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MASTER PAPER FOR THERMAL PAGE PRINTER

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ABSTRACT OF THE DISCLOSURE

The novel heat sensitive element of this invention comprises a support, preferably a flexible backing such as paper, upon which is coated at least one layer of a novel composition in a state of at least partial crystallization. In the state of at least partial crystallization the composition is substantially nontacky, nonfluid, and solid at room temperature. When heated to a temperature substantially elevated above room temperature, the heat sensitive novel coating of this invention undergoes a transition to an amorphous state and thereafter, for a substantial period of time, e.g., twenty minutes, exhibits a tackifying state at a temperature substantially below the original tackifying temperature. Since only the image areas in the heat-sensitive layer are selectively heated by conductive heat transfer to a temperature above the original tackifying temperature, only the image areas of the heat-sensitive coating are activated. After activation, the material in the image areas remain tacky at substantially lower temperatures while the unactivated background areas remain nontacky at this lower temperature.

The range of the components of the composition of this invention is set forth as follows:

	Percentage by weight, dry basis
(I) N-ethyl-p-toluene sulfonamide	50–70
(II) Glycerol ester of hydrogenated rosin	5–10
(III) Chlorinated rubber	2.5–4
(IV) Diazo dye	2–15
(V) Carbon black	1–10
(VI) Casein	1–5
(VII) Vinylacetate polymer, modified	6–12
(VIII) Sodium silicate	1–5

The present invention relates to thermal printing ink. More specifically, this invention relates to a thermal printing ink that provides a tacky, adhesive, transferable, colored material, that has the propery of remaining tacky when heated to the tackifying temperature and remaining in a tacky state for an interval of time after being cooled to a temperature less than the tackifying temperature.

The printing inks of the prior art encompass those such as set forth in Letters Patent No. 2,740,896 to Carl S. Miller on Apr. 3, 1956. Such methods require that heat-reducing radiation must fall on the printed characters of the document to be copied, which in turn produces a visible change in a heat-sensitive material coated upon a transparent copying paper. In such methods very little of the radiation is absorbed and converted on the unprinted portions of the page, thus the temperature does not increase at such unprinted areas and the copying paper remains unaffected. The printed portions of the page absorb radiation and by converting said radiation to heat results in an elevated-temperature pattern corresponding to the printed characters on the document to be copied. Only a single copy is made therefrom.

The foregoing method is similar to that described in Letters Patent No. 2,808,777 to Allen I. Roshkond, issued Oct. 8, 1957, which sets forth the manufacture of a duplicating master by positioning an original from which copies are desired to be made in surface contact with a base sheet comprising a sufficiently continuous layer formed of material displacable at elevated temperatures and then directed a sufficient quantity of radiation rich in infrared onto the original to generate a heat pattern and cause displacement of the heat displaceable material directly to the base sheet to form the corresponding printing areas in the duplicating master.

Letters Patent No. 3,261,023 to William A. Light et al., which issued on July 12, 1966, shows a matrix comprising a sheet support having coated thereon a layer of normally nontacky thermoplastic material at room temperature. The coating composition has the property of undergoing transition from a partially crystalline state to a tacky amorphous state at a temperature called the original tackifying temperature and remaining in said tacky state at a temperature below the original tackifying temperature for at least long enough to permit transfer of tackified material from the matrix to produce a transfer print on a receiving surface at a transfer temperature below said original tackifying temperature. That invention also requires that heat be generated by infrared absorption by the printed characters of the document to be copied and that that heat be transmitted to an adjacent polymer area on the matrix, raising the temperature of those areas above the original tackifying temperature of the polymer layer. The matrix is then separated from the document to be copied and placed in contact with a receiving sheet. The method is limited to printed areas that are absorbent of infrared radiation, which are distinguished from background areas that are relatively nonabsorbent of infrared radiation. The essence of the Light invention lies in the fact that a single matrix can be activated thermographically more than one time, and after each activation a transfer print different from the last-imposed thermographic image can be made.

The persistent tacky state of an otherwise nontacky composition was disclosed in an adhesive in U.S. Pat. No. 2,462,029 to Lloyd M. Perry, which issued on Feb. 15, 1949, and has now expired. In that invention, particles of polymer material and a potential plasticizer therfor were mixed into a coating composition, which, when applied to paper, dried, and elevated in temperature, became tacky due to the solvent action of the plasticizer on the polymer material. Upon cooling, a slow reversion took place in which the plasticizer crystallized.

