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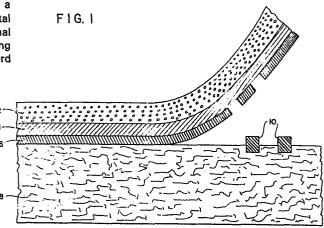
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- 71) Applicant: Exxon Research and Engineering Company P.O.Box 390 180 Park Avenue Florham Park New Jersey 07932(US)
- (72) Inventor: Luebbe, Ray Henry, Jr. 165 Lake Destiny Trail Maitland Florida(US)

- 72 Inventor: Miro, Frank 241 Canterclub Trail Longwood Florida(US)
- 72 Inventor: Robbins, David J. 8687 Chevington Chase Pickerington Ohio(US)
- (2) Inventor: Palermiti, Frank Michael 23 Locke Drive Pittsford New York(US)
- (72) Inventor: Carter, Mark Allen 1001 Esplanada Way 36-D, Casselberry Florida(US)
- (4) Representative: Pitkin, Robert Wilfred et al, ESSO Engineering (Europe) Ltd. Patents & Licences Apex Tower High Street New Malden Surrey KT3 4DJ(GB)

(54) Electrosensitive transfer film.

(57) An electric discharge transfer film material comprising at least two layers, the first of which is (a) an electrically anisotropic support layer (2) having electroconductive particles dispersed in a resin matrix. The electroconductive particles can be graphite particles having a particle size between 0.1 to 20 microns, carbon black particles having a particle size between 25 to 500 millimicrons, or metal powders, and (b) at least one thermal or electrothermal transfer layer (4) in the form of a resin layer capable of being broken by electrical discharge and transferred to a record sheet, e.g., paper.



1 BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a composite 4 electrosensitive transfer material, and more particu-5 larly, to a reusable electrosensitive transfer film.

6 2. Description of the Prior Art

7 In recent years, various systems have been 8 proposed for the rapid transmission and/or recording of 9 information. One such system is an electric discharge 10 recording system.

The electric discharge recording system is a 11 process which comprises applying an electrical signal of 12 several hundred volts and several watts in the form of 13 an electric voltage, and breaking a semiconductive 14 recording layer on the surface of a recording layer by 15 electric discharge, thereby to form an image on the 16 recording layer or on a substrate superimposed on the 17 recording layer. This process is a "direct imaging" 18 process which does not require processing operations 19 such as development and fixation, and is in widespread 20 use as a simple recording process. For example, the 21 process finds applications in facsimile systems, various 22 measuring instruments, recording meters, record displays 23 in computers, and processing of electrostencil master 24 sheets. 25

In the electric discharge recording, a discharge recording stylus is directly contacted with the recording surface of an electric discharge recording material. Discharging is performed through the stylus to break the recording layer, and to form an image on the recording surface.

A more recent development is disclosed by 1 Nakano et al in U.S. Patent 4,163,075 and relates to the use of an electrosensitive transfer film. To record 3 with this type of film it is laid over an untreated sheet of a receiving medium, such as paper, and an 5 electric discharge stylus is moved in a regular pattern across the back of the transfer film. Provision is generally made to ground either one edge or the front surface of the transfer film. When a voltage on the 9 order of 150 to 200 volts is applied to the stylus, 10 current flows through the sheet and matter is caused to 11 be transferred to the receiving sheet, e.g., paper. 12

The film disclosed by Nakano et al in U.S.
14 Patent 4,163,075, comprises three layers, namely a film
15 support layer and two transfer layers. The support
16 layer is composed of a metal powder-containing resin
17 layer, e.g., electrolytic copper powder having an
18 average diameter of 2 microns dispersed in a vinyl
19 chloride resin.

Numerous disadvantages appear to exist with 20 the use of the products disclosed in the Nakano et al 21 For example, the use of small metal particles 22 in the support layer results in a high cost product 23 affecting the commercial success of the product. A 24 need therefore exists for a transfer sheet exhibiting 25 improved image quality that can be produced at a low 26 cost compared to other commercially available products. 27

SUMMARY OF THE INVENTION

28

It is an object of this invention to provide 30 an electric discharge transfer film which is free from the disadvantages described hereinabove.

According to the present invention, an elec-1 tric discharge recording material is provided which 2 comprises (a) an electrically anisotropic support 3 layer having electroconductive particles dispersed in a 4 resin matrix wherein said electroconductive particles 5 graphite particles having a particle size 6 between 0.1 to 20 microns, (2) carbon black particles 7 having a particle size between 25 to 500 millimicrons. or (3) metal powders; and (b) at least one thermal or 9 electrothermal transfer layer in the form of a resin 10 layer capable of being broken by electrical discharge 11 and transferred to a record sheet. A preferred resin 12 matrix comprises a phenoxy resin of the formula: 13

18 where n is about 100.

