

1

3,519,463

ADHESIVE INK

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No Drawing. Filed Mar. 1, 1967, Ser. No. 619,609

Int. Cl. B41c 1/06; B41m 5/02

U.S. Cl. 117—36.1

1 Claim

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 a 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, exhibits a tackifying 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 coating composition of this invention remains tacky while the tacky coating is brought into contact with a plurality of copy papers to which copy papers the heat-sensitive coating is selectively transferred in the image areas.

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

	Percentage by weight, dry basis
(I) Hydrogenated rosin	5-20
(II) Polyvinylacetate copolymer	5-20
(III) Film-forming transfer regulator	1-4
(IV) Plasticizer	50-70
(V) Carbon black	4-15
(VI) Diazo dye	2-15

The present invention relates to thermal printing composition. More specifically, this invention relates to a potentially tacky, adhesive, transferable, colored composition that has the property of remaining tacky-adhesive when heated to a tackifying temperature and remaining in a tacky-adhesive state for a substantial interval of time after being cooled to a temperature less than the original tackifying temperature required to render the composition tacky, so that the composition when coated onto a substrate can be depleted in stratigraphic, discrete decrements.

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 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 by unprinted portions of a page, thus the temperature does not increase at such areas and the copying paper remains unaffected in such areas. 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.

The persistent tacky state of an otherwise nontacky composition was disclosed in an adhesive in U.S. Pat. No.

2

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 therefor 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 transfer inherent in sealing an adhesive material to a receptor surface.

The object of this invention is to provide a potentially adhesive composition which can be coated upon a substrate to form a matrix which upon heating by heat other than infrared radiation, that is, by conduction, changes 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 changed to a tacky state.

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

Another object of this invention is to provide an ink coating composition in which no impact printing 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 transfer of tackified material from the matrix thus formed successively 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 scribe, thus avoiding thermal diffusion and obtaining a well-resolved tacky image in the heat-sensitive layer. Copies can be made from the tacky layer after an initial, instantaneous 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.

An extended tacky state at a temperature lower than the tackifying temperature after activation is an idiosyncratic characteristic of the composition of this invention.

The thermally sensitive paper is coated on the side facing the copy paper and away from the printing head with a novel composition characterized in that when heated, it becomes tacky or sticky, and retains this tackiness or stickiness for an extended period of time after the novel

composition has been reduced to a temperature below that initially required to render it tacky. Upon activation of a thermal pattern in the printing head, corresponding areas of the coating of the novel composition of this invention become tacky and adhere to copy paper placed in contiguous juxtaposition with the thermally sensitive paper. The copy paper and the thermally sensitive paper are subsequently separated. Upon separation, the copy paper carries with it a discrete stratum of the novel coating composition from those areas delineated by the heat pattern produced by the printing head of U.S. Pat. No. 3,161,457 which issued Dec. 15, 1964.

The tackiness of the composition of this invention is accounted for, partially by a cunctative recrystallization after activation. 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 thermal plastic polymer composition the tackifying temperature is the first order transition temperature, and for a completely amorphous thermal plastic 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, and 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 term "delayed tack" is hereby defined as an inherent idiosyncrasy of a composition having (a) at normal conditions a crystalline or semicrystalline state, (b) the capability of transition, upon heating to an original tackifying temperature, to an essentially noncrystalline, amorphous state in which the composition has a substantially reduced tackifying temperature, (c) the property of remaining for a substantial period of time after said transition in said state having a substantially reduced tackifying temperature, and (d) the property of stratigraphic transferability at a temperature above the reduced tackifying temperature and below the original tackifying temperature.

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 laminae, electrically nonconducting material, each laminae 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. While this invention is denominated a planographic heating element, the planographic member which gives rise to this invention is the master sheet and not the planographic printing head.

The instant invention does not involve infra-red 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 composi-

tion 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 data in terms of a temperature above that of room temperature. Such printing members include relief surface, hot-type bodies, such as branding irons, thermographic plano-sheets, and type bodies having a planar surface which is differentially heated.

