

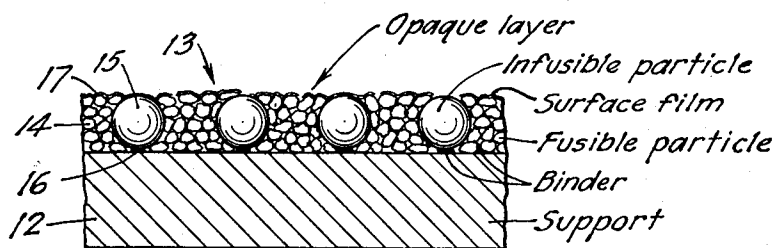
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HEAT-SENSITIVE COPYING-PAPER

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HEAT-SENSITIVE COPYING-PAPER

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4 Claims. (Cl. 117—36)

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This invention is concerned with duplicator sheet material or copying-paper useful in preparing copies of printed matter or the like. The invention particularly contemplates coated sheet material having a heat-sensitive transparentizable opaque layer consisting essentially of a fusible inherently transparent matrix material and a light-scattering transparent infusible particulate material in partial contact therewith.

Heat-sensitive copying-papers of the type here contemplated are of particular utility in making copies of graphic subject-matter such as printing, drawings, diagrams, pictures, etc. by methods to be described. Such methods involve the irradiation of the graphic subject-matter with intense radiant energy of proper wave-length, the resultant formation of an elevated-temperature pattern corresponding to the graphic matter irradiated, and the utilization of such elevated-temperature pattern in directly producing a corresponding visible pattern in the copying-paper.

Depending on the desired appearance of the finished copy, we may employ a transparent, dyed, pigmented, or other type of base sheet material for our novel copying-paper, provided the sheet has a low degree of heat-conductivity. For most purposes, we prefer to use writing-paper having on one surface a thin but opaque colored coating. To this sheet we apply a thin uniform layer of a mixture of fusible waxy particles and infusible siliceous particles in a solution of a film-forming infusible transparent binder. The volatile vehicle is then removed by evaporation at a temperature below the melting-point of the waxy particles. The dried coating is opaque, and the coated sheet is quite resistant to surface marring.

In making a copy of graphic subject-matter, e. g. of a typewritten page, we place the copying-paper, prepared as described above, in close and heat-conductive contact with the unprinted surface of the page. We then briefly expose the typewritten surface to intense radiant energy. On removing and examining the copying-paper, it is found to contain a visible copy of the printed message, appearing in the color of the base sheet against a background of unchanged wax-silica coating.

Suitable radiant energy for such copying methods may be obtained from electrically-heated incandescent filaments, electric arcs, focused sunlight, etc. and is largely within the infra-red or near infra-red range. The most convenient source is the electric filament, par-

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tially enclosed by a suitable reflector, and the copying-paper is therefore designed to print at temperatures above normal room and storage temperatures, which it is possible to reach safely by irradiation of the graphic material from such source of radiant energy.

Cellophane or other transparent film material may constitute the flexible support for the fusible layer, in which case the copy will appear as transparent areas in an opaque background. Paper or other fibrous sheet material, as well as the non-fibrous films, may be used either in the natural color or after being colored with an appropriate dye, this colored backing then being visible through the transparent spaces obtained in the opaque coating during the copying process. For the most intense copy, however, we prefer to coat the flexible backing with an opaque colored contrast-layer as previously disclosed. A composition suitable for this purpose may consist of lamp-black dispersed in a binder of cellulose acetate lacquer. Various colored pigments, e. g. nigrosine, ultramarine, toluidine toner, etc., may replace the lamp-black, and other cellulosic lacquers, spirit varnishes, elastomer solutions, or the like may be used in place of the cellulose acetate. The coating must adhere well to the flexible backing, must provide a surface to which the fusible layer may adhere, and must provide adequate visual contrast when present as an extremely thin film.

The waxy particles must remain in particulate form at normal room and storage temperatures, but must melt and fuse together at temperatures obtainable in the copying process, to form a continuous transparent waxy layer which remains transparent on cooling to room temperature. Natural ester-type waxes (such as carnauba wax), hydrocarbon waxes, and other waxy materials or mixtures thereof, which are suitably transparent and melt within the approximate range of 60–150° C., or preferably 70–120° C., may be employed. Water-insoluble salts of higher fatty acids have been found to give excellent results. One such waxy material is cadmium stearate, prepared by the reaction of a soluble cadmium salt with the water-soluble sodium salt of commercial triple-pressed stearic acid. Other examples are lead myristate and lead palmitate.

