Oct. 15, 1963 T. G. WARTMAN 3,107,174

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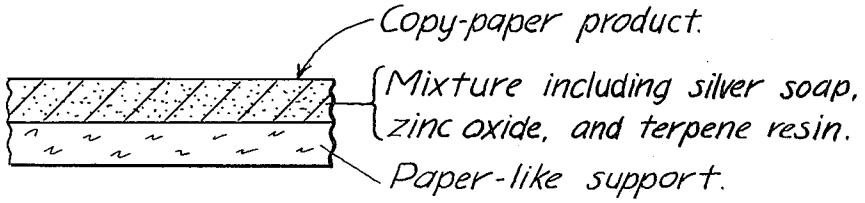
Filed July 12, 1961



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United States Patent Office 3,107,174 Patented Oct. 15, 1963

3,107,174

HEAT SENSITIVE COPY SHEET AND METHOD OF MAKING

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Filed July 12, 1961, Ser. No. 123,528
7 Claims. (Cl. 117—36.2)

This invention relates to heat-sensitive copy-papers useful in the thermographic copying of graphic originals having differentially radiation, absorptive image and background areas. This application is a continuation-in-part of my copending application Serial No. 768,091, filed October 20, 1958, now abandoned.

Heat-sensitive copy-sheets are known in which a heat-image, produced by brief intense irradiation of a graphic original in intimate heat-conductive contact with the copy-sheet, is developed into a visible copy through reaction at the heated areas between inter-reactive components of the copy-sheet such for example as silver behenate and protocatechuic acid. With proper formulation, such sheet materials are capable of providing copies having dense black or brownish-black images on white backgrounds. Under normal handling and storage, the background areas remain white, the copies therefore retaining high visual contrast and pleasing appearance. Under conditions of high humidity and elevated temperature, and particularly in conjunction with protracted illumination and under extensive handling, these copy-sheets are found to undergo undesirable discoloration. One particularly undesirable manifestation appears as "finger-printing," in which discoloration appears at areas contacted by the operator's hands or finger-tips. The latter phenomenon is presumably due to the effect of perspiration residues on the reactant system.

The present copy-paper, while based on silver compounds as essential image-producing components, is found to be highly resistant to discoloration under the conditions mentioned and particularly to fingerprinting, while providing the desirable reactivity and image-forming appearance factors characteristic of such copy-sheets. There is provided a copy-sheet having a strikingly white initial appearance, capable of producing high contrast black-on-white copy under thermographic copying procedures, and capable of undergoing protracted exposure to light, high humidity, and moderately elevated temperature, without any significant darkening or discoloration even at areas subjected to extensive handling.

These and other advantages are obtained, in accordance with the present invention, by incorporating with the silver soap composition a substantial amount of a normally solid, fusible, pure hydrocarbon thermoplastic terpene resin of zero acid number. A series of beta-pinene polymers of various melting points meeting the requirements just stated is available commercially as "Piccolyte" resins. "Piccolyte" S–85, S–100, and S–135, the numbers, designating the nominal melting points in degrees centigrade, are typical and are preferred. In addition to the resinous component, my preferred heat-sensitive copy-sheets contain significant amounts of zinc oxide.

A useful accelerated test procedure for determining the resistance of the copy-sheet to finger-printing and to discoloration on aging involves subjecting the sheet to contact with the fingers which have first been rubbed over oily skin, and then maintaining the sheet at 95% relative humidity, 95° F., and under irradiation from a G.E. 15 watt "B.L." fluorescent lamp at 5 inches distance, for a period of 120 hours. Under such a test, typical copy-sheets containing a silver soap reactant, and with or without a phenolic reducing agent, are found to darken extensively to a purplish brown color, the finger-printed area being still darker. With added Piccolyte resin, finger-printing is greatly reduced but the sheet assumes a brownish yellow color. With added zinc oxide but in the absence of the resin, the sheet darkens only slightly but the fingerprinted areas become an intense dark brownish purple. However with the addition of both the resin and the zinc oxide, and within the proper proportional limits, the sheet remains brilliantly white with no more than a faint smudginess being observable at the finger-print areas.

