexadecylhydroquinone are ball-milled in 0.6 gram of ethyl cellulose and 60 cc. of trichloroethylene.

Solution B.—7.0 grams of 2-methyl - 5 - n-hexadecylquinone are dissolved in 30 cc. of trichloroethylene.

Solution B is then added to Solution A and the mixture dispersed in 150 cc. of a 1% aqueous gelatin solution containing 1.5 cc. of a 10% aqueous solution of a dispersing agent, such as sodium isobutylnaphthalene sulfonate. The diseprsion is then coated on a thin paper support and dried.

Exposure of the dried coating to a graphic original containing line copy produces a sharp image of execllent contrast. Apparatus suitable for such an exposure is shown in Miller U.S. Patent 2,740,895, issued Apr. 3, 1956.

Example 91

5.0 grams of 2-methyl-5-n-hexadecylhydroquinone are dissolved in 150 cc. of acetone. The solution is then coated by dip-coating on a paper coating machine useing a 0.5-inch air knife pressure to give a uniform distribution of materials. The coating is then dried until substantially all acetone has been removed.

5.0 grams of 2-methyl-5-n-hexadecylquinone are dissolved in 100 cc. of trichloroethylene and the solution added to 50 cc. of a 5% (by weight) solution of ethyl cellulose in trichloroethylene. The mixture is coated over the dried layer containing the hydroquinone, by a dip-coating technique using a 0.5-inch knife pressure to obtain uniform coating.

The resulting coating, after drying, has a very faint yellow color. Exposure of the coating to a printed letter by reflex on a thermographic copying machine of the type shown in U.S. Patent 2,740,895 gives an excellent reproduction having good blue color with low yellow D-min. A bireflex exposure made in the same manner also gives a good reproduction, but not as sharp as the reflex exposure. The temperature required to bring about the thermographic reaction is about 86° C.

Example 92

4.0 grams of 2-methyl-5-n-hexadecylhydroquinone are combined with 45 cc. of trichloroethylene and the solution added to 25 cc. of a 5% ethyl cellulose solution in trichloroethylene. The resultant dispersion is ball-milled for 18 hours to give a fine slurry of the hydroquinone compound. A solution of 4.0 grams of 2-methyl-5-n-hexadecylquinone in 10 cc. of trichloroethylene is added to the fine slurry.

Coatings are prepared from the above dispersion by absorbing a portion thereof into a cotton swab and wiping onto Fidelity bond onion skin paper. After drying, the coating has a very faint yellow color. Bireflex exposure of the dried coating to a printed letter gave an excellent copy wherein the facsimile portions are blue in color. The copy is right-reading.

Example 93

A flask of methanol is warmed on a steam bath to produce a vapor-rich atmosphere above the liquid. Image-bearing thermographically exposed copying sheets containing the quinone and dihydroxybenzene compounds as set forth in Examples 1 to 92 are passed briefly through the fumes. The images are cleanly erased in a matter of seconds. When reexposed to heat, the erased sheets record the heat pattern in substantially the same manner as virgin copying sheets containing the same quinone and dihydroxybenzene compounds.

Example 94

A flask of acetone is warmed on a steam bath to produce a vapor-rich atmosphere above the liquid. Image-bearing thermographically exposed copying sheets containing the quinone and dihydroxybenzene compounds as set forth in Examples 1 to 92 are passed briefly through the fumes. The images are cleanly erased in a matter of seconds. When re-exposed to heat, the erased sheets record the heat pattern in substantially the same manner as virgin copying sheets containing the same quinone and dihydroxybenzene compounds.

Example 95

A flask of cyclohexane is warmed on a steam bath to produce a vapor-rich atmosphere above the liquid. Image-bearing thermographically exposed copying sheets containing the quinone and dihydroxybenzene compounds as set forth in Examples 1 to 92 are passed briefly through the fumes. The images are cleanly erased in a matter of seconds. When re-exposed to heat, the erased sheets record the heat pattern in substantially the same manner as virgin copying sheets containing the same quinone and dihydroxybenzene compounds.