The infusible siliceous particles are substantially transparent and have a refractive index approximately the same as that of the waxy material. Fibrous or acicular infusible transparent particles such as asbestine may be used. Crushed

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silica, crushed glass, or glass spherules offer additional advantages. These materials are infusible at temperatures required to fuse the wax.

Mixtures of wax particles and small glass beads or the like, when deposited from a non-solvent volatile liquid vehicle, produce thin opaque coatings which are transparentizable by heating. However, when an attempt is made to produce copies of printed pages or the like by methods herein described, it is found that the fused portions of the coating adhere to the printed page or other contiguous surface and subsequently are pulled away from the copying-sheet. Furthermore, these two-component coatings are susceptible to removal by rubbing, brushing, or flaking. A small amount of a film-forming binder is therefore dissolved in the volatile vehicle, and serves to hold the particles together and to the base sheet without seriously reducing the opacity of the particulate coating. Cellulose acetate and ethyl cellulose are examples of film-forming binder materials soluble in volatile liquid vehicles which are non-solvents for the preferred waxy materials. These binders, like the siliceous particles, are infusible at temperatures required to fuse the wax, and have approximately the same refractive index as the wax.

The opacity of the coating is due partially to the waxy particles, and partially to the infusible siliceous particles. The individual small particles are held in place by partial contact with each other and with the binder, but are largely separated so that light impinging on the layer of particles is diffused and scattered. With the surface coating in this condition, the colored contrast layer beneath it cannot be seen.

As previously noted, graphic subject-matter may be directly copied by placing the copying-paper against the reverse side of the printed sheet and strongly irradiating the printed surface. In explanation of this effect, it is believed that the radiant energy directed against the printed page or the like is largely reflected from the unprinted surface but is absorbed and converted to heat at the printed areas. The resulting elevated temperature pattern at the irradiated surface is sufficient to produce a corresponding elevated-temperature pattern within the fusible layer and to cause fusion of said layer at the heated areas. The fusible material, which as a solid is immobile, in the fused or liquid form immediately wets and flows around the adjacent infusible siliceous particles, forming a matrix in which the particles are embedded on cooling. The infusible binder remains attached to the siliceous particles and distributed throughout the waxy matrix, and in addition a portion appears to remain as a film at the outer surface of the matrix. Since all three components have substantially the same refractive index, the resulting compacted composite layer is transparent and does not cause objectionable optical distortion. The underlying layer of the copying-paper is thus exposed to view through this transparentized portion of the opaque coating, and a facsimile of the original graphic subject-matter is obtained.

Placing the opaque particulate surface of the copying-paper against the reverse side of the printed sheet results in the production of a direct copy of the original, and is ordinarily preferred. The copying-paper may, however, be otherwise positioned if desired. Thus, placing the uncoated surface of the copying-paper against the reverse side of the printed sheet makes possible the

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formation of a reversed copy of the original graphic subject-matter.

In the figure, which is a diagrammatic enlarged vertical cross-section, not necessarily to scale, of one embodiment of our novel heat-sensitive copying-paper, the sheet is seen to consist of a flexible contrasting support 12 coated with an opaque layer 13 consisting of a mixture of particles 14 of fusible waxy material and particles 15 of siliceous infusible particles (in this case represented as small glass spheres), held together and to the supporting base by a small amount of infusible binder 16. A portion of the binder forms a semi-continuous surface film 17.

Various modifications of the exemplary copying-paper here described and illustrated will be apparent to those skilled in the art, particularly in view of the discussion herewith presented. Thus, the support 12 may be coated on either surface with a color layer, or may be dyed or pigmented; or if transparent, the copy may be held against an illuminated transparent surface or against an opaque contrasting surface, in order to provide desired visibility of the copy. However, the support 12 should be low in heat conductivity, hence metal foil and the like is excluded. Although not ordinarily desirable, an additional light surface film of binder material may be added to fortify the film 17.

The presence of the infusible particles 15 is found to provide a number of advantages. Substitution of the quite inexpensive crushed glass or analogous particles for the relatively expensive wax particles effects a desirable saving in costs. The infusible particles provide a hard outer surface for the heat-sensitive layer. When the heat-sensitive surface is pressed against a sheet of paper in making a copy, the infusible particles assist in preventing the melted wax from flowing to and into the paper.

Example

Paper was first provided with a black contrast layer of lamp-black and cellulose acetate, as previously described, and over the contrast layer was applied a coating of a heat-sensitive composition comprising lead palmitate, ethyl cellulose, and small glass beads.