A preferred copy-sheet structure as shown in the appended drawing contains the silver soap, reducing agent, toners and other auxiliary components, together with the terpene resin and zinc oxide, uniformly intimately dispersed within a resinous binder as a coating on a paper or paper-like carrier. A protective surface coating may be applied over the color-forming coating; where the protective layer is opaque, a transparent film or paper is employed as the carrier member. The principal reactants, i.e. the silver soap and the organic reducing agent, may alternatively be applied to separate carriers and the two sheets then placed in face-to-face contact, the pair serving as a heat-sensitive copy-sheet; in such structure the terpene resin and the zinc oxide are incorporated in the silver soap coating.

The amount of terpene resin found necessary in the copy-sheets of the invention ranges from about two parts by volume to about 12 parts, based on five volumes of the silver soap component. At less than about 1½ to 2 parts of the resin, severe fingerprinting occurs in the test hereinbefore described, even at maximum zinc oxide content; while with much more than about twelve parts the image density may be significantly reduced. The amount of zinc oxide is likewise preferably held between approximately one and eight volumes for each five volumes of the silver soap component. Within these limits, yellowing is substantially prohibited while full image density is still obtained.

Example 1

A mixture of equal mol percent of silver behenate and behenic acid is prepared by reacting together one mol of silver nitrate and two mols of sodium behenate, made from commercial behenic acid, in aqueous medium and in the presence of nitric acid. The resulting water-insoluble precipitate is recovered on a filter and is washed and dried to produce a fine powder. The powder fuses at about 135° C. and melts to a liquid at about 175° C. Silver behenate and behenic acid, prepared separately from the same sodium behenate, melt at about 220° C. and about 70° C. respectively. The co-precipitate will be hereinafter referred to as "silver soap reactant" of which one-half, on the molar basis, is silver behenate in the present example.

A quantity of "Piccolyte" S–135 pure hydrocarbon thermoplastic terpene resin having a zero acid number and a softening point of about 135° C. is ground to a fine flour-like powder by milling in a hammer mill, taking care to avoid exceeding the melting point of the resin.

To a ball mill of suitable size, charged with ceramic balls, there is added 100 parts by weight of zinc oxide pigment, 26 parts of the silver behenate-behenic acid silver soap reactant, 90 parts of the powdered resin, 46 parts of polyvinyl acetate, 4 parts phthalazinone, and 446 parts of acetone. The mixture is milled until smooth and homogeneous, and is then removed from the ball mill. Just prior to coating, there is added to the above mixture a solution of 10 parts of methyl gallate in 278 parts of acetone. The mixture is stirred until homogeneous and is coated on white 37 pound (24 x 36—500 basis) bleached kraft paper, using a knife or bar type coater at a coating orifice of approximately 3 mils. The solvent is removed by evaporation at room temperature. The

resulting sheet is white and uniform in appearance, but the coating has a slight tendency to powder and abrade from the paper during handling. The coating is also slightly tacky, particularly at elevated temperatures. Abrasion resistance may be improved without loss of printing quality by increasing the amount of binder, for example to 92 parts of polyvinyl acetate. Heating the sheet, as in back-printing as above described, produces black or brownish-black image areas on a white background. The sheet is resistant to discoloration under illumination and under severe handling and fingerprinting.

The sheet as thus prepared may be moistened with a volatile solvent for the resinous component, for example with heptane, and again dried, without significantly reducing the resistance to discoloration. The porosity of the coating is decreased. The particulate nature of the resin is altered, to a relatively continuous web-like structure, by such treatment; and the opacity of the sheet is slightly reduced.