The composition of this invention is illustrated by the four examples, A, B, C, and D set forth below:

	Percentage by weight (dry coating basis)			
	A	B	C	D
(I) Hydrogenated rosin with a softening point range of 70-100° C. and an acid number of 100-200	20.03	19.95	17.50	18.00
(II) Polyvinylacetate copolymer	12.50	12.43	8.90	11.00
(III) Casein	2.20	2.53	.00	.00
(IV) Polyvinylalcohol	.00	.00	1.20	1.00
(V) Plasticizer	56.00	55.87	64.60	50.00
(VI) Carbon black	4.99	4.97	4.90	15.00
(VII) Diazo dye	3.00	3.02	2.90	5.00
(VIII) Defoaming agent	0.10	0.18	.00	.00
(IX) Surfactant	0.20	0.18	.00	.00
(X) Anti-blocking agent	0.93	0.97	.00	.00

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

Percentage by weight,
dry basis

(I) Plasticizer	50-70
(II) Hydrogenated rosin	5-20
(III) Diazo dye	2-15
(IV) Carbon black	4-15
(V) Casein or polyvinylalcohol	1-4
(VI) Polyvinylacetate copolymer	5-20

(I) The hydrogenated wood rosin is comprised predominantly of mixtures 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% leopimaric acid, dihydroabietic acid, tetrahydroabietic acid, and 7-10% pimaric acid, 10-14% isopimaric acid as well as other homologues of abietic acid.

Since good color stability is desired in the composition of this invention, hydrogenated rosin is used. Hydrogenation is one of the more satisfactory methods for decreasing the susceptibility of rosin to air oxidation.

The hydrogenation of wood rosin can be performed by the methods set forth in U.S. Pat. No. 1,167,264, which issued Jan. 4, 1916, to B. T. Brooks; U.S. Pat. No. 2,174,651, which issued May 17, 1937, to R. J. Byrkit, Jr.; and U.S. Pat. No. 2,094,117, which issued Sept. 28, 1937, and was reissued as Reissue No. 21,448, on May 14, 1940, to R. J. Byrkit, Jr.

A typical analysis of the various types of acids in 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 rosin 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 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 re-

sult, hydrogenated wood rosins are dihydroabietic and tetrahydroabietic acids.

The hydrogenated wood rosin used in the composition of this invention is dispersed in ammonium hydroxide. The percentage of solids, i.e., rosin, in the dispersion is approximately forty-five. An advantage in the use of ammonium hydroxide is that ammonium resinate, being extremely tacky, imparts rapid initial wet tack upon application. The hydrogenated rosin should exhibit an acid number ranging from 100 to 200; a saponification number in a range from 100 to 200; a color conforming to that of grades (U.S. rosin standard) X, WW, WG, N, M, or K, which are terms of the 1931 I.C.I. colorimetric coordinate system with its standard observer and standard illuminant C; (Grades I, H, G, F, E, and D can be used where the color is compatible with that of other addenda to the composition), a softening point being in the range from 70° C. to 100° C.; and a refractive index at 20° C. in the range of 1.52 to 1.55. The hydrogenated wood rosin dispersion of the preferred embodiment is sold as "Dresinol 205" by Hercules Powder Company, Wilmington, Del., U.S.A.

(II) The polyvinyl acetate copolymer (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 c.p.s. in a concentration of 86 gm./1000 cubic centimeters of ethyl alcohol at 20° C., using an Ostwald viscometer, and is used as a hot melting adhesive. The preparation of the polyvinylacetate copolymer is set forth in U.S. Pat. No. 2,413,239 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, which issued Feb. 10, 1948 (Reissue No. 23,164, Nov. 1, 1949) to N. G. Tompkins, and U.S. Pat. Nos. 2,508,341 and No. 2,508,343, which issued May 16, 1950, to W. K. Wilson.

(III) 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; and U.S. Pat. No. 2,044,282, which issued June 16, 1936, to H. F. Clickner. The precipitating agent may be lactic, sulfuric, or hydrochloric acid.

Commercial acid casein is obtained from skim milk by selective precipitation with lactic acid followed by whey removal. Solutions of acid casein are prepared by soaking casein in water and subsequently adding alkali, heating and stirring at 40-50° C. The minimum quantities of alkalis 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. 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.

(IV) Polyvinylalcohol can be used in place of casein or combined with casein as a film-forming transfer regulator in the practice of this invention. The polyvinyl alcohol suitable for the composition of this invention can be prepared in the processes set forth in U.S. Pat. No. 2,424,110 which issued July 15, 1947, to G. O. Morrison and T. P. G. Shaw and in U.S. Pat. No. 2,478,431 which issued Aug. 9, 1949, to G. S. Stamatoff. The polyvinyl alcohol should exhibit a specific gravity of 1.27 to 1.31; a specific

volume of 22.9 cubic inches per pound to 21.1 cubic inches per pound; a refractive index of 1.49 to 1.53 n_D^{25} ; and a specific heat of 0.4 calorie per gram per degree centigrade. A commercial grade of polyvinyl alcohol suitable for the composition of this invention is that sold as "Elvanol® 50-42" by E. I. Du Pont de Nemours & Co., Inc., Wilmington, Del. U.S.A.

(V) 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.

(VI) Carbon blacks are usually prepared by the impingement 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").

(VII) The diazo dye of the preferred embodiment is Oil Black BT (for example, that sold by Allied Chemical and Dye Corporation), which has 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.

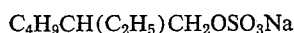
(VIII) The defoaming agent of the preferred embodiment is a mixture of a hydrocarbon and a nonionic fatty compound (sold as "Nopco NDW" by Nopco Chemical Company, Newark, N.J., U.S.A.). It is a dark yellow liquid exhibiting a moisture content of 0.5%, an acid value of 8.0, and a specific gravity range 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," and from the General Electric Co., Silicone Products Division, Schenectady, N.Y.

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, U.S. Pats. No. 2,453,351 and No. 2,453,352, which issued Nov. 9, 1948, to H. E. Tremain and L. R. Bacon; organic phosphates, metallic soaps and, of course, kerosene.

(IX) The gross effects of surface-active compounds are styled as detergency, wetting, dispersion and emulsification. The surface-active agent of the preferred embodiment of this invention is 2,4,7,9-tetramethyl-5-decyne-4,7-diol, a ditertiary acetylenic glycol, (sold as "Surfynol® 104" by Air Reduction Chemical & Carbide Co., a Division of Air Reduction Company, Inc., 150 E. 42nd St., New York, N.Y.). It is a white solid compound which will undergo volatilization without degrading when heated to its boiling point, 260° C. Its melting point is 37-38° C.

The compound 3,6-dimethyl-4-octyne-3,6-diol (sold as "Surfynol® 82" by Air Reduction Company, Inc.) can also be used as a nonionic, nonfoaming surface-active agent.

Among the other surfactants which can be used in this invention are: Sodium alkyl-naphthalenesulfonate (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 oleylisothionate (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.);



(sold as "Tergitol 08" by Union Carbide Corporation, New York, N.Y.); $\text{p-C}_8\text{H}_{17}\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_2\text{OSO}_3\text{Na}$ (sold as "Triton W-30" by Rohm & Haas Co., Philadelphia, Pa.); $\text{p-C}_8\text{H}_{17}\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_n\text{OH}$ (sold as "Triton X-100" by Rohm & Haas Co., Philadelphia, Pa.).

(X) Antiblocking agents are used to prevent the sticking or blocking of coated surfaces in contact with each other at temperatures lower than the tackifying temperature. The use of an antiblocking agent obviates slipsheeting and has no tendency to rub off.