A variation of the foregoing Perry composition is encompassed in U.S. Pat. No. 2,608,543, which issued on Aug. 26, 1952, to Charles M. Wiswell. The Wiswell composition included a ground-particle solid eutectic polymer and a plasticizer. The Wiswell composition exhibited a lower activating temperature range than the Perry composition. Neither the Perry patent nor the Wiswell patent made any disclosure of the transfer of material from one sheet to another sheet, except that nonimage-delineating transfer is inherent in sealing an adhesive material to a receptor surface.

The object of this invention is to provide a coating of heat absorbing material ink on a sheet which can be heated other than by infrared radiation absorption in an image pattern, that is, by conduction, from a normally nontacky state to a tacky state, and which has the property of remaining in a tacky state at temperatures substantially lower than the temperature at which the ink composition originally reached a tacky state.

Another object of this invention is to provide an ink coating which will be stratigraphically depleted of successive decrements of the adhesive ink.

Another object of this invention is to provide an ink

coating composition in which no impact printing or radiation application pressures are required in making the original matrix or in making copies from the matrix.

The preferred form of the instant invention has a paper sheet base coated with a composition of distinctive color which qualifies it for a marking material. The composition of this invention being, substantially solid, nontacky, and nontransferable to another sheet in contact therewith at room temperature, but which changes into a tacky-adhesive, contact-transferable state when heated to a temperature elevated above room temperature, and which exhibits the property of remaining in a state having a tackifying temperature substantially lower than the original tackifying temperature for at least long enough to permit successive transfer of tackified material from the matrix thus formed to a plurality of transfer sheets.

The instant invention provides a solid phase transfer for reproduction of multiple copies from a single activation of the heat-sensitive element. The copies can be made on ordinary paper. The invention provides means by which a heat-sensitive matrix can be activated with the support for the heat-sensitive layer in direct contact with a heat-conductive printing head or hot scriber, thus avoiding thermal diffusion and obtaining a high resolution tacky image in the heat-sensitive layer. Copies can be made from the tacky layer after an initial activation of the layer without need for further preferential heating of the image areas during the sequential transferring steps of the process. The present invention provides for preparation of multiple copies from a single heat-sensitive element of prints suitable for archive use.

The prolonged tacky state at a temperature lower than the original tackifying temperature after an initial activation is an idiosyncratic characteristic of the composition of this invention. It is accounted for, partially, by delay of recrystallization after activation. While recrystallization probably would occur, at least to some extent, in activated unmixed amorphous materials, it is a characteristic of the composition of this invention that the rate of recrystallization at temperatures below the original tackifying temperature is sufficiently slow that for a substantial period of time after activation the activated material remains in a state having substantially the same transfer characteristics as if the material were at temperature elevated above the tackifying temperature.

By "tackifying temperature," as the term is used in the specification, is meant the lowest temperature (or temperature range) at which the material in the state being described will become tacky. For a completely crystallized thermoplastic polymer composition the tackifying temperature is the first order transition temperature; and for a completely amorphous thermoplastic polymer composition the tackifying temperature is the second order transition temperature, sometimes called "glass transition temperature." In a composition that is partially amorphous and partially crystalline, the tackifying temperature will be a hybrid first order transition temperature and be somewhat below the true first order transition order temperature, the disparity between the true first order transition temperature and the hybrid first order transition temperature being dependent on the degree of crystallization. The term, "tackifying temperature" is used to denote both true first order transition temperatures, true second order transition temperatures, and varying hybrids of the foregoing orders.

The instant invention does not pertain to infrared radiation, thermography, simultaneous printing material, light reflex printing, visible light patterns, free-standing patterns of tacky ink, the solvent or drying principles of printing, or chemical action in the sense of forming colored material or the decoloration of the colored material. The matrix formed of the adhesive ink composition of this invention is preferably heated by a thermal printing unit similar to that disclosed in U.S. Pat. No. 3,161,457 to H. Schroeder et al., which issued on Dec. 15, 1964. The ink composition can be heated by any printing member device which has an outline or delineation of the data in terms of a temperature above that of room temperature. Such printing members include relief surface, hot-type bodies, such as branding iron, thermographic plano-sheets, and type bodies having a planar surface which is differentially heated.

