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COPY-SHEET

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ABSTRACT OF THE DISCLOSURE

A copy-sheet or image-sheet containing a silver soap and a light-stable reducing agent, and which forms an image when heated with small amounts of a photosensitive reducing agent, is found to give increased image density with a combination of mono- and bis-phenol light-stable reducing agents.

This invention relates to the copying of graphic originals and to copy-sheet materials useful therein.

U.S. Pat. No. 3,218,166 describes a copy-sheet or image-forming sheet on which a copy may be produced by heat-induced reaction therewith of traces of a volatilizable reducing agent at image areas. A typical sheet includes an image-forming reactant layer containing an organic silver soap, a toner for the silver image, and a light-stable ditertiaryalkyl-substituted phenol first reducing agent for the silver ion. The volatilizable reducing agent typically is photosensitive substituted alpha-naphthol which when exposed to light becomes non-reactive with the silver ion. Thus it may be present in an intermediate sheet coating and rendered ineffective at light-exposed areas, in which case reaction at unexposed areas occurs when the two sheets in face-to-face contact are uniformly heated; or alternatively, both reactants are present in a unitary sheet, an image is produced by localized heating, for example by thermographic copying procedures, and the background is then desensitized against subsequent heat-induced change by exposure to light.

It has now been found possible significantly to improve the density and contrast of the image obtained with copy-sheets or composites as just described, by employing a mixture of tertiary-alkyl-substituted monophenol and bisphenol compounds in place of the single di-tertiary-alkyl-substituted phenol reducing agent of the patent. The ratio of the two is within the approximate range of five to fifteen parts by weight of monophenol to one part of bisphenol.

Alternatively, the practice of the invention makes possible a reduction in the amount of silver soap required per unit area of the copy-sheet in order to obtain an adequately dense image; or the available image density is increased without concomitant darkening at background areas. The invention also makes possible increased latitude in exposure of the photosensitive intermediate, by requiring significantly lesser amounts of the photosensitive reducing agent for initiating the image-forming oxidation-reduction reaction than has heretofore been found necessary.

The invention will now be further illustrated by means of specific examples in which all proportions are in parts by weight unless otherwise stated.

EXAMPLE 1

Image sheets are prepared by coating bond paper with the following mixtures, the coating weight after drying being 1.2 gm./sq. ft.

	A	B	C
Silver behenate half-soap	1.6	1.6	1.6
Behenic acid	1.6	1.6	1.6
Zinc oxide	8.6	8.6	8.6
Stannous stearate	.0021	.0021	.0021
Polyterpene resin ("Piccolyte S-135")	1.4	1.4	1.4
Cellulose fiber ("Solka Floc")	.7	.7	.7
Polyethyl methacrylate	7.5	7.5	7.5
Cellulose acetate	1.2	1.2	1.2
Polyvinyl acetate	2.9	2.9	2.9
Cellulose acetate propionate	2.9	2.9	2.9
Tetrachlorophthalic anhydride	.085	.085	.085
Phthalazinone	1.9	1.9	1.9
Acetone	128.8	128.8	128.8
2,6-di-t-butyl-p-cresol	1.7	------	1.7
4,4'-methylene-bis-(2,6-di-t-butylphenol)	------	0.2	0.2

An intermediate sheet is separately prepared by coating a thin paper with a solution of 0.2 part of 4-methoxy-1-naphthol, 0.088 part of erythrosin, and 10 parts of ethyl cellulose in 90 parts of methylethyl ketone at about 0.7 gm./sq. ft. after drying. The sheet is placed in face-to-face contact with a printed graphic original which is then exposed through the intermediate, i.e., by reflex exposure, to intense illumination from a tungsten filament lamp. The exposure is just sufficient to desensitize all of the photosensitive substituted naphthol in the areas overlying the white background, a portion of the still sensitive compound remaining at the areas corresponding to the printed image. Portions of the exposed intermediate are then placed in face-to-face contact with the three image sheets and the composites heated so as to provide maximum image density without change in background density. The image formed with Sheet C is darker and more easily readable than that formed with Sheet A which in turn shows substantial improvement over that formed with Sheet B.

Silver behenate half soap is a mixture of equal molar proportions of commercial behenic acid and the silver salt thereof and melts to a liquid at about 175° C.