Lead palmitate is a water-insoluble metal salt of a long-chain fatty acid, and is a waxy material melting at approximately 99–101° C. It was dispersed in acetone, in the form of fine particles within the approximate size range of ½–25 microns, by prolonged ball milling. The concentration was 20%. An ethyl cellulose soluble in acetone was used, and it was added as a pre-formed solution in acetone, at a concentration of 10%. No. 19 glass beads, of about 3 mils diameter, were employed. The two solutions and the dry beads were mixed in various proportions, and the mixtures coated on the prepared backing and dried at room temperature. The coating was found to fuse and become transparent when briefly heated to about 95–105° C. The sheets were then tested as heat-sensitive copying-papers according to the method described herein for making direct copies.

With 10 parts by weight of beads and 100 parts of the wax, best results were obtained with three parts of ethyl cellulose binder. Less than about one part of the binder was insufficient to prevent dusting and rub-off of the heat-sensitive layer. More than about six parts of ethyl cellulose reduced the opacity of the coating, and copies made

with these sheets were undesirably low in contrast.

With 50 parts of beads and 100 parts of wax, somewhat the same results were obtained over the range of 1-6 parts of binder except that there was a slight reduction in detail of the copies. Rub-off occurred with less binder. At nine parts of binder, flaking was noted; apparently the film strength of the coating exceeded the adhesion between backing and coating.

Still higher ratios of beads to wax, up to equal parts of each, gave good results with the lower proportions of binder, but at six parts binder to 100 each of wax and beads, flaking again occurred. Above about 100 parts of beads, flaking and reduced detail made the coatings ineffective for most copying purposes.

The foregoing tests were on sheet material coated on a knife coater at an orifice of six mils, which was found to be the minimum coating weight at which full opacity and maximum contrast was obtained. At three mils, the sheet appeared grey in color, due to the contrast layer showing through the partially translucent coating. Furthermore, the composition was difficult to apply at that thickness due to the size of the glass beads. At nine mils, the opacity was no better than at six mils, and the detail of the copy was obscured.

Larger size particles also reduced the amount of detail obtainable, and tended to make the copy "fuzzy" and difficult to read. No. 14 beads, with a diameter of about four mils, represent an approximate maximum size. Much smaller particles may be used, but the increased surface area of fine powders per unit of weight requires that the amount of such materials be limited. Mixtures of various sizes and types of infusible transparent particles sometimes provide additional advantages.

The product of our invention, in its preferred form, is thus seen to consist of a visibly contrasting thin flexible poorly heat-conductive support member coated with a heat-sensitive opaque layer of a mixture of insoluble siliceous particles and fusible waxy particles held in place with an infusible film-forming binder, the components being suitably selected and proportioned in accordance with the requirements and disclosures herein set forth. The product is stable to light, being capable of prolonged exposure to actinic radiation without change, and is not activated at normal room or storage temperatures. At higher temperatures, and particularly within the range of about 60-150° C., or preferably within the more restricted range of about 70-120° C., which temperatures may be readily and safely attained by intense irradiation of a contiguous printed page with infra-red rays, the heated opaque layer is irreversibly converted to a transparent condition,

permitting the visibly contrasting support member to be seen.

This application is a continuation-in-part of our copending application Serial No. 747,341, filed May 10, 1947, now abandoned.

What we claim is as follows:

1. A light-stable, heat-sensitive copying-paper adapted to provide clear and sharp copies of type-written messages by methods herein described, comprising a thin flexible visibly contrasting support member having low heat conductivity and a thin opaque heat-transparentizable surface coating comprising a mixture of: (a) one hundred parts by weight of particles of transparent waxy material fusible at about 60-150° C.; (b) about 10-100 parts by weight of transparent infusible siliceous particles less than about four mils in diameter; and (c) sufficient transparent flexible organic film-forming binder, within the range of about one to about six parts by weight, to provide good resistance to dusting and rub-off of the coating without causing flaking thereof; the wax, siliceous particles, and binder each having substantially the same refractive index, and said binder being infusible at the fusion temperature of said wax.

2. Product of claim 1 in which the waxy material is a water-insoluble metal salt of a long-chain fatty acid and is fusible at about 70-120° C.

3. Product of claim 2 in which the waxy material is lead palmitate.

4. A light-stable, heat-sensitive copying-paper adapted to provide clear and sharp copies of type-written messages by methods herein described, comprising a thin flexible visibly contrasting support member having low heat conductivity and a thin opaque heat-transparentizable surface coating comprising a mixture of: (a) one hundred parts by weight of particles of transparent waxy material fusible at about 60-150° C.; (b) about 10-100 parts by weight of transparent glass beads of about three mils diameter; and (c) sufficient transparent flexible film-forming cellulosic binder, infusible at the fusion temperature of the waxy material, and in an amount within the range of about one to about six parts by weight, to provide good resistance to dusting and rub-off of the coating without causing flaking thereof; the wax, glass beads, and binder each having substantially the same refractive index.

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