The use of radiant heat is not only unnecessary in the practice of this invention, but is undesirable. In the particular printing member of the aforementioned Pat. No. 3,161,457, the planar surface is formed of the edges of stacked lamina of electrically-nonconducting material, each lamina having one or more resistance supports on its edge. Selective choice of resistance on the laminae for electric energization will produce a corresponding high-temperature pattern which, in contact with the master sheet, will make a corresponding tacky pattern in the transfer coating. An uncontrolled source of infrared radiation cannot be used in this process, and thermographically-formed patterns in a controlled sheet will not usually have sufficient heat content satisfactorily to raise the temperature of the composition of this invention to its tackifying temperature. While this invention is a planographic system, the planographic member which gives rise to this denomination is the master sheet and not the planographic printer head.

The tacky material in the activated areas of the heat-sensitive layer has an optical density and can be transferred seriatim by layers from the activated areas to each of a plurality of receiving surfaces to produce a plurality of images, produced seriatim.

The composition of this invention has the characteristic property of remaining in a state of being tacky for a substantial time after once being heated to the original tackifying temperature.

The preferred composition of this invention consists of the following:

	Percentage by weight (dry basis)			
(I) N-ethyl-p-toluene sulfonamide	60.290	56.4	57.51	59.00
(II) Glycerol ester of hydrogenated rosin with a softening point range of 80°-88° C. and an acid number of 8.0	7.076	6.7	6.77	7.00
(III) Chlorinated rubber	3.516	3.3	3.38	3.48
(IV) Diazo dye	9.346	10.9	11.09	9.25
(V) Carbon black	5.752	7.6	7.71	5.72
(VI) Casein	0.750	2.1	-------	2.09
(VII) Vinylacetate polymer, modified	9.730	9.6	9.73	9.60
(VIII) Sodium silicate	3.540	3.5	3.44	3.48
(IX) Surface active agent	Trace	Trace	0.18	-------
(X) Defoaming agent	Trace	Trace	0.18	-------

The range of the components of the composition of this invention is set forth as follows:

	Percent by weight, dry basis
(I) N-ethyl-p-toluene sulfonamide	50–70
(II) Glycersol ester of hydrogenated rosin	5–10
(III) Chlorinated rubber	2.5–4
(IV) Diazo dye	2–15
(V) Carbon black	1–10
(VI) Casein	1–5
(VII) Vinylacetate polymer	6–12
(VIII) Sodium silicate	1–5

(I) N-ethyl-p-toluene sulfonamide acts as a plasticizer for the resins of the preferred composition. The compound exhibits a melting point of 58° C. and a boiling point of 340° C. (It is sold as "Santicizer 3" by Monsanto Chemical Corporation, St. Louis, Mo.) The molecular weight is 199.3; the density is 1.253 grams per cubic centimeter; the specific gravity should range from 1.166 to 1.176; the refractive index should range from 1.512 to 1.532 at 65° C.; the vapor pressure should be 0.8 millimeter of mercury at 160° C.

(II) The glycersol esters of hydrogenated wood rosins

are predominantly mixtures of the glycerol esters of dihydroabietic acids. The degree of saturation should be greater than fifty percent of that theoretically possible.

The resin acids in wood rosin comprise approximately 30–37% abietic acid, 5–17% palustric acid, 2–13% neoabietic acid, 3–9% dehydroabietic acid, less than 2 percent levopimaric acid, 7–10% pimaric acid, 10–14% isopimaric acid, as well as other homologues of abietic acid.

Since good color stability is desired, the glycersol ester of a stabilized rosin, i.e. hydrogenated rosin, is used. Hydrogenation is one of the more satisfactory methods for decreasing the susceptibility of rosin to air oxidation. A typical analysis for content of the various types of acids in glycerol esters of hydrogenated wood rosins shows only two changes from the unreduced form, viz, a decrease in the two-double-bond abietic-type acids from 53 to 3%, and an increase in dihydroabietic acids from 11 to 60%; hence, the overall change is conversion of the former to the latter.