The antiblocking agent of the preferred embodiment of this invention is comprised (by weight) of 75% octadecanamide (stearamide), 22% hexadecanamide (palmitamide), and 3% 9-octadecanamide (oleamide). The maximum quantity of unreacted fatty acid is 5% (by weight). The minimum melting of the mixture is 98° C.; the maximum codine value is 5. The mixture exhibits a specific gravity of approximately 0.960; 0.5% moisture; a flash point of approximately 225° C.; and a fire point of approximately 250° C. The fatty acid derivatives of the preferred embodiment are sold as "Armud HT" by Armour Industrial Chemical Company, a division of Armour and Company, 110 N. Wacker Drive, Chicago, Ill.

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 including 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; plasticizers, tackifiers, and surfactants.

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 thick-

ness 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 scribes, or any pattern source of all heat which may be pressed into the master sheet.

EXAMPLE

A heat-sensitive element of the instant invention was prepared as follows: 40 pounds of N-ethyl-p-toluene sulfonamide, 59.53 pounds of polyvinylacetate copolymer in a 15% aqueous ammoniacal solution (8.93 pounds of solids), (sold as "Gelva C5-V16R" by Monsanto Chemical Company, St. Louis, Mo., U.S.A.); 3.56 pounds of carbon black; 2.14 pounds of Oil Black BT dye; 10.00 pounds of a 15% solution of casein in an aqueous ammoniacal solution (1.5 pounds of casein solids), (sold as "Casein FF-30" by The Borden Co., New York, N.Y., U.S.A.); 0.07 pound of a defoaming agent (sold as "Nopco NDW" by Nopco Chemical Company, Newark, N.J., U.S.A.); 0.14 pound of surface-active agent (sold as "Surfynol® 104" by Air Reduction Chemical & Carbide Co., a division of Air Reduction Company, Inc., 150 E. 42nd St., New York, N.Y., U.S.A.); 0.70 pound of antiblocking agent (sold as "Armud HT" by Armour Industrial Chemical Company, a division of Armour and Company, 110 N. Wacker Drive, Chicago, Ill., U.S.A.) were mixed together for two hours in a 30-5 attritor. 31.78 pounds of hydrogenated rosin emulsion (45% solids by weight), (sold as "Dresinol 205" by Hercules Powder Company, Wilmington, Del., U.S.A.) and 10.30 pounds of water were added to the foregoing composition. After the thoroughly mixing, the above composition was coated onto base paper consisting of 8 pound (20 x 30/480) Tuscan WS Grade from the Peter J. Schweitzer Division of the Kimberly Clark Corporation at a thickness such that the dry coating weight was approximately thirteen pounds per ream 25 x 38/500 (3300 sq. ft.). The coating was then dried. 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 Dec. 15, 1964. The coating composition was heated by said printing member causing the coating layer to become tacky in those areas corresponding to the character areas of the printing head. The heat-sensitive element was simultaneously exposed to a copy sheet of highly absorbent sheet paper supported by rollers. The transfer of tacky material produced a good black-blue pattern on the copy paper. The transfer step was repeated five times seriatim on five additional copy sheets from a single activation of the heat-sensitive coating.

What is claimed is:

1. A heat-sensitive master sheet for use in a thermal printing process, said master sheet comprising in combination

(A) a paper support;

(B) a coating on said support having a composition comprising:

(1) hydrogenated rosin

(2) vinyl acetate polymer modified by carboxyla-

tion to be soluble in ammonium hydroxide solution

- (3) casein as a film-forming transfer regulator
- (4) N-ethyl-p-toluenesulfonamide as a plasticizer
- (5) an organic dye
- (6) carbon black wherein in the dry composition the weight of hydrogenated rosin ranges from 5% to 20% of the dry coating composition, the weight of vinyl acetate polymer modified by carboxylation ranges from 5% to 20%, the weight of casein ranges from 1% to 4%, the weight of N-ethyl-p-toluenesulfonamide ranges from 50% to 70%, the weight of the organic dye ranges from 2% to 15%, and the weight of carbon black ranges from 4% to 15%.

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MURRAY KATZ, Primary Examiner

U.S. Cl. X.R.

15 101—470, 473; 117—138.8, 155; 260—27