One embodiment of the present invention is an 19 electric discharge recording material which comprises: 20 (a) a semiconductive resin layer capable of being 21 broken by electric discharging which has a surface 22 resistance of 10^5 to 10^{16} ohms and a volume resistance 23 of 10^3 to 10^{14} ohms-cm; (b) an electroconductive elec-24 trically anisotropic resin layer containing electro-25 conductive particles such as graphite, carbon black or 26 metal powders as described above, which is laminated on 27 one surface of the semiconductive resin layer (a); and 28 a conductive layer having a surface resistance of not 29 more than 10^4 ohms and a volume resistance of not more 30 than 10^2 ohms-cm, which is laminated on the other 31 surface of the semiconductive resin layer (a). 32

- Another embodiment of the present invention is an electric discharge recording material which comprises at least one resin layer capable of being thermally or electrothermally transferable to another substrate, and an electrically anisotropic carbon black or graphitecontaining resin layer which is laminated on one surface of one resin layer.
- Still another embodiment of the present 8 invention is an electric discharge recording material, 9 e.g., film, which comprises at least one resin layer 10 capable of being thermally or electrothermally trans-11 ferred to another substrate and an electrically aniso-12 tropic carbon black or graphite-containing support 13 The graphite and carbon black particles exhibit 14 particle sizes previously defined herein. 15 layer is laminated onto one surface of the resin layer. 16
- Other objects, features and effects of this invention will become more apparent from the following detailed description considered with the drawings wherein:
- 21 Figure 1 is an expanded sectional view of the 22 transfer film of this invention.

23 DETAILED DESCRIPTION OF THE INVENTION

- The film structure, as illustrated in FIGURE 1, comprises an electrically anisotropic (unidirectionally conductive) electroconductive particle-support layer 2 and two transfer layers, namely layers 4 and 6.
- When a graphite-containing resin is employed as layer 2, it generally contains between 5 to 65% and preferably between 15 to 45% by weight graphite based

on the weight of the resin. Best results are obtained 1 when the layer contains between 25 and 35% by weight 2 graphite, based on the weight of the resin. The par-3 ticle diameter of the graphite used in this layer 4 is also critical to the successful practice of the 5 subject invention. Generally, the particle size is 6 generally between 0.1 to 20 microns, and preferably 7 between 0.1-5 microns, with best results being achieved 8 with particles between 0.1 and 1 microns. 9

According to an embodiment of this invention, 10 graphite particles useful in the anisotropic support 11 layer can be prepared by grinding the graphite particles 12 in the presence of water or other solvent having sub-13 stantially the same freezing and vapor pressure proper-14 ties as water, e.g., tertiary butyl alcohol, cyclohexane, 15 benzene, dioxane, and para-xylene. Generally, between 16 about 70 and 80% by weight of the slurry is water or 17 solvent, as defined herein, the balance being solids, 18 namely the graphite particles. It is understood 19 that the amount of water or solvent employed is not 20 critical and can vary over wide ranges both below 70% 21 and above 80% because the solvent or water is eventually 22 driven off in accordance with this process. Grinding 23 takes place for a period of time sufficient to achieve 24 substantially complete dispersion of the graphite 25 particles in the solvent or water. Generally, such 26 grinding takes place between 8 and 16 hours to achieve 27 the substantial dispersion of the graphite particles. 28 The term "substantial", as used in this context, means 29 at least 95% of the graphite being dispersed in the 30 water or solvent with as little as possible agglomeri-31 zation of the graphite being present. Grinding is 32 generally accomplished by subjecting the slurry to a 33 ball mill, sand mill or any other dispersion technique 34 well-known to those of ordinary skill in the art. 35

- 1 is particularly preferred to reduce agglomerates of
- 2 graphite and to obtain substantial dispersion of the
- 3 graphite particles with an "ATTRITOR", Model 01, made by
- 4 Union Process Company, Dayton, Ohio.
- A binding polymer is added to the graphite
- 6 slurry, either during the grinding step or immediately
- 7 after the grinding step for the purpose of forming a
- 8 film or coating on the individual particles of graphite.
- 9 The polymer employed is to be soluble in the water or
- 10 solvent of the slurry. Suitable polymers include, e.g.,
- 11 polyvinyl alcohol, gelatin or methyl cellulose.
- 12 Freezing of the slurry is achieved by lowering
- 13 the temperature to a point wherein the physical state of
- 14 the solvent changes from liquid to solid. The frozen
- 15 slurry is then dried, under conditions such that the
- 16 water solvent present is caused to sublime, i.e., the
- 17 solid is directly converted to the vapor form, without
- 18 passage through the liquid state. The process results
- 19 in the formation of a substantial amount of undamaged
- 20 polymeric coated graphite particles having a diameter of
- 21 at least 0.2 microns. By substantial amount, it is
- 22 intended that at least 90% of the particles have a
- 23 diameter of at least 0.2 microns.
- Sublimation of water, or other solvents used
- 25 in place of water, which exists in the solid state,
- 26 can be caused to change to a gaseous phase without an
- 27 intermediate phase, under well-known changes in pressure
- 28 alone, temperature alone, or a change in both temper-
- 29 ature and pressure. Generally, sublimation can be
- 30 produced under the influence of a high-pressure vacuum.
- It is critical that the graphite particles be
- 32 dispersed in the resin in such a manner the graphite is