The chief effects of hydrogenation of rosins are to partially or totally remove the double bonds present in the resin acids thus stabilizing the product, and to destroy color bodies found in natural wood rosins. The degree of saturation of glycersol esters of hydrogenated wood rosins is greater than 50 percent of that theoretically possible, assuming that the resin acids found in wood rosin have an average of two double bonds, typical of which is abietic acid. As a result of hydrogenated wood rosins are dihydroabietic and tetrahydroabietic acids.

The glycerol ester of rosin, usually called *ester gum,* has decided advantages over both the raw material, rosin, and the metal-hardened rosins with regard to durability, moisture resistance, and freedom from livering with basic pigments. Livering is a defect found in inks in which the pigments react chemically with vehicle constituents. It causes the ink to body up and finally to gel completely. The composition of this invention shows no evidence of livering.

The ester gum of optimum physical properties is that in which three moles of resin acids combine with one mode of glycerol to produce glycerol triabietate. Commercial ester gum is composed of both the mono- and the diglycerides as well as the completely esterified product. Unreacted glycerol in the finished product is to be avoided if an ester of proper hardness and water resistance is to be obtained. A suitable ester gum, with acid number 5–10, is produced by heating rosin with glycerol at 250° C. The reaction can be carried to completion at 290° C. in a vessel provided for the removal of the water produced. The glycerol ester of hydrogenated rosin should exhibit medium relative viscosity, negligible odor, good oxidation resistance and only slight coloration. (The mixture is sold as "Staybelite Ester No. 10" by the Hercules Powder Company, Wilmington, Del.)

(III) The chlorinated natural rubber used in the composition of this invention is the product of the chlorination of polyisoprene rubber and acts as a tackifier. It is odorless and shows excellent clarity in film form. The chlorination of natural rubber which is a polymer made up of isoprene units, takes place in a complex fashion with addition and substitution of chlorine occurring as well as cyclization along the polymer chains and the cleavage of the polymer chains into shorter chains. The chlorination process terminates when the unsaturated characteristics of the rubber have been exhausted. The chlorine content is approximately 67% and is great enough to insure an optimum of stability, compatibility and resistance to fire. The viscosity of the chlorinated rubber ranges from 9 to 14 centipoises. (The chlorinated rubber of the preferred embodiment of this invention is sold as "Parlon 10" by the Hercules Powder Company, Wilmington, Del., U.S.A.)

(IV) The diazo dye of the preferred embodiment is Oil Black BT (for example, that sold by Allied Chemical and Dye Corporation). The dye used in the composition is of the diazo type such as that having a Color Index No. 26150. The preferred dye does not exclude compositions embodying other dyes such as aryl amine dyes having Color Index Nos. 26200, 26210, 26270, 26300, 26315, 26330, 26380, 26405, 26750, and 26950.

Other suitable coloring addenda include the following materials available from the Allied Chemical and Dye Corporation: Azo Oil Black, Alizarin Blue G.R.L. Base, Oil Scarlet 60, Oil Red G.R.O., Oil Red O, Oil Orange 2311, Plasto Oil M.G.S., Insol Black Ultra Blue 9775A, and Azo Oil Blue Black B. Other coloring addenda include Nile Blue Hydroxide, Methyl Red, Prussian Blue Pigment, Iron Oxide, Peacock Blue, Phloxine, Chrome Yellows, etc.

(V) Carbon blacks are usually prepared by the impingement of small natural gas flames. They consist chiefly of 88.4% carbon with 0.4% hydrogen and 11.2% oxygen. Any of the 25 grades of manufactured carbon black can be used in this invention such as that sold by Sterling Chemical Co. as Grade "R."

(VI) The lactic acid casein (sold as Casein FF–30 by The Borden Co., New York, N.Y., U.S.A.), was modified especially to be low foaming and is used as a film-forming transfer regulator.

Preparation methods for acid precipitation of casein are set forth in U.S. Pat. No. 1,716,799 which issued June 11, 1929, to W. H. Sheffield; U.S. Pat. No. 1,892,233, which issued Dec. 27, 1932, to F. L. Chappell; U.S. Pat. No. 1,992,002, which issued Feb. 19, 1935, to F. L. Chappell; U.S. Pat. No. 2,044,282, which issued June 16, 1936, to F. H. Clickner. The precipitating acid may be lactic, sulfuric, or hydrochloric.