EXAMPLE 2

In order to obtain more precise measurements of density differences, a further series is tested in which the image areas are increased in size so that the density at both image and background areas may be determined with a reflectometer. The intermediate sheet is prepared as in Example 1. In the present example the image sheet coatings contain 27 parts by weight of silver soap dispersion together with the following reducing agents in the amounts indicated:

	A	B	C
2,6-di-t-butyl-p-cresol	0.24	------	0.24
4,4'-methylenebis (2,6-di-t-butylphenol)	------	0.038	0.038
Image density	1.16	0.99	1.27
Background density	0.07	0.07	0.02

The silver soap dispersion has the following composition:

Silver behenate half soap	3.25
Zinc oxide	8.39
Stannous stearate	.001
Polyterpene resin ("Piccolyte S-135")	1.35

Cellulose fiber ("Solka Floc")	.65
Polyethyl methacrylate	4.32
Cellulose acetate	.62
Polyvinyl acetate	1.50
Cellulose acetate propionate	1.50
Tetrachlorophthalic anhydride	.04
Phthalazinone	.95
Acetone	83.56

EXAMPLE 3

This example is the same as Example 2 except for the substitution of a different pair of reducing agents and in different amounts, as tabulated.

	A	B	C
2,4-dimethyl-6-t-butylphenol	.15		.14
4,4'-methylene-bis (2-methyl-6-t-butylphenol)		.02	0.2
Image density	1.02	.99	1.17
Background density	.07	.07	.07

EXAMPLE 4

This example is similar to Examples 2 and 3 but again using different specific reducing agents. In addition the image is developed by heating at 245° F. whereas a temperature of 255° F. is employed in the previous examples. The amounts of materials are as indicated based on a composition containing 27 parts of the silver soap dispersion.

	A	B	C
2,6-ditertiarybutylphenol	.28		.26
4,4'-(2,6-di-t-butylphenol)		.02	.02
Image density	1.06	.90	1.11
Background density	.07	.08	.08

EXAMPLE 5

A transparent copy-sheet useful in the preparation of projection transparencies is prepared by coating a transparent polyester film with a homogenized mixture containing:

Silver behenate full soap	35.31
Polyethyl methacrylate	17.73
Polymethyl methacrylate	17.66
Cellulose acetate propionate	17.73
Tetrachlorophthalic anhydride	.88
Phthalazinone	5.3
2,6-di-t-butyl-4-methylphenol	4.6
4,4'-methylenebis (2,6-di-t-butylphenol)	.77

in sufficient acetone for coating purposes. The coating weight after drying is 0.6 gram/sq. ft. A further coating of a mixture of:

Cellulose acetate butyrate	98.9
2,6-di-t-butyl-4-methylphenol	.99
4,4'-methylenebis (2,6-di-t-butylphenol)	.16

applied from solution in methylethyl ketone is applied and dried, the added dry coating weight being 0.08 gm./sq. ft.

Silver behenate full soap contains essentially no free behenic acid.

A thin intermediate sheet containing 4-methoxy-1-naphthol as described under Example 1 is placed in contact with a printed original and after exposure to light is then briefly heated in contact with the coated film. Dense black images are produced, and the copy is effective as a projection transparency for use on an overhead projector.

EXAMPLE 6

The additional image density made possible by the incorporation of both mono- and bis-phenol compounds is particularly useful in connection with the reproduction process described in U.S. Pat. No. 3,360,367.

A master sheet is prepared by coating a paper base on one surface with a mixture of:

Ethyl cellulose	6.5
Mixture of o- and p-toluene sulfonamides ("Santicizer 9")	52
Benzil	8
Powdered silica ("Hi-Sil 233")	16.1

applied from acetone to a dry weight of about one gm./sq. ft. The reverse surface is coated with a composition containing:

Silver behenate full soap	35.19
Polyethyl methacrylate	8.99
Polymethyl methacrylate	17.59
Cellulose acetate propionate	21.99
Tetrachlorophthalic anhydride	1.19
Phthalazinone	8.80
2,6-di-t-butyl-4-methylphenol	5.86
4,4'-methylenebis (2,6-di-t-butylphenol)	.59

applied from acetone to a dry weight of about .8–.9 gm./sq. ft.