not reduced in size to dust particles (under 0.1 micron).

Graphite particles are therefore dispersed in a resin,

generally in a molten state, by means of a high sheer

blender, e.g., a Waring blender, Cowl or Greer blenders,

rather than by impact grinding methods, e.g., ball

milling or dispersing in an attritor. The latter

methods cause the graphite particles to break up into

particles less than 0.1 micron size, adversely affecting

the electrically anisotropic properties of the layer.

10 When the electroconductive particles are 11 carbon black particles, the electrically conductive 12 carbon-black-containing resin of layer 2 contains 13 generally between 60 to 70% by weight carbon black. 14 Best results are obtained when the layer contains 65% by 15 weight carbon black, based on the weight of the resin 16 and carbon black. The particle diameter of the carbon 17 black used in this layer is also critical to the suc-18 cessful practice of the subject invention. Generally, 19 the particle size is generally between 25 and 500 20 millimicrons, with best results being achieved with 21 particles of about 350 millimicrons.

Carbon black is available from numerous commercial sources. For the present invention, channel blacks, furnace blacks, and thermal blacks are useful in the practice of the invention. Examples of suitable carbon blacks include those sold under the mark THERMAX.

The resin which constitutes the resin matrix in which the electroconductive particles of the anisotropic layer are dispersed may be any thermoplastic or thermosetting resin which has film-forming ability and electrical insulation (generally having a volume resistance of at least 10^7 ohms-cm). Generally, the matrix resin preferably has a great ability to bind the elec-

- 1 tro-conductive particle and can be formed into sheets or
- 2 films having high mechanical strength, flexibility and
- 3 high stiffness.
- A preferred resin that is useful in the resin 5 matrix, in which the electro-conductive particles are 6 dispersed, is a phenoxy resin of the formula:

- 11 wherein n is about 100.
- 12 A suitable phenoxy resin is sold by Union
- 13 Carbide Corporation under the tradename "PKHH". This
- 14 resin has the following characteristics:

15	Approximate Molecular Weight	20,000 to 30,000
16	Specific Gravity	1.18
17	Melt Flow (g/10 minutes at 220°C)	2.5-10
18	Ultimate Tensile Strength, psi	9,000-9,500
19	Ultimate Tensile Elongation,	50-100
20	Softening Temperature	100°C
21 22	Moisture Vapor Transmission	3.5 gms/mil/ 24 hrs/100 in.
23	Molecular Structure	As shown above

Generally, the matrix resin preferably has a great ability to bind the electroconductive particles, e.g., graphite, carbon black or the metal powders disclosed in U.S. Patent 4,163,075 or other useful electroconductive particles that may be used. These resins can be formed into sheets or films having high mechanical strength, flexibility and high stiffness.

Examples of suitable resins that can be used 1 in this invention are thermoplastic resins such as 2 polyolefins (such as polyethylene or polypropylene), 3 polyvinyl chloride, polyvinyl acetal, cellulose acetate, polyvinyl chloride, polyvinyl acetal, cellulose acetate, 5 polyvinyl acetate, polystyrene, polymethyl acrylate, polymethyl methacrylate, polyacrylonitrile, thermo-7 plastic polyesters, polyvinyl alcohol, and gelatin; and 8 thermosetting resins such as thermosetting polyesters, 9 epoxy resins, and melamine resins. The thermoplastic 10 resins are preferred, and polyethylene, polyvinyl 11 acetal, cellulose acetate, and thermoplastic polyesters 12 are especially preferred. 13

As is conventional in the art, additives such as plasticizers, fillers, lubricants, stabilizers, antioxidants or mold releasing agents may be added as needed to the resin in order to improve its moldability, storage stability, plasticity, tackiness, lubricity, etc.

Examples of the plasticizers are dioctyl 20 phthalate, dibutyl phthalate, dicapryl phthalate, 21 dioctyl adipate, diisobutyl adipate, triethylene glycol 22 di(2-ethyl butyrate), dibutyl sebacate, dioctyl azelate, 23 and triethylhexyl phosphate, which are generally used as 24 plasticizers for resins. The amount of the plasticizer 25 can be varied over a wide range according, for example, 26 to the type of the resin and the type of the plasticizer. 27 Generally, its amount is at most 150 parts by weight, 28 preferably up to 100 parts by weight, per 100 parts 29 by weight of the resin. The optimum amount of the 30 plasticizer is not more than 80 parts by weight per 100 31 parts by weight of the resin. 32

- Examples of fillers are fine powders of calcium oxide, magnesium oxide, sodium carbonate, potassium carbonate, strontium carbonate, zinc oxide, titanium oxide, barium sulfate, lithopone, basic magnesium carbonate, calcium carbonate, silica, and kaolin. They may be used either alone or as mixtures of two or more.
- The amount of the filler is not critical, and can be varied over a wide range according to the type of the resin, the type of the filler, etc. Generally, the amount is up to 1000 parts by weight, preferably not more than 500 parts by weight, more preferably up to 200 parts by weight.
- Usually its thickness is at least 3 microns.

 The upper limit of the thickness is not strict, but is
 advantageously set at 100 microns for the reason stated
 above. Preferably, the thickness is 5 to 60 microns,
 more preferably 10 to 40 microns.
- The semiconductive resin layer 4 laminated on the electroconductive particle-containing resin layer is broken by discharging. It has a surface resistance of 10 to 10^9 ohms, preferably 10^3 to 10^7 ohms, more preferably 10^4 to 10^6 ohms and a volume resistance of 1^1 to 10^6 ohms-cm, preferably 1^{10} to 10^5 ohms-cm, more preferably 10^2 to 10^4 ohms-cm.
- The semiconductive resin layer 4 can be formed by dispersing a conductivity-imparting agent in a resin matrix.
- The resin matrix forming a substrate for the semiconductive resin layer 4 may be chosen from those which have been described hereinabove about the non-

recording layer composed of an electroconductive particle-containing resin. The thermoplastic resins are especially suitable, and polyethylene, cellulose acetate and polyvinyl acetal are used advantageously. As needed, the resin may contain additives of the types described hereinabove such as plasticizers and fillers in the amounts described.

When a filler having a different conductivity 8 from the conductivity-imparting agent, generally having 9 a lower conductivity than the conductivity-imparting 10 agent, is included in the semiconductive resin layer 4, 11 the breakdown of the semiconductive resin layer 4 by 12 electric discharging occurs more sharply, and a recorded 13 image which is clearer and has a higher contrast can 14 Suitable fillers of this kind are fine be obtained. 15 powders of inorganic substances such as magnesium oxide, 16 calcium oxide, sodium carbonate, potassium carbonate, 17 strontium carbonate, titanium oxide, barium sulfate, 18 lithopone, basic magnesium carbonate, calcium carbonate, 19 silica, kaolin clay, and zinc oxide. They can be used 20 singly or as a mixture of two or more. 21 titanium oxide and calcium carbonate are especially 22 The average particle diameter of the filler 23 is generally 10 microns at most, preferably not more 24 25 than 5 microns, more preferably 2 to 0.1 microns. amount of the filler can be varied over a wide range 26 according to the type of the resin, etc. The suitable 27 amount is generally 10 to 2,000 parts by weight, prefer-28 ably 20 to 1,000 parts by weight, more preferably 50 to 29 400 parts by weight, per 100 parts by weight of the 30 resin. 31

The conductivity-imparting agent to be dis-33 persed in the resin to impart semiconductivity may be 34 any material which has conductivity and gives the

surface resistance and volume resistance described above to the resin layer. Generally, suitable conductivity-2 imparting agents have a specific resistance, measured 3 under a pressure of 50 kg/cm², of not more than 10⁶ ohms-cm. Examples of such a conductivity-imparting 5 agent include carbon blacks; metals such as gold, 6 silver, nickel, molybdenum, copper, aluminum, iron 7 and conductive zinc oxide (zinc oxide doped with 0.03 8 to 2.0% by weight, preferably 0.05 to 1.0% by weight, 9 based on the zinc oxide, of a different metal such as 10 aluminum, gallium, germanium, indium, tin, antimony or 11 iron); conductive metal-containing compounds such as 12 cuprous iodide, stannic oxide, and metastannic acid; and 13 zeolites. Of these, carbon blacks, silver, nickel, 14 suprous iodide, conductive zinc oxide are preferred, 15 and carbon blacks and conductive zinc oxide are more 16 preferred. The carbon blacks which also act as a 17 coloring agent are most preferred. 18

- Carbon blacks differ somewhat in conductivity according to the method of production. Generally, acetylene black, furnace black, channel black, and thermal black can be used.
- The conductivity-imparting agent is dispersed 23 usually in the form of a fine powder in the resin. 24 average particle diameter of the conductivty-imparting 25 agent is 10 microns at most, preferably not more than 5 26 microns, especially preferably 2 to 0.005 microns. 27 a metal powder is used as the conductivity-imparting 28 agent, it is preferably in a microspherical, dendric 29 or microlumpy form. Moreover, since a resin sheet 30 having the metal powder dispersed therein tends to be 31 electrically anisotropic if its particle diameter 32 exceeds 0.2 micron. Hence, the particle size of a metal 33 34 powder in the above-mentioned form to be used as a

conductivity-imparting agent for the semiconductive resin layer 4 or the conductive layer 6 should be at most 0.5 micron, preferably not more than 0.2 micron, more preferably 0.15 to 0.04 micron. Scale-like or needle-like powders can also be used, but should be combined with powders of the above forms.

The amount of the conductivity-imparting agent 7 to be added to the resin can be varied over a very wide 8 range according to the conductivity of the conductivity-9 imparting agent, etc. The amount is that sufficient 10 to adjust the surface resistance and volume resistance 11 of the semiconductive resin layer 4 to the above-12 For example, carbon blacks are mentioned ranges. 13 incorporated generally in an amount of 1 to 300 parts by 14 weight, preferably 2 to 200 parts by weight, more 15 preferably 3 to 150 parts by weight, per 100 parts by 16 weight of the resin. The other conductivity-imparting 17 agents are used generally in an amount of 3 to 500 parts 18 by weight, preferably 5 to 400 parts by weight, more 19 preferably 10 to 300 parts by weight, per 100 parts by 20 weight of the resin. 21

- The thickness of the semiconductive resin layer 4 is not critical, and can be varied over a wide range according to the uses of the final product, etc. Generally, its thickness is at least 2 microns, preferably 3 to 50 microns, more preferably 5 to 20 microns.
- According to the present invention, the conductive layer 6 is laminated on the other surface of the semiconductive resin layer 4.
- The conductive layer 6 plays an important role in performing electric discharge breakdown with high

accuracy by converging the current flowing through the 1 semiconductive resin layer at a point immediately 2 downward of the electric discharge recording stylus. 3 The conductive layer 6 has a surface resistance of not 4 more than 10^4 ohms, preferably not more than 5 x 10^3 ohms, more preferably 10^{-1} to 2 x 10^3 ohms and a volume 6 resistance of not more than 102 ohms-cm, preferably not 7 more than 50 ohms-cm, more preferably not more than 20 8 ohms-cm. 9

The conductive layer 6 having such resistance characteristics may be a conductive resin layer comprising a thermoplastic or thermosetting resin and a conductivity-imparting agent dispersed in it, a vacuum-deposited metal layer, or a metal foil layer.

The thermoplastic or thermosetting resin that 15 can be used in the conductive resin layer can also be 16 selected from those described hereinabove in connection 17 Of these, the thermowith the non-recording layer. 18 plastic resins, especially polyethylene, cellulose 19 acetate and polyvinyl acetal, are used advantageously. 20 The conductivity-imparting agent to be dispersed in the 21 resin may be chosen from those described above in 22 connection with the semiconductive resin layer. 23 blacks and metal powders are especially suitable. 24 Carbon blacks are particularly preferred over metals in 25 view of cost factors. 26

The conductivity-imparting agents are added in amounts which will cause the resin layer to have the electrical resistance characteristics described above.

The amounts vary greatly according to the type of the conductivity-imparting agent. For example, carbon blacks are used in an amount of generally at least 10 parts by weight, preferably 20 to 200 parts by weight,

- 1 more preferably 30 to 100 parts by weight; the other
- 2 conductivity-imparting agents especially metal powders,
- 3 are used in an amount of at least 50 parts by weight,
- 4 preferably 100 to 600 parts by weight, more preferably
- 5 150 to 400 parts by weight, both per 100 parts by weight
- 6 of the resin.
- 7 . As needed, the conductive resin layer may
- 8 contain the aforesaid additives such as plasticizers and
- 9 fillers in the amounts stated.
- 10 The thickness of the conductive resin layer is
- 11 not critical, and can be varied widely according to the
- 12 uses of the final products, etc. Generally, it is at
- 13 least 3 microns, preferably 3 to 50 microns, more
- 14 preferably 5 to 20 microns.
- The conductive layer 6 may be a vacuum-
- 16 deposited metal layer. Specific examples of the metal
- 17 are aluminum, zinc, copper, silver and gold. Of these,
- 18 aluminum is most suitable.
- The thickness of the vacuum-deposited metal
- 20 layer is not critical. Generally, it is at least 4
- 21 millimicrons, preferably 10 to 300 millimicrons,
- 22 more preferably 20 to 100 millimicrons. By an ordinary
- 23 vacuum-depositing method for metal, it can be applied to
- 24 one surface of the semiconductive resin layer 4.
- The conductive layer 6 may also be a thin
- 26 metal foil, for example, an aluminum foil. It can be
- 27 applied to one surface of the semiconductive resin layer
- 28 4 by such means as bonding or plating.
- It is understood that at least one of the
- 30 layers 4 and 6 may contain a coloring substance. Useful

- 1 coloring substances are carbon black, inorganic and 2 organic pigments, and dyes.
- Carbon black has superior conductivity and 3 4 acts both as a coloring substance and a conductivityimparting agent as stated above. Thus, when the semi-5 6 conductive resin layer or the conductive resin layer already contains carbon black as a conductivity-impart-7 8 ing agent, it is not necessary to add a further coloring The inclusion of other suitable coloring 9 substance. 10 substance is of course permissible.
- 11 Examples of pigments other than carbon black 12 include inorganic pigments such as nickel yellow, 13 titanium yellow, cadmium yellow, zinc yellow, ochre, 14 cadmium red, prussian blue, ultramarine blue, zinc 15 white, lead sulfate, lithopone, titanium oxide, black iron oxide, chrome orange, chrome vermilion, red iron 16 oxide, red lead and vermilion, and organic pigments of 17 18 the phthalocyanine, quinacridone and benzidine series such as aniline black, naphthol yellow S, hanza yellow 19 10G, benzidine yellow, permanent yellow, Permanent 20 21 Orange, Benzidine Orange G, Indanthrene Brilliant Orange GK, Permanent Red 4R, Brilliant Fast Scarlet, Permanent 22 Red F2R, Lake Red C, Cinquasia Red Y (Dup) (C. I. 46500), 23 Permanent Pink E (FH) [Quido Magenta RV 6803(HAR)], 24 and Phthalocyanine Blue (C.I. Pigment Blue 15). 25
- Examples of useful dyes are azoic dyes, 27 anthraquinonic dyes, thionidigo dyes, quinoline dyes, 28 and indanthrene dyes.
- The pigments and dyes described are used 30 either alone or in combination according to the color 31 desired to be formed on a transfer recording sheet.

The amount of the pigment or dye can be varied over a wide range according to the type, color intensity, etc. of the coloring substance. Generally, it is at least 1 part by weight, preferably 2 to 1,000 parts by weight, more preferably 3 to 500 parts by weight, per 100 parts by weight of the resin.

When the pigment or dye is to be incorporated in both of the semiconductive resin layer 4 and the conductive resin layer 6, it is desirable that pigments or dyes be of an identical color or have colors of the same series.

The composite electric discharge recording material of this invention can be formed by known methods, for example a melt-extrusion method, a melt-coating method, a melt-calendering method, a solution casting method, an emulsion casting method or combinations of these methods.

The composite electric discharge recording material of this invention described above is useful as an electric discharge transfer recording material or an electric stencil master sheet.

The electric discharge transfer recording 22 mediums of the present invention are generally employed 23 by superimposing the transfer recording medium onto a 24 recording sheet 8, e.g., cellulosic paper, a synthetic 25 paper-like sheet or a plastic sheet so that the conduc-26 tive layer 6 contacts recording sheet 8. When electric 27 discharge recording is performed by a discharge record-28 ing stylus in accordance with an ordinary method from 29 the side of the electroconductive powder-containing 30 resin layer 2, the semiconductive resin layer 4 and the 31 conductive layer 6 are simultaneously broken by electric 32

- 1 discharging, and the broken pieces 10 are transferred to
- 2 the record sheet and fixed thereon, thereby achieving
- 3 transfer recording.
- According to a further embodiment of the
- 5 present invention, a color coupler may be put in one or
- 6 more transfer layers to react with a material in the
- 7 recording material or paper, to generate a colored
- 8 image, e.g., bisphenol A and leuco dye.
- 9 It is understood that the electric discharge
- 10 transfer film of this invention can be processed to any
- 11 desired width or length in accordance with its desired
- 12 use. For example, the transfer film can be used in the
- 13 form of a narrow tape, such as a typewriter ribbon.
- In electric discharge recording, the semi-
- 15 conductive resin layer and the conductive layer of the
- 16 composite electric discharge transfer recording material
- 17 are broken down, but the electroconductive powder-
- 18 containing resin layer is not broken because of its
- 19 electric anisotropy and remains substantially unchanged.
- 20 Accordingly, dissipation of any offensive odor issued
- 21 at the time of electric discharge breakdown is inhibited,
- 22 and soot or a coloring substance such as carbon black is
- 23 prevented from scattering and adhering to the discharge
- 24 recording stylus. The troublesome inspection and
- 25 maintenance of the discharge recording stylus can be
- 26 markedly reduced, and recording can be performed with
- 27 high reliability. The term "electrical anisotropy"
- 28 refers to the low resistance of support layer or
- 29 electroconductive particle containing resin layer 2 in
- 30 the through direction and the high resistance of this
- 31 layer in the lateral direction.

- The use of the composite electric discharge recording material can afford a sharp recorded image, and in electric discharge transfer recording, a transfer recorded image having a high density, a natural appearance and a soft tone can be obtained.
- The composite electric discharge recording material of this invention can be used a plurality of times.
- The composite electric discharge recording material of this invention can be conveniently used in facsimile systems, terminal recording devices in electronic computers, automatic recording devices of automatic measuring instruments, and various types of printers, etc.
- In the present specification, the terms
 16 "surface resistance" and "volume resistance" is deter17 mined in accordance with the method described by H. R.
 18 Dalton in U.S. Patent 2,664,044.
- 19 In the detailed description of the present invention, a transfer film comprising a support layer 20 and two transfer layers is disclosed. It is understood 21 that the present invention also encompasses the use of 22 a support layer, as disclosed herein, having only one 23 or possibly more than two resin layers provided that 24 at least one of the layers is thermally or electro-25 thermally transferable to another substrate, e.g., a 26 27 paper sheet.
- The following examples further describe the present invention.

1 · EXAMPLE 1

2 A transfer sheet in accordance with this 3 invention was prepared as follows.

A stock solution (A-1) containing 27.5 grams 4 Estane 5715 (polyurethane) sold by B. F. Goodrich Co., 5 and 72.5 grams methyl ethyl ketone was mixed together and stirred until complete dissolution was achieved. 7 A second solution containing 10 grams of particulate 8 graphite, sold as Micro 650 by Asbury Graphite, 90 grams resin solution, 40 grams methyl ethyl ketone, and 2.1 10 grams Byk Special sold by Mallinckrodt Chemical Company, 11 was blended with the first solution in a chilled Waring 12 blender for 15 minutes and then allowed to settle for 15 13 14 minutes.

The resulting solution was coated on a release sheet with a gap coater to a dry thickness of 1.1 mils, air dried for 5 minutes and then dried in a oven at 65°C for 15 minutes.

Another solution (B) was prepared by intro-19 ducing 22.5 grams poly-n-butyl methacrylate, sold as 20 ELVACITE 2044 by E.I. du Pont de Nemours & Co., and 74.4 21 grams TOLUSOL 25, sold by Shell Chemical Company, into 22 an 8 oz. plastic bottle. The bottle was rolled on a 23 jar null until the contents were dissolved. 7.5 grams 24 Black Pearls L which is carbon black, sold by Cabot 25 Corporation, and 600 grams of 1/4" stainless steel (Type 26 440) shot was added to the solution and the same was 27 milled for 16 hours. The resulting solution was coated 28 over the first coating to a dry thickness of 0.5 mil 29 using a Mayer rod (about #22). The product was oven 30 31 dried at 65°C for 3 minutes.

A final solution (C-1) was prepared by introducing 25.0 grams Aquadag E (graphite dispersion, 22%
solids in water) and 75.0 grams ethanol in an 8 oz.
bottle. The contents were stirred rapidly for 60
minutes with vortex blades. This solution was coated
over the second coating (from solution B) to a dry
thickness of 0.3 mil using a Mayer rod (about #18)
and oven dried at 65°C for 3 minutes.

EXAMPLE 2

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A transfer sheet was prepared in accordance . 10 with Example 1 except that a solution (C-2) containing 11 25.0 grams AQUABLACK 548-17 (24% carbon black in water) 12 or 428-238, sold by Borden Chemical Co., 2.0 grams 13 Rhoplex P-376 (acrylic resin dispersion in water, 50% 14 15 solids) and 27.0 grams water was substituted for solution C-1 and processed in the same manner as solution 16 17 C-1.