The somewhat porous coated sheet may be further improved by applying over the coated surface, at a coating thickness of about 2 mils, a second and much thinner coating of a composition formed by mixing together, in a ball mill, behenic acid 100 parts by weight, fine silica powder 50 parts, cellulose acetate 250 parts, polyvinyl acetate 250 parts, phthalazinone 100 parts, and acetone 9250 parts, and drying as before. The resulting sheet is dull white and cannot readily be distinguished in appearance from untreated plain white paper. The resistance to light and fingerprinting is still further improved. The surface tackiness and tendency to powder or abrade under normal handling are eliminated, and the surface readily accepts pencil markings. When subjected to thermographic back-printing, the sheet produces dense black image areas on a white background. The image areas show excellent sharpness and resolution. The reproduction prepared from an original typewritten on onion skin or similar white paper is scarcely distinguishable, on visual inspection, from a similar original typed on heavy white bond paper.

Silver stearate has been successfully substituted for silver behenate, and silver salts of many other organic acids have also been found useful in these heat-sensitive compositions and copying-papers. A partial list of such organic acids includes oleic, lauric, hydroxystearic, acetic, phthalic, terephthalic, butyric, m-nitrobenzoic, salicylic, phenylacetic, pyromellitic, p-phenylbenzoic, undecylenic, camphoric, furoic, acetamidobenzoic and o-aminobenzoic. Where suitable, an appropriate quantity of the free acid may accompany the silver soap, as in the silver behenate-behenic acid material; or some other waxy organic acid or other waxy component may be substituted; or the wax-like silver soap may be used in the substantial absence of any additional waxy materials. Where the proportion of silver soap to free acid or the like differs greatly from a 1:1 molar ratio, it is to be understood that the relative proportions of silver soap and terpene resin are to be appropriately adjusted.

The phthalazinone is a preferred example of a toner material which acts to darken the image produced by the reaction of the silver soap with the methyl gallate or equivalent. A less effective but still useful substitute is phthalic anhydride.

Methyl gallate may likewise be replaced by equivalent reducing agents for the silver compounds, such for example as protocatechuic acid or hydroquinone.

The polyvinyl acetate binder employed in Example 1 is effective in bonding the reactants and other materials to the base sheet without causing undue curling. Increasing the amount of polyvinyl acetate binder, as suggested in connection with the first coating, causes slight tackiness in the resulting product, which is particularly disadvantageous in connection with mechanically feeding the sheets from a stack of the same in continuous duplicating operations, and when separating the duplicate from the original following the thermographic copying operation. The tackiness is overcome, without causing undue curling of the sheet product, by incorporation of cellulose acetate or equivalent either in the first coat or as already described in connection with the second coat. Other binders which are non-reactive with the other components of the coating and which effectively bond these components to the supporting web are also contemplated.

Example 2

White machine finish sulfite 37 lb. tablet paper is coated on one surface, at a coating weight of 0.8–1.05 grams per sq. ft. on the dry basis, with a composition containing, in 130 parts by weight of acetone, 7.5 parts of the silver soap reactant of Example 1, 6 parts of "Piccolyte S–135" terpene resin, 3 parts of phthalazinone, 30 parts of zinc oxide, 4.5 parts of polyvinyl acetate, and 9.0 parts of cellulose acetate. On the volume basis, this corresponds closely to the following:

	Volumes
Silver soap	5
Terpene resin	6
Toner	3
Zinc oxide	5.45
Polyvinyl acetate	3.75
Cellulose acetate	7.50

Separately a thin porous paper is sparingly coated on both surfaces with a dispersion of about 20 parts by weight of corn starch in a solution of about 20 parts methyl gallate and one part of polyvinyl acetate in a solvent mixture of methylisobutylketone and acetone. The dried sheet is provided with a preferentially radiation-absorptive image by typing, thereby forming both a graphic original and a component of the copy-sheet system. The sheet is placed with its back or image-free surface in contact with the coated surface of the silver sheet and the printed surface is subjected to brief intense radiation by thermographic copying procedures. A copy of the typed original is produced on the silver sheet in the form of black letters on a white background.

The silver sheet is separately tested for fingerprinting and discoloration in the accelerated test procedure described hereinbefore. Essentially no discoloration or fingerprinting is observed.

The same results are obtained in the accelerated aging test with sheet materials of otherwise identical formulation but in which equal amounts of Piccolyte S–100 or of Piccolyte S–85 terpene resins are substituted for the Piccolyte S–135.

The terpene resins herein employed are insoluble in the ketone solvents and accordingly are well adapted to application in powdered or particulate form. Although somewhat less effective, these specific resins are still useful in decreasing the fingerprinting tendency of the silver soap sheet materials when applied in solution rather than dispersion form. For example, the particles may be coalesced by means of solvents applied to the coated sheet; or a sheet containing no terpene resin may be protected by application of a thin coating of the resin applied from solution in a volatile solvent. Although the added opacity normally provided by the resin powder is thereby lost, a high resistance to fingerprinting is still observed. Surprisingly, no such effect has been found possible with other resinous additives; the effect appears to be specific to the terpene resins as hereinbefore identified. Examples of other resinous or polymeric materials which have been tested and found inoperative in preventing fingerprinting include "Pentalyn X" pentaerythritol abietate resin, "V–950 Versamid" polyamide resin, "Piccolastic E 125" thermoplastic polystyrene resin, limed "Polypale" polymerized rosin type resin, and various silicone resins. Many of these materials might be expected to provide improved protection against fingerprinting; but in no case are the results at all comparable to those obtained with the terpene resins.

The combination of film-forming binders employed in the silver sheet of Example 2 is advantageous in retaining the remaining components on the surface of the paper backing in position for reaction while avoiding any tendency toward curling of the coated sheet or tackiness of the coating. Polyvinyl acetate as used in the sheet of Example 1 or in the methyl gallate sheet of Example 2 is a soft flexible binder which causes substantially no curling when coated on a paper sheet but which is rendered undesirably tacky at thermographic copying temperatures. In the two structures mentioned, this tackiness is avoided by the application of a further protective surface coating or by the inclusion of a masking component. In the silver sheet of Example 2, the cellulose acetate binder component, which by itself would cause undesirable curling, in conjunction with the polyvinyl acetate provides a curl-resistant and heat-resistant binder component. The proportions given in the example are illustrative; the quantity of either binder may be varied by as much as about one-fifth of the specific amounts shown without significant changes in properties of the copy-sheet product. Useful silver sheets may also be prepared in the absence of added binder components, employing a waxy silver soap reactant which itself presumably serves to retain the unity of the sheet product, as shown by the following illustrative example.

Example 3

Bond paper is uniformly coated with a powdery mixture of 5 parts by weight of mixed silver behenate-behenic acid, 2 parts phthalazinone, 5 parts of zinc oxide, and 5 parts of "Piccolyte S–135" terpene resin. The powdered surface is brushed vigorously, producing a smooth and uniform coating which is visibly reactive with the methyl gallate paper of Example 2 under localized heat and contact in thermographic copying procedures. The sheet is highly resistant to discoloration and fingerprinting under normal aging conditions and in the accelerated aging test hereinbefore described.

What I claim is as follows:

1. A sheet product useful in the thermographic reproduction of graphic originals and highly resistant to discoloration under illumination and under handling and fingerprinting, said sheet including as an essential image-producing reactant component five parts by volume of finely divided particulate silver soap reactant and, homogeneously associated therewith, from about one to about eight parts of zinc oxide and from about two to about twelve parts of solid fusible pure hydrocarbon thermoplastic terpene resin of zero acid number.

2. A sheet product useful in the thermographic reproduction of graphic originals and highly resistant to discoloration under illumination and under handling and fingerprinting, said sheet including a paper-like backing and a thin uniform silver-containing coating comprising a film-forming binder, about five parts by volume of finely divided particulate silver soap reactant, from about one to about eight parts of zinc oxide, and from about two to about twelve parts of solid fusible pure hydrocarbon thermoplastic terpene resin of zero acid number.

3. A visibly heat-sensitive copy-sheet, useful in the thermographic reproduction of graphic originals by back-printing at temperatures available in the thermographic process, capable of providing copies of high image density in said process, and highly resistant to fingerprinting and to discoloration under illumination, said copy-sheet comprising a paper-like support member and a heat-sensitive coating thereon of a visibly heat-sensitive mixture comprising a binder, a finely divided particulate silver soap reactant and a reducing reactant therefor as essential image-producing components, and, based on five parts by volume of said silver soap reactant, from about one to about eight parts of zinc oxide, and at least about two parts of solid fusible pure hydrocarbon thermoplastic terpene resin of zero acid number.

4. A visibly heat-sensitive copy-sheet suitable for thermographic reproduction of graphic originals by back-printing at temperatures available in the thermographic copying process, capable of providing copies of high image density in said process, being resistant to discoloration under illumination and under handling and fingerprinting, being capable of being fed mechanically from a stack of said sheets, and separated from copy-contact with an original, without sticking, and having a pencil-mark-receptive surface; said copy-sheet having, in order: a paper support web; a heat-sensitive coating thereon comprising a visibly heat-sensitive mixture of a finely divided particulate silver soap reactant and a reducing reactant therefor, a powdered solid fusible pure hydrocarbon thermoplastic terpene resin of zero acid number in an amount of at least about two volumes for each five volumes of said silver soap reactant, zinc oxide in an amount of about one to about eight volumes for each said five volumes, and a binder; and a thin surface coating comprising a waxy material, a finely divided particulate inorganic filler, and a binder.

5. Method of making a discoloration-resistant heat-sensitive copy-sheet capable of providing copy of high image density in the thermographic copying process and having a visibly heat-sensitive layer of a binder-containing composition including as an essential image-producing component a finely divided particulate silver soap reactant and a reducing reactant therefor, comprising homogeneously incorporating in said composition in coatable liquid form an amount by volume, based on 5 volumes of said silver soap reactant, of at least about two volumes of powdered pure hydrocarbon thermoplastic terpene resin of zero acid number and about one to about eight volumes of zinc oxide, coating the composition on a backing member, and solidifying the coating; said coating being visibly changed on brief heating at temperatures available in the thermographic copying process.

6. A visibly heat-sensitive copy-sheet having: a paper-like backing; a heat-sensitive coating comprising, in approximate proportions by weight, particulate silver soap reactant 26 parts, zinc oxide 100 parts, solid fusible pure hydrocarbon thermoplastic terpene resin of zero acid number 90 parts, phthalazinone image toner 4 parts, methyl gallate 10 parts, and polymeric resinous binder 46 to 92 parts; and a dull transparent thin protective surface coating capable of accepting pencil markings and comprising, in approximate proportions by weight, waxy fatty acid 100 parts, silica powder 50 parts, phthalazinone toner 100 parts, and polymeric resinous binder 500 parts; the coated sheet having essentially the dull white appearance of untreated plain white paper, being strongly resistant to degradation by light and fingerprinting under accelerated test conditions as herein described, and producing copies having dense black image areas on a white background by back-printing from thin graphic originals in the thermographic copying process.

7. A sheet product including a paper-like backing and a thin uniform surface coating consisting essentially, in approximate proportions by weight, of silver soap 7.5 parts, "Piccolyte S–135" thermoplastic terpene resin 6 parts, phthalazinone 3 parts, zinc oxide 30 parts, polyvinyl acetate 4.5 parts, and cellulose acetate 9 parts; said sheet product being strongly resistant to degradation by light and fingerprinting under accelerated test conditions as herein described, and said sheet product providing copies of high image density when briefly heated at image areas in contact with a source of methyl gallate.

References Cited in the file of this patent

UNITED STATES PATENTS

2,910,377	Owen	Oct. 27, 1959
3,031,329	Wingert	Apr. 24, 1962