Commercial acid casein is obtained from skim milk by selective precipitation with lactic acid and whey removal. Solutions of acid casein are prepared by soaking casein in water and subsequently adding alkali and heating and stirring at 40–50° C. The minimum quantities of alkalies required for dissolving acid casein (in parts per 100 parts of casein) are as follows: 3% sodium hydroxide; 3% ammonium hydroxide; 5% sodium carbonate; 12% sodium phosphate, and 15% sodium bromate or sodium borate. Alkaline solutions of casein form continuous films on drying. Commercial acid casein is about 80–84% pure casein. The principal nonprotein materials, besides moisture, are ash constituents (largely calcium phosphate) lactose, and fat.

Preservatives for casein include phenols, chlorophenols, 2-naphthol, benzoates and salicylates.

Pine oil can be used as a combined preservative, wetting agent (surfactant), and defoamer.

(VII) The vinyl acetate polymer (sold as Gelva C5–V16R by Monsanto Chemical Corp., St. Louis, Mo.), modified to be soluble in ammonium hydroxide solution, exhibits a softening point of 134° C. and a viscosity of 13–18 cps. in a concentration of 86 gm./1000 cubic centimeters of ethyl alcohol at 20° C., using an Ostwald viscometer. It is used as a hot melting adhesive. The preparation of the vinyl acetate polymer is set forth in U.S. Pat. No. 2,412,239 which issued Dec. 24, 1946, to G. J. Manson; U.S. Pat. No. 2,486,855 which issued Nov. 1, 1942, to E. Lavin and C. L. Boyce; U.S. Pat. No. 2,435,-909 (Reissue No. 23,164, Nov. 1, 1947) to N. G. Tompkins, and U.S. Pats. Nos. 2,508,341 and 2,508,343 which issued May 16, 1950, to W. K. Wilson.

(VIII) The sodium silicate used in this invention exhibits a weight ratio of silicon dioxide to sodium oxide of 2.5 to 3.4; the percentage of sodium oxide can range from 5 to 20; the percentage of silicon dioxide can range from 20 to 40; the viscosity at 68° F. can range from 100 centipoises to 1,000 centipoises. The chemical formula is $Na_2O.xSiO_2$ where x ranges from 3 to 6.

(IX) The gross effects of surface-active compounds are styled as detergency, wetting, foaming, dispersion, and emulsification. The surfactants or wetting agents of the

preferred embodiment of this invention are alkylaryl polyether alcohols such as isooctylphenoxyethanol (sold as "Triton N–100" by Rohm & Haas Company, Philadelphia, Pa., U.S.A.).

Among the other surfactants which can be used in this invention are: Sodium alkylnaphthalenesulfonate (sold as "Alkanol B" by the Du Pont Corporation, Wilmington, Del., U.S.A.); sodium cetylsulfate (sold as "Avitex SF" by the Du Pont Corporation of Wilmington, Del.); sodium oleyl sulfate (sold as "Duponol LS" by the Du Pont Corporation of Wilmington, Del., U.S.A.); sodium N-methyl-N-oleyltaurate (sold as "Igepon T" by General Aniline Film Corporation of New York, N.Y.); sodium oleylisethionate (sold as "Igepon A" by General Aniline Film Corporation of New York, N.Y.); sodium dodecyl benzenesulfonate (sold as "Santomerse No. 1" by the Monsanto Chemical Corp., St. Louis, Mo.); sorbitan monopalmitate (sold as "Span 40" by the Atlas Powder Company, Wilmington, Del.);

$$C_4H_9CH(C_2H_5)CH_2OSO_3Na$$

(sold as "Tergitol 08" by Union Carbide Corporation, New York, N.Y.);

$$P—C_8H_{17}C_6H_4(OCH_2CH_2)_2OSO_3Na$$

(sold as "Triton W–30" by Rohm & Haas Co., Philadelphia, Pa.); $P—C_8H_{17}C_6H_4(OCH_2CH_2)_nOH$ (sold as "Triton X–100" by Rohm & Haas Co., Philadelphia, Pa.

(X) The silicone defoamer used in the preferred composition of this invention is sold by Nopco Chemical Co., Newark, N.J., as Nopco NDW. It is a dark yellow liquid silicone having a minimum of 0.5% moisture content and a specific gravity range of 0.87 to 0.91.