Example 96

A flask of ethyl acetate is warmed on a steam bath to produce a vapor-rich atmosphere above the liquid. Image-bearing thermographically exposed copying sheets containing the quinone and dihydroxybenzene compounds as set forth in Examples 1 to 92 are passed briefly through the fumes. The images are cleanly erased in a matter of seconds. When re-exposed to heat, the erased sheets record the heat pattern in substantially the same manner as virgin copying sheets containing the same quinone and dihydroxybenzene compounds.

The invention will be more fully understood upon consideration of the drawing wherein:

FIG. 1 is a sectional view of a virgin copying sheet of the quinone-dihydroxybenzene thermographic system with which the instant invention is useful;

FIG. 2 is a sectional view of an exposed copying sheet such as that shown in FIG. 1, and

FIG. 3 is a sectional view of an erased and regenerated exposed copying sheet such as that shown in FIG. 2.

The thermographic copying sheet with which the instant invention is useful is generally illustrated in FIG. 1 as a virgin copying sheet having a support **10** and a heat-sensitive layer **11** coated thereon. Heat-sensitive layer **11** contains distinct particles of dihydroxybenzene compound **12** and quinone compound **13**. When exposed to heat such as infrared radiation, the particles of dihydroxybenzene compound **12** and quinone compound **13** combine to form a heat-darkened portion in the area of heat exposure as shown in FIG. 2. Heat-exposed layer **11** is generally considered to be stable though of course further darkening will occur if heat-sensitive areas other than darkened portion **14** are further exposed to heat. However, heat-darkened portion **14** can be erased and reformed into its constituent parts dihydroxybenzene compound **12** and quinone compound **13** as shown in FIG. 3 by subjecting the exposed heat-sensitive layer **11** to a mist or vapor of an organic solvent. For practical purposes, the erased and regenerated copying sheet shown in FIG. 3 is identical to the virgin copying sheet shown in FIG. 1.

Summarily, the instant invention concerns the simple but unique process which enables thermographic copying sheets containing the quinone-dihydroxybenzene compounds to reused. In addition to providing a means for reusing the copying sheets when the information recorded thereon is no longer needed, the proces obviously has use in information retrieval systems in which information is stored or displayed in graphc form for only relatively short periods of time. Other uses for reusable thermographic paper will be readily apparent to those skilled in the art.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A process for erasing and regenerating thermographic copying sheets containing an image area of a complex

formed from quinone and dihydroxybenzene components comprising (A) dissociating the complex into the corresponding quinone and dihydroxybenzene products by subjecting the complex to an organic solvent and (B) substantially removing the organic solvent from the copying sheet.

2. A process as set forth in claim 1 wherein the copying sheet is exposed to a mist of the organic solvent.

3. A process as set forth in claim 1 wherein the copying sheet is exposed to vapors of the organic solvent.

4. A process as set forth in claim 3 wherein the organic solvent vapors are saturated.

5. A process for regenerating thermographic copying sheets containing image areas formed by a complex of quinone and dihydroxybenzene components comprising (A) dissociating the complex into the corresponding quinone and dihydroxybenzene products by subjecting the complex to an organic solvent selected from the group consisting of methanol, ethanol, acetone, tetrahydrofuran, benzene, acetonitrile, ethyl acetate, methylene chloride, chloroform, carbon tetrachloride, hexane, cyclohexane, acetic acid, dialkyl ethers and mixtures of two or more thereof, and (B) substantially removing the organic solvent from the copying sheet.

6. A process as set forth in claim 5 wherein the copying sheet is exposed to a mist of the organic solvent.

7. A process as set forth in claim 5 wherein the copying sheet is exposed to vapors of the organic solvent.

8. A process as set forth in claim 5 wherein the organic solvent is removed from the copying sheet solely by evaporation.

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