An image is developed on the sensitive reverse surface by heating in contact with a reflex-exposed intermediate sheet containing a photosensitive active-hydrogen aromatic organic reducing agent as previously described. The image has a density of 1.5 and is highly absorptive of infra-red. The imaged sheet is placed with its non-imaged coated surface against a sheet of untreated paper and the image is briefly exposed to intense infra-red. The sheet of paper is removed and is dusted with toner powder, preferably consisting of spherical particles of fusible resin containing carbon black. A reproduction of the image is obtained. Several additional copies may be made by repeating the process using additional sheets of paper.

In the absence of the bisphenol, additional heating of the composite of master and intermediate is required to obtain the degree of infra-red absorptivity here obtained. The additional heating causes an increase in background density and results in darkening of the background in the resulting copies.

Combinations of the various monophenol and bisphenol compounds may be used. As one illustration, substitution of 4,4'-methylene-bis (2-t-butyl-6-methylphenol) for the 4,4'-methylene-bis (2,6-di-t-butylphenol) of Example 1 produces an image density of 1.19 as compared with the value of 1.20 obtained in the example. In the absence of either bisphenol the image density is reduced to 1.10.

It will be appreciated that increased image density may be obtained in these examples by additional heating, e.g., by increasing the time, or the temperature, or both; but only at the expense of simultaneous severe increase in background color. Thus the comparative values in each instance represent maximum contrast available, since image development is carried to the point at which the first visible change in background occurs. In most of the examples, development is carried out mechanically at a fixed time and temperature, and a series of coatings made with varying proportions of the reducing agents is tested in order to obtain sheets which under such conditions will produce a desired minimum background density.

A particularly important and unexpected feature of the invention is that it makes possible the development of full image density with unusually small amounts of added photosensitive reducing agent. The danger of over-exposure of the photosensitive intermediate sheet is therefore greatly decreased and the exposure latitude accordingly greatly improved.

It will also be seen that the invention makes possible a significant increase in image density and contrast by means of an unexpected synergistic effect whereby the combination of monophenol and bisphenol reducing agents increases the available image density beyond the value obtainable with either one alone, without at the same time causing any increase in the accompanying background density.

It will be understood that the formulations herein described may be incorporated in unitary heat-sensitive copy-sheets which are desensitized by light, by combining the photosensitive substituted α-naphthol with the mono- and bis-phenol reducing agents in a single sheet, e.g., of the type described in U.S. Pat. No. 3,218,166.

What is claimed is as follows:

1. Sheet material useful in copying processes, including a reactant layer comprising a silver soap of an organic acid, a tertiary-alkyl-substituted monophenol, and a tertiaryalkyl-substituted bisphenol, said substituted phenols each being a reducing agent for the silver ion and being characterized as forming with an equal weight of silver behenate and one-fifth said weight of phthalazinone a uniformly blended trace deposit requiring at least six seconds preheat at 100° C. before rapidly darkening at that temperature.

2. Sheet material of claim 1 wherein said monophenol is selected from the class consisting of 2,6-ditertiarybutylphenol, 2,4-dimethyl-6-tertiarybutylphenol and 2,6-ditertiarybutyl-4-methylphenol.

3. Sheet material of claim 1 wherein said bisphenol is selected from the class consisting of 4,4'-(2,6-ditertiarybutylphenol), 4,4' - methylenebis (2-methyl-6-tertiarybutylphenol), and 4,4'-methylenebis-(2,6-ditertiarybutylphenol).

4. Sheet material of claim 1 wherein said monophenol is selected from the class consisting of 2,6-ditertiarybutylphenol, 2,4-dimethyl-6-tertiarybutyl-phenol and 2,6-ditertiarybutyl-4-methylphenol, and said bisphenol is selected from the class consisting of 4,4'-(2,6-ditertiarybutylphenol), 4,4'-methylenebis (2-methyl-6-tertiarybutylphenol), and 4,4' - methylenebis (2,6 - ditertiarybutylphenol) and wherein the amount of said bisphenol is from about one-fifth to about one-fifteenth the amount of said monophenol.

5. Sheet material of claim 1 useful as a unitary heat-sensitive light-desensitizable copy-sheet and including a photosensitive active-hydrogen aromatic organic reducing agent in an amount no greater than the amount of said substituted phenol reducing agents.

6. Sheet material of claim 5 wherein said photosensitive reducing agent is 4-methoxy-1-naphthol.

7. Sheet material of claim 1 useful in the making of projection transparencies and having a transparent reactant layer on a clear transparent supporting film.

References Cited

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