Some of the most effective antifoam agents are among the dimethyl silicones. Minimum concentrations of 9 parts per million are effective in the practice of this invention. The dimethyl silicone fluids are obtainable from the Dow Corning Corporation under the trade designation "200 Fluids," from the General Electric Co., Silicone Products Division.

Other foam preventing agents which can be used in the practice of this invention include 2-ethylhexanol, frequently referred to as "octyl alcohol"; diisobutylcarbinol (2,6-dimethyl-4-heptanol). Additional antifoaming agents are fatty acids and fatty acid esters such as those set forth in U.S. Pat. No. 2,304,304, which issued on Dec. 8, 1942, and in U.S. Pat. No. 2,390,212, which issued on Dec. 4, 1945, both to J. H. Fritz; pine oil, alkyl lactates; higher ethers such as 2-(di-tert-amylphenoxy) ethanol, as set forth in U.S. Pat. No. 2,407,589, which issued on Sept. 10, 1946, and U.S. Pats. Nos. 2,453,351 and 2,453,352, which issued Nov. 9, 1948, to H. E. Tremain and L. R. Bacon; organic phosphates and metallic soaps.

The heat-sensitive element of this invention comprises a heat-sensitive coatable composition containing at least two specific polymeric components coated on a suitable support by a well-known manner, such as extrusion, hopper coating, dip coating, doctor blade coating, etc. Suitable supports include paper, e.g., 8 pound (20 x 30/480) Tuscan WS Grade from the Peter J. Schweitzer Division of the Kimberly Clark Corporation; glassine, vegetable parchment; film base, e.g., cellulose acetate butyrate, cellulose acetate propionate, etc.; polyester film base, e.g., polyethylene terephthalate, etc.

To the polymer-containing composition can be added addenda to accomplish a variety of purposes, such as agents to modify the flexibility of the layer, to modify the surface characteristics, to impart color to the layer; to modify the adhesivity of the heat sensitive layer to its support; other plasticizers, tackifiers, and surfactants. A variety of dyes may be added to achieve specific colors.

Water is an excellent dispersing medium for the components of this invention.

The above addenda may, without affecting crystallization, have beneficial effects to both surfaces of the heat-sensitive layer, for example, increasing its adhesion to its support; while on the surface facilitating intimate contact between the coating layer and the copy paper document during transfer of the coating, at the same time preventing optical contact.

In preparing the heat-sensitive elements according to the invention, a single coating of the polymeric coating composition is normally applied to the support at a thickness to give a predetermined thickness when dried. Alternatively, the coating layer can be built up of two or three coats. The dry thickness of the heat-sensitive layer can vary over a wide range. For example, a suitable coating thickness can be in a range of about 0.05 to about 5.0 mils. A preferred coating thickness is found to be in a range of about 0.10 to about 3.0 mils.

The preferred method for activating heat areas of the heat-sensitive coating, as noted supra, is to contact the heat-sensitive coating with a printing element such as that described in U.S. Pat. No. 3,161,457, which issued on the application of Hans Schroeder et al., on Dec. 15, 1964, and in which high-temperature images of selected configuration can be made in an otherwise substantially planar cool surface of the type member. In the embrace of the concept of the invention there may be supplied for the hot pattern for the impression means of the master sheet hot letter press type, hot scribers, or any pattern source of all heat which may be pressed into the master sheet. An uncontrolled source of infrared radiation cannot be used in this system since thermographically-formed patterns in a control sheet, generally, will not have sufficient heat content to work satisfactorily with the master sheet coating contemplated by this invention.

EXAMPLE I

A heat-sensitive element of the instant invention was prepared as follows: 17 grams of N-ethyl-p-toluene sulfonamide, 2 grams of the glycerol ester of hydrogenated rosin, 1 gram of chlorinated rubber, 2 grams of Oil Black BT dye, and 1 gram of carbon black were mixed together, heated until a homogeneous dispersion was formed at a temperature of approximately 60° C. The dispersion was recrystallized upon a lowering of the temperature.