CLAIMS:

1	1.	An	electric	discharge	transfer	material
2	characterized	by	comprising:			

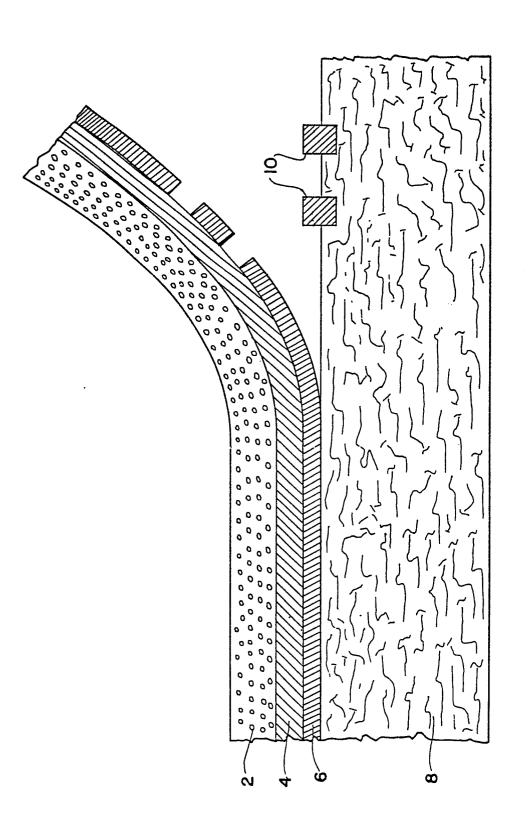
- 3 (a) an electrically anisotropic support layer 4 having electroconductive particles dispersed in a resin 5 matrix wherein said electroconductive particles are:
- 6 (1) graphite particles having a particle 7 size between 0.1 to 20 microns,
- 8 (2) carbon black particles having a particle size between 25 to 500 millimicrons, or
- 11 (3) metal powders; and
- (b) at least one thermal or electrothermal transfer layer in the form of a resin layer capable of being broken by electrical discharge and transferred to a record sheet.
- 2. An electric discharge transfer material according to claim 1 further characterized by comprising:
- (a) a semiconductive resin layer capable of 19 being broken by electric discharging which has a surface 20 resistance of 10^5 to 10^{16} ohms and a volume resistance of 10^3 to 10^{14} ohms-cm;
- (b) an electroconductive electrically anisotropic resin layer containing said electroconductive particles, said electroconductive resin layer being laminated on one surface of the said semiconductive resin layer (a); and

- (c) a conductive layer having a surface resistance of not more than 10^4 ohms and a volume resistance of not more than 10^2 ohms-cm, said conductive layer being laminated on the other surface of the said semiconductive resin layer.
- 3. An electric discharge transfer material according to claim 2 further characterized in that at least one of the semiconductive resin layer (a) and the conductive layer (c) contains a coloring substance.
- 4. An electric discharge transfer material according to claim 3 further characterized in that the coloring substance is carbon black.
- 5. An electric discharge transfer material according to any one of claims 1-4 further characterized in that the semiconductive resin layer capable of being broken by electric discharging comprises a thermoplastic or thermosetting resin and carbon black and a filler dispersed therein.
- 6. An electric discharge transfer material according to any one of claims 1-5 further characterized in that the said electrically anisotropic resin layer comprises between 60 to 70% by weight carbon black having a particle size between 25 and 500 millimicrons, based on the total weight of the resin and carbon black.
- 7. An electric discharge transfer material according to any one of claims 1-5 further characterized in that the said electrically anisotropic resin layer comprises between 5 and 65% by weight graphite having a particle size between 0.1 and 20 microns, based on the weight of the resin.

1 8. An electric dischage transfer material 2 according to any one of claims 1-7 further said resin 3 matrix comprises a phenoxy resin of the formula:

- 8 wherein n is about 100.
- 9. A method for making an electrically 10 anisotropic support layer useful in the electric 11 discharge transfer materials of claim 7 or claim 7 12 characterized by comprising the steps of:
- 13 (a) grinding a slurry of graphite particles 14 in the presence of water or solvent having freezing and 15 vapor pressure properties similar to water for a period 16 of time sufficent to substantially completely disperse 17 the graphite particles in said water or solvent;
- (b) adding a binding polymer to said graphite slurry, either as part of step (a) or immediately after step (a), wherein said polymer is soluble in said water or solvent;
- 22 (c) freezing said slurry;
- (d) drying said slurry wherein said water or 24 solvent present is caused to sublime resulting in the 25 formation of polymeric coated graphite particles wherein 26 at least a substantial portion of these particles have a 27 diameter of at least 0.2 microns; and
- (e) casting said coated graphite particles into a support layer for an electroconductive transfer film.

- 1 . 10. A method according to claim 9 further
- 2 characterized by solvent casting said coated graphite
- 3 particles into a support layer for an electroconductive
- 4 transfer film.
- 5 ll. A method according to claim 9 or claim 10
- 6 further characterized in that the said water-soluble or
- 7 solvent soluble binding polymer is polyvinyl alcohol,
- 8 gelating or methyl cellulose.
- 9 12. A method according to any one of claims
- 10 9-11 further characterized in that the said solvent is
- 11 t-butyl alcohol, cyclohexane, benzene, dioxane, or
- 12 p-xylene.



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