To 20 grams of the mixture prepared supra was added 42.7 grams of a 15% solution of polyvinylacetate in ammonia solution, 10 grams of water, 1 drop of isooctylphenoxyethanol, and 1 drop of dimethyl silicone antifoaming agent. The composition mixture was ground in an attritor until the particle size was homogeneous. After thoroughly mixing the above composition while holding it at a temperature of about 25° C., the composition was doctor blade coated onto a sheet of base paper consisting of 8 lb. (20 x 30/480) Tuscan WS Grade from the Peter J. Schweitzer Division of the Kimberly Clark Corporation at a thickness such as the dry coating weight was approximately 13 lbs. per ream, 25 x 38/500 (3300 sq. ft.). The coating was then dried to remove the water and calendered to give a flat, smooth surface. The finished product was exposed to a printing head of the type set forth in U.S. Pat. No. 3,161,457, to H. Schroeder et al., which issued on Dec. 15, 1964. The ink-containing coating was heated by said printing member causing the layer to become tackified in those areas corresponding to the character areas of the printing head. The heat-sensitive element while retaining its tacky state was exposed to copy sheets of paper, supported by rollers. The transfer of tacky material produced a good black-blue production of a pattern on the copy paper. The transfer step was repeated several times on several copy sheets from a single activation of the heat-sensitive coating.

EXAMPLE II

595 grams of N-ethyl-p-toluene sulfonamide, 70 grams of the glycerol ester of hydrogenated rosin, 35 grams of

chlorinated rubber, 70 grams of Oil Black BT dye, and 35 grams of carbon black were mixed together, heated until a homogeneous dispersion was formed at a temperature of approximately 60° C. The material was at least partially recrystallized upon a lowering of temperature.

To 18 grams of the above composition was added 1 gram of Oil Black BT, 1 gram of carbon black, 15 grams of a 15% solution of polyvinylacetate copolymer in ammonia solution, 15 grams of water, 2.1 grams of sodium silicate in alkaline solution, 1 drop of dimethyl silicone defoamer, and 1 drop of isooctylphenoxyethanol. The composition mixture was ground in an attritor until the particle size was homogeneous. After thoroughly mixing the above composition while holding it at a temperature of 25° C., the composition was doctor blade coated onto a sheet of base paper consisting of 8 lb. (20 x 30/480) Tuscan WS Grade from the Peter J. Schweitzer Division of the Kimberly Clark Corporation at a thickness such as the dry coating weight was approximately 13 lbs. per ream, 25 x 38/500 (3300 sq. ft.). The coating was then dried to remove moisture and calendered. The finished product was exposed to a printing head of the type set forth in U.S. Pat. No. 3,161,457 to H. Schroeder et al., which issued on Dec. 15, 1964. The ink-containing coating was heated from the back (uncoated) side by said printing member causing the layer to become tackified in those areas corresponding to the character areas of the printing head. The heat-sensitive element while retaining its tacky state was exposed to copy sheets of paper supported by rollers. The transfer of tacky material produced a good black-blue production of a pattern on the copy paper. The transfer step was repeated several times on several copy sheets from a single activation of the heat-sensitive coating.

EXAMPLE III

26.6 grams of N-ethyl-p-toluene sulfonamide, 3.14 grams of the glycerol ester of hydrogenated wood rosin, 1.56 grams of chlorinated rubber, 4.14 grams of Oil Black BT dye, and 2.56 grams of carbon black were mixed together and heated until a homogeneous dispersion formed at a temperature of approximately 60° C. The components were recrystallized by lowering the temperature of the dispersion.

To 20.0 grams of the above composition was added: 15.0 grams of a 15% solution of polyvinylacetate copolymer in ammonium hydroxide; 15.0 grams of water, 2.1 grams of a 38% solution of sodium silicate in sodium hydroxide, 1 drop of 2,4,7,9-tetramethyl-5-decyne-4,7-diol, and 1 drop of a dimethylsilicone antifoaming agent. The foregoing mixture was ground in an attritor until the composition exhibited a homogeneous particle size. After thoroughly mixing the above composition while holding it at a temperature of 25° C., the composition was doctor blade coated onto a sheet of base paper consisting of 8 lb. (20 x 30/480) Tuscan WS Grade from the Peter J. Schweitzer Division of the Kimberly Clark Corporation at a thickness such as the dry coating weight was approximately 13 lbs. per ream, 25 x 38/500 (3300 sq. ft.). The coating was then dried to remove the water and calendered. The finished product was exposed to a printing head of the type set forth in U.S. Pat. No. 3,161,457 to H. Schroeder et al., which issued on Dec. 15, 1964. The ink-containing coating was heated by said printing member causing the layer to become tackified in those areas corresponding to the character areas on the printing head. The heat-sensitive element while retaining its tacky state was exposed to copy sheets of highly absorbent sheet paper supported by rollers. The transfer of tacky material produced a good black-blue production of a pattern on the copy paper. The transfer step was repeated several times on several copy sheets from a single activation of the heat-sensitive coating.

EXAMPLE IV

The heat-sensitive composition of the present invention was prepared as follows: 42.7 pounds of N-ethyl-p-toluene sulfonamide, 5.02 pounds of the glycerol ester of hydrogenated rosin, 2.51 pounds of chlorinated rubber, 6.65 pounds of Oil Black BT dye, and 4.12 pounds of carbon black were mixed together and heated until a homogeneous dispersion formed at circa 60° C. The composition was then cooled until a state of at least partial crystallization was achieved. To the foregoing was added 1.5 pounds dry of casein in solution and 6.9 pounds of a 15% solution of polyvinylacetate copolymer in ammonium hydroxide solution, and 2.5 pounds of a 32% solution of sodium silicate. The mixture was ground in an attritor until the particle size was homogeneously small.

Some of the advantages of the present invention have been described in the foregoing part of the specification. Many others are apparent. For example, the elements produced by the present invention are permanent in storage; the heat-sensitive layers are unusually resistant to wear, abrasion, crackling, etc. The process in which the elements are employed are normally completely dry, thus not requiring chemicals, solvents and the like. Moreover, the process for copies reproduced do not require a stabilizing step. The copies produced by process of the invention are permanent and are not affected by high temperature or humidity. The copies are ideally suited for archival storage for these reasons. Since high resolution and high quality are obtained in the copies, they are also acceptable for use in the fields of industry and commerce.

What is claimed is:

1. A heat-sensitive element for use in a thermal printing process using hot printing members in heat-conductive contact with the element, said element comprising a support of paper, a heat-sensitive layer of a thermoplastic composition coated on said support, said composition comprising at least three organic filming materials capable of at least partial crystallization, said film-forming materials comprising at least one organic acid ester, and at least one modified vinyl acetate polymer; a tackifier for said film-forming materials, at least one plasticizer for said film-forming materials; at least one organic dye; carbon black particles; and at least one alkali metal silicate; said composition having an original tackifying temperature, at which temperature said composition will undergo transition from a state of at least partial crystallinity to an amorphous state, said composition having the property of remaining for a substantial period of time after said transition to the amorphous state at a temperature substantially below said original tackifying temperature, wherein said organic film-forming materials comprise from 12 to 27%, by weight, of said composition; said tackifier comprises from 2.5 to 4%, by weight, of said composition; said plasticizer comprises from 50 to 70%, by weight, of the said composition, and wherein said organic dyes comprise from 2 to 15%, by weight, of said composition, all weights being on a dry basis; and wherein the plasticizer is N-ethyl-p-toluene sulfonamide, the organic acid ester is glycerol ester of hydrogenated rosin, the tackifier is chlorinated rubber, the vinyl acetate polymer is modified by carboxylation until soluble in ammonium hydroxide, and the metal silicate is sodium silicate.

References Cited

UNITED STATES PATENTS

2,462,029	2/1949	Perry.	
2,678,284	5/1954	Holt.	
2,885,307	5/1959	Rigterink et al.	
3,117,100	1/1964	Cox et al.	260—27
3,260,612	7/1966	Dulmage et al.	117—36.1
3,261,023	7/1966	Light et al.	117—36.1
3,342,623	9/1967	Dulmage et al.	117—36.1

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101—470, 473; 117—138.8, 155; 260—27

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,519,464 July 7, 1970

Lester Alfred Balster et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 58, "heat-reducing" should read -- heat-inducing --. Column 3, line 1, after "printing" insert -- pressures --; line 2, "application" should read -- applications --; same line 2, cancel "pressures".

Signed and sealed this 16th day of February 1971.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents