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(54) **Multilayered thermal transfer medium from water-based formulations**

Mehrschichtiges thermisches Übertragungsmaterial aus wässrigen Zusammensetzungen

Feuille multicouche pour le transfert thermique obtenue à partir de compositions aqueuses

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Description

[0001] The present invention relates to thermal transfer printing technology wherein data or images are produced on a receiving substrate by selectively transferring portions of a pigmented layer from a donor film to the receiving substrate by heating extremely precise areas with heating elements typically comprised of thin film resistors. More particularly, the present invention relates to thermal transfer printing with multi-layer ribbons, wherein the viscosity and adhesive properties of the layers are distinct. Such multi-layer ribbons are advantageously used with high speed printers such as "near edge", "true edge", "corner edge" or "Fethr™" thermal transfer printers wherein the thin film resistors (heating elements) are positioned right at the edge of the thermal print head allowing rapid separation of the donor film from the receiving substrate after the thin film resistors are fired. These multi-layer ribbons also enable greater variation in the properties and performance of the print obtained from conventional thermal transfer printing processes and equipment since the requirements of the transferred print are shared between two layers. An example is providing print on rough stock using these multi-layer ribbons in conventional processes and equipment.

[0002] Thermal transfer printing is widely used in special applications such as in the printing of machine readable bar codes, either on labels or directly on articles to be encoded. The thermal transfer process employed by these printing methods provides great flexibility in generating images allowing for broad variations in the style, size and color of the printed images, typically from a single machine with a single thermal print head.

[0003] As the use of thermal transfer printing grows into new applications, the requirements for the ribbons become broader and more strict. Conventional general purpose ribbons with a single layer often cannot meet these requirements since the requirements can conflict with one another. For example, single layer coated ribbons have not performed satisfactorily in printers known in the art as "near edge", "true edge" and "Fethr™" printers, referred to herein collectively as "high speed printers", due to the rapid separation of the ribbon from the substrate once the print head heating elements have been fired.

[0004] Since the ribbon and receiving substrate are separated almost instantaneously after the thin film resistors are fired, there is very little time for waxes and/or resins to melt/soften and flow onto the surface of the receiving substrate before the ribbon is separated from the receiving substrate. With conventional ribbons, the adhesion of the molten/softened material to the receiving substrate is typically lower than its adhesion to the supporting substrate of the ribbon at the time of separation with a high speed printer. As a result, the functioning thermal transfer layer is usually split and the transfer incomplete, resulting in light printed images where the functioning layer is an ink layer.

[0005] The use of an adhesive layer, comprising polycaprolactone and no pigment, on top of a functioning layer is disclosed by Obata et al. in U.S. 5,240,781. Such a configuration has been found not to provide the best offset resistance and darkest density of printed images for other formulations. A new configuration is desired for thermal transfer ribbons which does not require a polycaprolactone adhesive layer, which is more resistant to offset and provides high density images.

[0006] European Patent Application No. 0 194 860 A2 in the name of General Company Ltd discloses a heat-sensitive transferring recording medium composed of a substrate, a heat-sensitive releasing layer and a heat-sensitive transferring ink layer.

[0007] German Patent Application No. 36 34 049 A1 in the name of Konishiroku Photo Industry Co., Ltd describes a thermal transfer medium comprising a first heat-fusible layer and a second colorant layer having a film thickness of not more than 2μm disposed on a substrate.

[0008] United States Patent No. 5,053,267 in the name of Ricoh Company Ltd discloses a thermosensitive image transfer recording medium comprising a support on which is disposed a peel-off layer comprising a thermofusible material and a transparent thermofusible ink layer comprising a plurality of different color thermofusible ink sections formed side by side in the form of a repeating unit on the peel-off layer.

German Patent Application No. 35 07 097 A1 in the name of Canon K.K. discloses a thermal transfer medium comprising a flexible substrate on which a first thermosensitive coating comprising a wax and a sensible material is formed and over which a second thermosensitive coating comprising a sensible material, a wax and a binder resin is formed.

[0009] It is also desirable to provide a system (coating formulation and thermal transfer medium) which is not dependent on the use of organic solvents. Extensive work has been done to develop water-rich systems to replace organic solvent-based systems. Water-based and water-rich coating formulations improve safety, reduce costs, and simplify compliance with environmental regulations and restrictions. For example, U.S. Patent No. 4,923,749, issued to Talvalkar, discloses a thermal transfer ribbon which comprises a thermal sensitive layer and protective layer, both of which are water-based. In these formulations, both the waxes and resins must be soluble, dispersible or emulsifiable in water. The present invention provides water-based multi-layer thermal transfer media with unique properties, such as being suitable for use in high speed printers.

[0010] It is an object of the present invention to provide a thermal transfer medium from water-based or water-rich coating formulations with a broader variation in properties.

[0011] It is another an object of the present invention to provide a thermal transfer medium such as a thermal transfer ribbon from water-based or water-rich coating formulations which produces high density images with high adhesion to a substrate.

[0012] It is an additional object of the present invention to provide a thermal transfer medium such as a thermal transfer ribbon from water-based or water-rich coating formulations which does not comprise polycaprolactone and which produces high quality images with reduced offset with "near edge", "true edge", "comer edge" or "Fethr™" thermal transfer printers and other high speed printers where the thermal transfer ribbon is separated from the receiving substrate almost instantaneously after the heating elements of the thermal transfer print head have been fired.

[0013] According to the invention a thermal transfer medium which transfers images to a receiving substrate when exposed to an operating print head of a thermal transfer printer, said thermal transfer medium comprising:

a flexible substrate;
a thermosensitive first coating positioned on said substrate comprising at least 75 wt.% of a water dispersible wax, based on dry components, a water-soluble, dispersible or emulsifiable binder resin and, optionally, a sensible material in an amount less than 20 wt.% based on dry components; and
a thermosensitive second coating positioned on said first coating comprising a sensible material, a water dispersible wax and at least 20 wt.% of a water-soluble, dispersible or emulsifiable binder resin having high hot tack properties, based on dry components;

characterized in that the first coating has a melt viscosity at least 10 times lower than that of the second coating and the first and second coatings are applied from water-based or water-rich formulations.

[0014] Also the invention resides in a thermal transfer printer which incorporates a thermal transfer ribbon, wherein said ribbon comprises:

a polyester substrate;
a thermosensitive first coating positioned on said polyester substrate and comprising from 75-97 wt.% of a water dispersible wax or mixture of waxes and 3-25 wt.% of a binder resin, all based on dry components;
a thermosensitive second coating positioned on said first coating comprising 5-26 wt.% coloring agent, about 20-75 wt.% of a water-soluble, dispersible or emulsifiable binder resin having high hot tack properties, all based on dry components, and a water dispersible wax or mixture thereof, and characterized in that
the first coating has a melt viscosity in the range of 25 to 1,500 mPa.s at 150°C and shear rate of 100 s^{-1}, and the second coating has a melt viscosity in the range of 5,000 to 30,000 mPa.s at 150°C at a shear rate of 100 s^{-1} and the first and second coatings are applied from water-based or water-rich formulations.

[0015] The invention will be described by way of example with reference to the accompanying drawings in which:-

Fig. 1 illustrates a thermal transfer medium of the present invention prior to thermal transfer, which has two thermosoftenable layers;
Fig. 2 illustrates a thermal transfer medium of the present invention having two thermosoftenable layers after thermal transfer;
Fig. 3 illustrates another embodiment of a thermal transfer medium of the present invention prior to thermal transfer, which has three thermosoftenable layers; and
Fig. 4 is a graph of viscosity values for various coating formulations vs. shear rate.

[0016] Thermal transfer ribbon 20, as illustrated in Figs. 1 and 2, is a preferred embodiment of this invention comprising a substrate 22 of a flexible material, preferably a thin smooth paper or plastic-like material. Tissue-type paper material or polyester-type plastic materials are preferred. Positioned on substrate 22 is a thermosoftenable first coating 26 also referred to herein as a "subcoat." The first coating contains a wax or wax blend, a minor portion of binder resin and optionally a sensible material, e.g., a pigment. The thermal transfer ribbon 20 also has a thermosoftenable second coating 24 positioned on first coating 26 which contains a binder resin with high hot tack properties, a sensible material and a wax. The melt viscosity and thermal sensitivity of the first coating 26 and second coating 24 is determined by the melting points of the binder resins and waxes therein and the amounts thereof in each. The first coating is formulated to have a melt viscosity lower than that of the second coating, preferably a value at least 25 times less than the second coating for high speed printers and a value at least 10 times less than the value of the second coating when used in conventional printers. With lower melt viscosity values comes lower cohesion within the coating. Lower cohesion allows for easier separation from the substrate. Reduced melt viscosity and cohesion ensure that exposure to heat from a thermal transfer head 30 will transfer both the first coating 26 and the second coating 24 to a receiving substrate 28 without splitting the first coating or separating the first and second coatings upon transfer, so as to form a multiple layer image 32.

[0017] Low softening points for the first coating also aids in the simultaneous transfer of the first and second coatings. The first coating 26 and second coating 24 preferably have a softening point below 200°C, typically below 150°C, and most preferably about 75°C. Such softening temperatures enable the thermal transfer medium to be used in high speed thermal transfer printers such as "near edge", "true edge" and "Fethr™" thermal transfer printers wherein the thermal transfer ribbon is separated from the receiving substrate almost instantaneously with the firing of the heating elements within the thermal print head. These heating elements (thin film resistors) are believed to operate at temperatures within the range of 100°C to 300°C. The actual operating temperatures are difficult to determine due to the small size of the heating elements. In preferred embodiments, the first coating has a higher softening temperature than the second coating so that the printed image obtained has higher abrasion/smear resistance. The difference in the softening temperature preferably falls within the range of 0°C-50°C.

[0018] Thermal transfer ribbon 120, as illustrated in Fig. 3, is another embodiment of this invention comprising a substrate 122 of a flexible material as described above, a thermosoftening first coating 126, a thermosoftening second coating 124 and a thermosoftening third coating 123. The first and second coatings are analogous in composition to coatings 26 and 24 in Figs. 1 and 2. Third coating 123 serves as a protective layer between the receiving substrate and the second coating which prevents scuffing during printing. Third coating 123 comprises at least 20 wt.% of binder resin with high hot tack properties and wax as in second coating 124 but is preferably free of coloring agent or other sensible material. The properties (viscosity, cohesion and softening point) and composition of third coating 123 are otherwise preferably equivalent to second coating 124.

[0019] A unique feature of the thermal transfer media of the present invention is the presence of a sensible material and high level of binder resin with high hot tack properties in the same coating so that this layer functions as both as an adhesive layer and ink layer in a multilayer system. This formulation helps provide better print quality, i.e., reduced offset and darker images in that complete and uniform transfer of the ink layer is simplified due to higher adhesion and proximity to the receiving substrate.

[0020] Another feature of the multi-layer ribbons of the present invention is the differentiation in melt viscosity and cohesion and preferably hot tack properties, between the first coating and second coating, with the first coating having a lower melt viscosity and cohesion (and hot tack properties) than that of the second coating. This simplifies separation of the coatings from the flexible substrate of the thermal transfer medium, which is required when operating with high speed printers such as "near edge", "true edge" and "Fethr™" thermal transfer printers. The features of this multilayered configuration allow the thermal transfer medium to provide high adhesion to the receiving substrate and low adhesion to the flexible substrate, which enhances the performance in high speed printers. These features also provide unique performance from conventional printers and processes such as the complete transfer of thick pigmented layers for high density images and high quality images on rough receiving substrates (rough stock) through improved adhesion to the substrate.

[0021] A three layer configuration does not detract from these features but adds the additional feature of providing a protective layer between the ink layer and receiving substrate to prevent scuffing and other machine marks.

[0022] The sensible materials employed in the thermal transfer media of this invention are present in the second coating and optionally also in the first coating. Thermal transfer media to be used in conventional printing processes preferably have sensible material in both layers. In high speed applications, sensible material in the first coating is typically undesirable. The third coating, when used, preferably does not contain any coloring agents or other sensible materials. Essentially, any sensible material used in thermal transfer printing which can be solubilized, dispersed or emulsified in water can be employed in the first or second coatings. These include water-soluble, dispersible or emulsifiable sensible materials which can be sensed by optical, visual, magnetic means, electroconductive means or by photoelectric means. The most common sensible materials are coloring agents such as colored pigments or dyes and magnetic pigments (e.g., iron oxide). Carbon black is the most common colored pigment and conventional dispersible or emulsifiable carbon blacks such as those provided by Environmental Ink and BASF. Preferred carbon blacks provide thermal transfer media which develop little or no static during use within the thermal transfer medium. The less common coloring agents include those described in U.S. Patent 3,663,278, leuco dyes which can react with phenolic resins to generate color, phthalocyanine dyes, fluorescent naphthalimide dyes, cadmium, primrose, chrome yellow, ultra marine blue, titanium dioxide, zinc oxide, iron oxide, cobalt oxide and nickel oxide.

[0023] Preferred magnetic pigments are the aqueous based ferrofluids which render printed image recognizable by magnetic ink character recognition (MICR) devices. Ferrofluids suitable for use in this invention are those classified as aqueous ferrofluids which comprise suspensions/dispersions/emulsions of magnetic particles, i.e., iron oxide particles such as Magnetite (Fe_3O_4), coated with a hydrophilic coating. The coating preferably reduces agglomeration of the magnetic particles. Such ferrofluids are known to be stable in water, i.e., homogeneously mixed with water in the preparation of magnetic tapes such as audio and video tapes. Suitable aqueous based ferrofluids include those disclosed by Thakur et al. in U.S. Patent 5,240,626. The colloidal suspension provided by Thakur et al. comprises magnetic particles (iron oxide/Magnetite-Fe_3O_4) which are coated with a carboxy functional polymer as an anti-agglomerating agent and preferably dispersed with the aid of a surfactant pair or surfactant and dispersant. The preferred sizes for these magnetic particles range from 2-20 nm (20 -200 Å), most preferably 2-9 nm (20-90 Å). Examples of suitable carboxy functional polymers include polymers with multiple carboxy groups in salt form (COO-M+) based on acrylic acid, isocrotonic acid, allylacetic acid, fumaric acid, maleic acid, citraconic acid, itaconic acid, vinyl acetic acid, methacrylic acid backbones and the like. The polymers preferably comprise between 20 and 40 wt.% carboxy groups. An example of a suitable commercially available polymer is Tamol-850, available from Rohm and Haas Co. The amount of polymer used preferably ranges from 50 to 95 wt.% of the weight of the magnetic particles (Magnetite).

[0024] The ferrofluid composition may contain a surfactant or dispersing agent to facilitate dispersion of the magnetic particles in the aqueous solution. Conventional anionic, cationic and non-ionic surfactants and dispersants are suitable. Most preferably, a surfactant pair (surfactant and dispersant) are used, one anionic and one non-ionic. These ferrofluids can be prepared by the conventional methods disclosed by Thakur et al. (U.S. 5,240,626).

[0025] Mixtures of aqueous ferrofluids are preferred. Suitable aqueous ferrofluids are available commercially from sources such as Georgia Pacific Corp.

[0026] The ferrofluids can be added to the formulation in a manner consistent with conventional methods for introducing conventional pigments. However, grinding is not a requirement. The amount of ferrofluid employed is preferably such that it provides an amount of magnetic particles sufficient to provide printed images which are recognizable by MICR devices. The ferrofluid is preferably employed in an amount that provides magnetic particles in the range of about 20 to 60 wt.%, most preferably about 20 to 40 wt.%, based on the weight of dry components. Those which can be solubilized, emulsified or dispersed in water can be used in the present invention.

[0027] Sensible materials other than coloring agents and magnetic pigments used in specialized applications include photochromic dyes, photochromic pigments and fluorescent pigments, which are water-soluble, dispersible or emulsifiable. Examples of suitable photochromic compounds are found in U.S. Patent 5,266,447.

[0028] The second coating may contain a loading of sensible material within the range of 5-60 wt.%, based on dry components. Preferred loadings of sensible material fall within the range of 5-20 wt.% so that the loading of sensible material does not differentiate the second coating from the first coating and inhibit the simultaneous transfer of both coatings to a receiving substrate when exposed to a thermal print head. Where the sensible material is carbon black, the amount employed in the second coating is most preferably about 10 wt.% based on the total weight of dry ingredients of the coating. As indicated above, the first coating is preferably free of sensible material in high speed application, but for ribbons used in conventional processes and printers, amounts of 5-15 wt.%, based on total dry ingredients of the coating, are preferred. Higher loadings of sensible material are not desired due to the increase in viscosity which accompanies high loadings of pigment.

[0029] Each of the coatings contain a water-soluble, dispersible or emulsifiable binder resin which serves to provide flexibility and resiliency to the coatings. The second and third coatings require the use of binder resins with high hot tack properties. Such binder resins are very tacky when softened. Such resins provide an adhesive strength measured as peel strength with an Instron 4411 of at least 2 times that of a general purpose ribbon as described in the examples herein. This provides higher adhesion to a receiving substrate both during transfer and after transfer by a thermal print head. High hot tack properties are manifested by high peel strength as discussed in the examples. Water-soluble, dispersible or emulsifiable binder resins with high hot tack properties include polyesters, acrylic acid-ethylene-vinyl acetate terpolymers, methacrylic acid-ethylene-vinyl acetate terpolymers, polyvinyl acetate, vinylchloride-vinyl acetate copolymers, ethylenevinylacetate copolymers, ethylene-ethylacetate copolymers, styrene copolymers, styrene butadiene block copolymers, polyurethane resins, ethylene-alkyl(meth)acrylate copolymers, and styrene-alkyl(meth)acrylate copolymers. Preferred resins include styrene copolymers such as vinyl toluene -methylstyrene copolymers.

[0030] Other water-soluble, dispersible or emulsifiable binder resins which may be present in any one of the coatings include those conventionally employed in thermal transfer media such as those described in U.S. Patent Nos. 5,240,781 and 5,348,348. These include polyvinylchloride, polyethylene, polypropylene, polyethylene oxide, ethylene-propylene rubber, polyvinyl alcohol, polylactones, polyketone resin, polystyrene, ethylene-propylene copolymers, ethylcellulose, polyamide, epoxy resin, xylene resin, polyvinylbutyryl, styrenebutadiene rubber, nitrile rubber, acrylic rubber, rosin esters and sucrose benzoate.

[0031] When preparing a thermal transfer ribbon for use with rough stock, higher loadings of binder resin are desired. These water-soluble, dispersible or emulsifiable resins preferably have a softening temperature of from 50°C to 250°C and can also be soluble, dispersible or emulsifiable in organic solvents. To obtain dispersions or emulsions, the binder resins are used as small particles, preferably of submicron size and are agitated at high shear in water or in an attritor.

[0032] Each coating may contain more than one binder resin to provide a specific property profile. For example, Piccotex™ 100 resin by Hercules is a styrene copolymer (vinyl toluene- -methylstyrene copolymer) that provides high hot tack properties desirable for the second coating in aiding adhesion to the receiving substrate upon a transfer. Other high hot tack binder resins that are suitable for the second coating include aqueous ethylenevinylacetate copolymer dispersions and aqueous polyester resin dispersions. These components can be used separately or blended as desired.

[0033] The water-soluble, dispersible or emulsifiable binder resins in the first and second coatings and, where applicable, third coatings can be the same but need not be to obtain excellent performance. While the binder resin in the first coating need not have high hot tack properties, it may be desirable to utilize the same binder resin in the first coating and second coating so as to provide similar thermosoftening characteristics. This enables all coatings to respond (soften) uniformly upon being heated by a thermal print head and assists in simultaneous transfer of all coatings to a receiving substrate upon application of heat from the print head of a high speed thermal printer. Where a third coating is used, employing identical resins to the second coating is preferred to prevent partial transfer of the second coating.

[0034] The coatings also contain a water dispersible wax. Suitable waxes are those within conventional water-based wax emulsions or dispersions. Examples include natural waxes such as carnauba wax, rice wax, bees wax and candelilla wax. Other suitable waxes include petroleum waxes such a paraffin waxes and synthetic hydrocarbon waxes such as low molecular weight polyethylene and Fisher-Tropsch wax. Less common waxes which are suitable are higher fatty acids such as myristic acid, palmitic acid, stearic acid and behenic acid; higher aliphatic alcohols such as stearyl alcohol and esters such as sucrose fatty acid esters. The less common waxes may complicate dispersion or emulsification. The preferred waxes include carnauba wax, montan wax, candelilla wax and paraffin waxes.

[0035] The wax-like substances preferably have a melting point of from 35°C to 200°C, more preferably 65°C to 130°C. The waxes are differentiated by their softening/melting point. Hard waxes such as carnauba wax, synthetic waxes and montan wax have high softening/melting points and as such, greater resiliency. A particular example of a hard wax is carnauba wax provided by Shamrock Technologies in Newark, New Jersey under the tradename "S-Nauba". Another is "Carnauba North Country No. 3" by Baldini & Co., Inc. of Millburn, New Jersey. In contrast, soft waxes such as candelilla wax provided by Stahl & Pitch of West Babylon, N.Y., and paraffin waxes have low melting/softening points and provide greater temperature sensitivity and flexibility. A blend of hard and soft wax is often preferred for the first layer in high speed printing. Hard wax typically has a melting point within the range of 80°C-200°C and soft wax has a melting/ softening point within the range of 40°C-80°C.

[0036] Each coating may contain a plasticizer to enhance flexibility and reduce the softening point. Water-soluble, dispersible or emulsifiable plasticizers used in binders of conventional thermal transfer ribbons such as those described in U.S. Patent No. 3,663,278 are suitable. These can include adipic acid esters, phthalic acid esters, chlorinated biphenyls, citrates, epoxides, glycerols, glycols, hydrocarbons, chlorinated hydrocarbons, phosphates, and the like. Each layer may contain other optional additives to enhance such properties as flexibility (oil flexibilizers), hot tack properties, cohesion, weatherability (U.V. absorbers), melt viscosity (fillers) and smoothness, if these additions are stable in solution.

[0037] The first coating of the thermal transfer medium of the present invention comprises at least 75 wt.% water dispersible wax, most preferably more than 85 wt.% wax based on total solids. This high level of wax provides a low melt viscosity and low softening temperature to simplify separation from the flexible substrate of the thermal transfer medium. Blends of waxes are preferred and preferably a blend of hard wax and soft wax is used in ratios ranging from about 4.0:1 to 0.5:1. The first coating also comprises a water-soluble, dispersible or emulsifiable binder resin, which need not have high hot tack properties. The amount of binder resin employed is preferably less than 20 wt.%, based on total solids to maintain a low melt viscosity value. Preferably, amounts of 3-15 wt.% resin binder are used, based on total dry components (solids). The first coating may optionally contain a water-soluble, dispersible or emulsifiable sensible material such as a colored pigment, in an amount less than 20 wt.% based on dry components. When used, the amount of pigment preferably ranges from 5-20 wt.%, preferably about 15 wt.%, based on total solid components. The melt viscosity of the first coating is at least 10 times lower than that of the the second coating and can range from 25-1500 mPa.s at 150°C and a shear rate of 100 s^{-1} (Haake RS150 reometer). Preferably, the melt viscosity has a value at least 25 times less than the melt viscosity value for the second coating of ribbons used in high speed printing and at least 10 times less than the melt viscosity value for the second coating of ribbons used in conventional printers. The melting/softening point of the first coating preferably ranges from 50 to 200°C.

[0038] The second coating comprises at least 20 wt.% of a water-soluble, emulsifiable or dispersible binder having high hot tack properties in addition to sensible material. Preferably, about 20 wt.% to 75 wt%, most preferably 30-50 wt.% of the second coating comprises a binder resin having high hot tack properties. To maintain similar softening characteristics consistent with the first coating, the second coating preferably contains 25 wt.% or more water dispersible wax, most preferably, 25-60 wt.% wax. Other water-soluble, emulsifiable or dispersible binder resins may be present in minor amounts of preferably about 0-15 wt.%. The melt viscosity of the second layer preferably falls within the range of 1,500 to 30,000 mPa.s measured at 150°C at a shear rate of 100 s^{-1} (Haake RS 150 Reometer).

[0039] The third coating, when used, preferably does not contain coloring agents or other sensible materials and comprises at least 20 wt.% water-soluble, emulsifiable or dispersible binder resin having high hot tack properties, which is preferably identical to that within the second coating. Other thermal plastic binder resins and waxes may be employed in amounts which preferably correspond to those given above for the second coating. The third coating softens at a temperature in the range of about 50 -200°C and preferably has a melt viscosity which ranges from 1000 to 30,000 mPa.s, measured at 150°C at a shear rate of 100 s^{-1} (Haake RS 150 reometer).

[0040] The proportion of resin binder and wax within each of the coatings can be adjusted to control the melt viscosity (cohesion), hot tack, softening temperature, resiliency and other properties. Additives may also be introduced to manipulate these properties. The difference in melt viscosity between the first and second coatings is preferably such that the melt viscosity of the second coating is over 25 times greater than that of the first coating for high speed print ribbons and over 10 times greater for conventional ribbons. This will provide reduced cohesion within the first coating, thus simplifying transfer. The second coating has higher hot tack properties to further simplify transfer of both layers to a receiving substrate.

[0041] The hot tack properties can be manifested and quantified by peel strength determinations wherein the strength of the coatings to a paper substrate is determined using a device such as an Instron 9411 as described in detail in the examples below. The second coating has a peel strength at least ten times greater than the first coating.

[0042] It is desirable to formulate the top coating to have a peel strength at least 2 times greater than the peel strength of the single layer of a general purpose a thermal transfer ribbon. Preferably, the peel strength is from 3 to 35 times the peel strength of a general purpose ribbon and higher. It is generally desirable for the subcoat to have a peel strength less than the peel strength of the single coating from a general purpose thermal transfer ribbon, preferably from .05 to 0.5 the peel strength of such a ribbon and lower.

[0043] The thermal transfer media of this invention are prepared from coating formulations that contain the above components in aqueous solution, dispersion or emulsion preferably at about 10-60 wt.% solids, most preferably 20-30 wt.% solids. In forming the coating formulation, the resin components may be added to an attritor wherein the solids are ground to a particle size of less than 10 μm at temperatures not to exceed 49°C (120°F). Such particle sizes are typically obtained in about 2 hours at 200-250 rpm. Emulsifiers may be used to help prevent precipitation of one or more components. A common emulsion may also be prepared by melting and resolidifying all solid components in the presence of the same emulsifier or combination thereof.

[0044] Suitable emulsifiers include some conventional resin emulsifiers and wax emulsifications available commercially and well known to those skilled in the art, examples of which include those available under the tradenames "Tween™", such as Tween™ 40, 60, 80", etc., "Surfynol", such as Surfynol 420, 440, 460", etc., "Morpholine", "Span", "Brig", "Triton", and propylene glycol. Mixtures of emulsifiers are preferred. One skilled in the art can readily determine whether a particular conventional emulsifier will emulsify the wax and/or thermoplastic resin selected by simply adding the emulsifier to fine particle dispersions of the wax and/or thermoplastic resin or forming such fine particles in the presence of emulsifier. The amount of emulsifier can vary widely and is preferably used in an amount of from 1 to 30 wt.% based on dry components.

[0045] The emulsions typically contain an aqueous solvent which can be essentially water, but may include a small portion of water miscible solvent such as an alcohol in an amount of less than 10 wt.%, based on the total liquid content. Examples include polypropylene glycol and N-propanol.

[0046] These coating formulations can be applied to substrates using conventional techniques and equipment such as a Meyer Rod® or like wire round doctor bar set up on a conventional coating machine to provide suitable coat weights. Thermal transfer media of the present invention are obtained via a two-layer process wherein the first coating is applied to a substrate such as polyester film, as a subcoat and the second coating applied over the first. To prepare a three-layer thermal transfer medium, the third coating is applied over the second after drying. The coat weight of the first coating as preferably maintained between about 1-2 g/m^2 and the coat weight of the second coating is preferably maintained between about

1.5-3.5 g/m^2. The third coating, when applied, is typically employed at a coat weight between about 0.2-1.5 g/m^2. The polyester film is typically from 18-24 gauge polyethyleneterephthalate film; however, the flexible substrates can vary widely and include those described in U.S. Patent 5,348,348.

[0047] The first coating is applied and preferably dried at a temperature of about 54°C - 121°C (130 F-250 F). Following drying, the second coating is applied at a temperature below the softening point (about 66°C (150 F)) to ensure adherence, and preferably dried at a temperature in the range of 60° C to 77° C (140 F-170 F).

[0048] The thermosensitive coatings can be fully transferred to a receiving substrate such as paper or synthetic resin at a temperature in the range of 75°C-300°C.

[0049] Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

Example 1

[0050] A first coating formulation (subcoating) is prepared by grinding within an attritor for 1 h the following: water, wax emulsions, resin and wetting agent in the proportions indicated in Table 1 at a temperature below 32°C (90 F) to provide a coating viscosity of 17.5 ± 1 seconds with a #2 Zahn cup.

TABLE 1

First Coating Formulation		
Ingredients	**Dry %**	**Wet Weight**
Water	---	126.0
Polyethylene Oxide Resin	9.0	9.0
Carnauba Emulsion at 25% solids	63.7	254.8
Candelilla Emulsion at 25% solids	27.3	109.2
Wetting Agent[1]	---	1.0
TOTAL	100.0	500.0

[1]Silwett L-77 Osi Specialities

[0051] A second coating formulation (top coating) is obtained by grinding in an attritor for 2 hours the following: water, resin, candelilla emulsion, grinding aid, aqueous EVA dispersion, polyester resin, carbon black and wetting agent in the proportions indicated in Table 2 at a temperature below 32°C (90 F) to provide a coating viscosity of 17.0 ± 1 second with a #2 Zahn cup.

TABLE 2

Second Coating Formulation		
Ingredients	**Dry %**	**Wet Weight**
Water	---	195.2
Polyethylene Oxide	3.0	3.0
Candelilla Emulsion at 25% solids	45.0	180.0
Grinding Aid[1]	3.0	3.0
Aqueous EVA Dispersion at 35% solids	20.0	57.1
Polyester Resin at 30% solids	14.0	46.7
Carbon Black	14.0	14.0
Wetting Agent[2]	1.0	1.0
TOTAL	100.0	500.0

[1]Grinding Aid from Air Products
[2]Silwet L-77 from Osi Specialities

Thermal Transfer Medium

[0052] A thermal transfer medium consistent with the present invention is prepared as follows: A first coating is formed on a 4.5 μm polyester film having a coat weight between 1-2 g/m^2 from the First Coating Formulation described above by applying said formulation to the substrate with a conventional coating machine at about 66°C - 93°C (150 F-200 F) and drying at less than 77°C (170 F). A second coating having a coat weight within the range of 1.5-2.5 g/m^2 is deposited on the dried first coating from the Second Coating Formulation described above with a conventional coating apparatus. The coated polyester film is dried following the application of the second coating at a temperature of about 66°C (150 F) to obtain a finished ribbon.

Example 2

[0053] A first coating formulation (subcoating) is prepared by adding all the ingredients listed below together under agitation and then mixing them for at least one hour. The viscosity of the coating formulation is about 17 seconds with a #2 Zahn cup.

First Coating Formulation		
Ingredients	**Dry %**	**Wet weight (g)**
Water		218.5
Paraffin Wax Emulsion at 25%[1] solids	30	120
Carnauba Wax Emulsion at 25% solids	60	140
Adhesive Dispersion at 44%[2] solids	9	20.5
Wetting Agent[3]	1	1
TOTAL	**100%**	**100%**

[1]Paraffin 1014 by IGI-Boler, in Wayne, PA
[2]#B7256A from Pearson Stevens, P.O. Box 1092, Buffalo, NY 14240
[3]Surfynol 104PA from Air Products

Second Coating Formulation		
A second coating formulation (top coating) is prepared in the same way as the above first coating formulation using the ingredients listed below to obtain viscosity of about 17 seconds with a #2 Zahn cup.		
Ingredient	**Dry %**	**Wet weight (g)**
Water		186.4
Paraffin Wax Emulsion at 25% solids	50	200
Hydrocarbon Resin dispersion at 55%[1]solids	14	25.5
Aqueous EVA Dispersion at 35% solids	20	57.1
Carbon Dispersion at 50%[2] solids	15	30
Wetting Agent[3]	1	1
TOTAL	**100%**	**500g**

[1]Hydrocarbon resin dispersion from Hercules, Inc.
[2]Carbon black dispersion from BASF.
[3]Surfynol 104PA from Air Products.

Example 3

[0054] An alternate first coating formulation (subcoating) is prepared by adding all the ingredients listed below together under agitation and then mixing them for one hour. The carbon black dispersion is used in this first coating formulation to enhance the density of printing images.

First Coating Formulation		
Ingredients	**Dry %**	**Wet Weight (g)**
Water		141
Polyethylene Oxide	8	8
Paraffin Emulsion at 25% solids	42	168
Carnauba Emulsion at 25% solids	42	168
Carbon Black Dispersion at 50%[1] solids	7	14
Wetting Agent[2]	1	1

[1]Carbon Black dispersion from BASF.
[2]Surfynol SE surfactant is a wetting agent from Air Products

(continued)

First Coating Formulation		
Ingredients	**Dry %**	**Wet Weight (g)**
Total	**100%**	**500g**

Example 4

[0055] A third coating formulation is prepared by adding all the ingredients listed below together under agitation and then mixing them for one hour. This coating formulation contains no carbon black and is for coating on the top of the second coating to eliminate or reduce scuffing.

Third Coating Formulation		
Ingredient	**Dry %**	**Wet Weight (g)**
Water		148
Candellila Emulsion at 25% solids	59	236
EVA Dispersion at 35% solids	25	100
Water-soluble polyester	15	15
Wetting Agent[1]	1	1
TOTAL	**100%**	**500G**

[1]Surfynol 104PA from Air Products

PEEL STRENGTH ANALYSIS OF VARIOUS TTR COATINGS

1. Sample Preparation

[0056] A 2.54 cm (1 inch) wide and 25.4 cm (10 inch) long stripe is cut from a thermal transfer ribbon, which is manufactured by applying the coating identified onto a polyester film. The stripe is taped to smooth (bond) paper and then is pressed together in the press at about 250 C for 0.5 seconds so the coating from the ribbon is melted into the paper substrate.

2. Test Conditions and Procedures

[0057]

Instrument	Instron 4411
Temperature	75°C
Relative Humidity	50%
Test Speed	5 cm/min. (2 in/min.)
Peel Angle	180

A test specimen was attached to the Instron by clamping the polyester film to one end and the paper substrate to another end. The film and the paper were separated at constant rate of 5 cm (2 inch) per minute at 180°. The force was recorded and the peel strength was calculated dividing this force by the sample width.

3. Test Results and Comparison

[0058] Peel strength is measured in gram/inch and the peel strengths of various ribbons are shown in the following:

	Peel Strength (g/cm (g/in))
General purpose ribbon(1)	3.5 (9)
Ribbon with sub-coating of Example 1 only:	0.4 (1)
Ribbon with top-coating of Example 1 only:	13.4 (34)
Ribbon with modified top-coating of Example 1[2]	48.4 (123)
Ribbon with modified top-coating of Example 1[3]	7.1 (18)

[1]single coated ribbon comprising carbon black, carnauba wax, ethylene vinyl acetate resin and polyethylene wax
[2]about 40 wt.% high tack resin
[3]about 20 wt.% high tack resin

[0059] As can be seen from the above, the peel strength of the top-coating of Example 1 is about four times higher than that of typical general-purpose ribbon formulation (GPR) while the peel strength of the Example 1 sub-coating is nine times lower than that of the GPR. The difference of peel strength between the sub-coating and top-coating is preferably about 11.8 g/cm (30 g/inch) for optimum printing. The low and high limits of peel strength for the top-coating are 7.1 and 48.4 g/cm (18 and 123 g/inch), respectively.

VISCOSITY MEASUREMENT

[0060] The melt viscosity of a coating can be measured using a Haake RS 150 Reometer at various shear rates as shown in Fig. 4 for:

a) a single coating of a general-purpose ribbon formulation;
b) a sub-coating from the formulation of Example 1 above; and
c) a top coating from the formulation of Example 1 above.

According to the graph of Fig. 4, the melt viscosity of the general purpose sub-coating of Example 1 and top-coating are 1426, 96 and 7528 mPa.s, respectively, measured at 150°C and a shear rate of 100 s^{-1} (see Fig. 4 graph).

[0061] It can be estimated that the difference between the melt viscosities of sub-coating and top-coating should be at least 25 times for high speed applications. Preferably, the melt viscosity of the sub-coating is about 10 times lower than that of a general purpose ribbon for high speed applications.

[0062] The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding example.

Claims

1. A thermal transfer medium which transfers images to a receiving substrate when exposed to an operating print head of a thermal transfer printer, said thermal transfer medium comprising:

a flexible substrate (22);
a thermosensitive first coating (26) positioned on said substrate comprising at least 75 wt.% of a water dispersible wax, based on dry components, a water-soluble, dispersible or emulsifiable binder resin and, optionally, a sensible material in an amount less than 20 wt.% based on dry components; and
a thermosensitive second coating (24) positioned on said first coating comprising a sensible material, a water dispersible wax and at least 20 wt.% of a water-soluble, dispersible or emulsifiable binder resin having high hot tack properties, based on dry components;

characterized in that the first coating has a melt viscosity at least 10 times lower than that of the second coating and the first and second coatings are applied from water-based or water-rich formulations.

2. A thermal transfer medium as in claim 1, wherein the melt viscosity of the second coating (24) is at least 25 times greater than that of the first coating (26).

3. A thermal transfer medium as in claim 2, wherein the binder resin and amount thereof within the first and second coatings (26, 24) are selected to provide hot tack properties for the second layer greater than the hot tack properties of the first layer, wherein hot tack properties are quantified by peel strength values in g/cm and the peel strength values for the first coating are at least 10 times less than the second coating.

4. A thermal transfer medium as in claim 1, wherein the melt viscosity of the second coating (24) is from 25-100 times greater than that of the first coating (26).

5. A thermal transfer medium as in any preceding claim which is derived from aqueous emulsions and is free of organic solvent.

6. A thermal transfer ribbon (20) comprising:

a polyester substrate (22);
a thermosensitive first coating (26) positioned on said polyester substrate and comprising from 75-97 wt.% of a water dispersible wax or mixture of waxes and 3-25 wt.% of a binder resin, all based on dry components;
a thermosensitive second coating (24) positioned on said first coating comprising 5-26 wt.% coloring agent, about 20-75 wt.% of a water-soluble, dispersible or emulsifiable binder resin having high hot tack properties, all based on dry components, and a water dispersible wax or mixture thereof, and **characterized in that** the first coating has a melt viscosity in the range of 25 to 1,500 mPa.s at 150°C at a shear rate of 100 s^{-1}, and the second coating has a melt viscosity in the range of 5,000 to 30,000 mPa.s at 150°C at a shear rate of 100 s^{-1} and the first and second coatings are applied from water-based or water-rich formulations.

7. A thermal transfer printer comprising a thermal transfer ribbon (20) as claimed in claim 6.

Patentansprüche

1. Thermoübertragungsmedium, das Bilder auf ein Empfangssubstrat überträgt, wenn es einem im Betrieb befindlichen Druckkopf eines Thermoübertragungsdruckers ausgesetzt wird, wobei das Thermoübertragungsmedium folgendes aufweist:

ein flexibles Substrat (22);
einen ersten thermoempfindlichen Überzug (26), der auf dem Substrat angeordnet ist, und mindestens 75 Gew-% eines wasserdispergierbaren Wachses, bezogen auf die trokkenen Bestandteile, ein wasserlösliches, -dispergierbares oder -emulgierbares Bindemittelharz und wahlweise ein empfindliches Material in einer Menge von weniger als 20 Gew-%, bezogen auf die trockenen Bestandteile enthält, und
einen zweiten thermoempfindlichen Überzug (24), der auf dem ersten Überzug angeordnet ist und ein empfindliches Material, ein wasserdispergierbares Wachs und mindestens 20 Gew-% eines wasserlöslichen, -dispergierbaren oder -emulgierbaren Bindemittelharzes mit starken Heißklebeeigenschaften, bezogen auf die trockenen Bestandteile, enthält,

dadurch gekennzeichnet, dass der erste Überzug eine Schmelzviskosität aufweist, die um das mindestens 10-fache geringer als diejenige des zweiten Überzugs ist und der erste und der zweite Überzug aus Zusammensetzungen auf Wasserbasis oder wasserreichen Zusammensetzungen aufgetragen ist.

2. Thermoübertragungsmedium nach Anspruch 1, worin die Schmelzviskosität des zweiten Überzugs (24) um das mindestens 25-fache größer als diejenige des zweiten Überzugs (26) ist.

3. Thermoübertragungsmedium nach Anspruch 2, worin das Bindemittelharz und seine Menge in der ersten und zweiten Beschichtung (26, 24) so gewählt sind, dass Heißschmelzeigenschaften für die zweite Schicht, die größer als die Heißschmelzeigenschaften der ersten Schicht sind, hergestellt werden, worin die Heißschmelzeigenschaften durch die Ablösefestigkeitswerte in g/cm quantifiziert sind und die Ablösefestigkeitswerte für den ersten Überzug um das mindestens 10-fache kleiner als der zweite Überzug sind.

4. Thermoübertragungsmedium nach Anspruch 1, worin die Schmelzviskosität der zweiten Beschichtung (24) um das 25 bis 100-fache größer als diejenige des ersten Überzugs (26) ist.

5. Thermoübertragungsmedium nach einem der vorangegangenen Ansprüche, das aus wässrigen Emulsionen abgeleitet ist und kein organisches Lösungsmittel enthält.

6. Thermoübertragungsband (20), das folgendes aufweist:

ein Polyestersubstrat (22);
einen ersten thermoempfindlichen Überzug (26), der auf dem Polyestersubstrat angebracht ist und 75 - 97 Gew-% eines wasserdispergierbaren Wachses oder einer Mischung aus Wachsen und 3 - 25 Gew-% eines Bindemittelharzes, alles auf die trockenen Bestandteile bezogen, enthält;
einen zweiten thermoempfindlichen Überzug (24), der auf dem ersten Überzug angeordnet ist und 5 - 26 Gew-% eines Farbmittels, etwa 20 - 75 Gew-% eines wasserlöslichen, -dispergierbaren oder -emulgierbaren Bindemittelharzes mit starken Heizklebeeigenschaften, alles auf die trokkenen Bestandteile bezogen, und ein wasserdispergierbares Wachs oder eine Mischung daraus enthält, und **dadurch gekennzeichnet ist, dass** der erste Überzug eine Schmelzviskosität im Bereich von 25 - 1.500 mPa·s bei 150°C und einer Scherrate von 100 s^{-1} aufweist und der zweite Überzug eine Schmelzviskosität im Bereich von 5.000 - 30.000 mPa·s bei 150°C und einer Scherrate von 100 s^{-1} aufweist und der erste und der zweite Überzug aus Zusammensetzungen auf Wasserbasis oder wasserreichen Zusammensetzungen aufgetragen ist.

7. Thermoübertragungsdrucker, der ein Thermoübertragungsband (20) nach Anspruch 6 aufweist.

Revendications

1. Support de transfert thermique qui transfère des images à un substrat récepteur lorsqu'il est exposé à une tête d'impression en fonctionnement d'une imprimante à transfert thermique, ce support de transfert thermique comprenant :

un substrat (22) souple ;
un premier revêtement (26) thermosensible placé sur le substrat et comprenant au moins 75 % en poids d'une cire dispersible dans l'eau par rapport aux matières sèches, une résine hydrosoluble, dispersible ou pouvant être émulsionnée formant liant et, le cas échéant, une matière sensible en une quantité représentant moins de 20 % du poids des matières sèches ; et
un deuxième revêtement (24) thermosensible placé sur le premier revêtement et comprenant une matière sensible, une cire dispersible dans l'eau et au moins 20 % du poids des matières sèches d'une résine hydrosoluble, dispersible ou pouvant être émulsionnée formant liant et ayant de bonnes propriétés de pégosité à chaud ;

caractérisé en ce que le premier revêtement a une viscosité à l'état fondu inférieure d'au moins 10 fois à celle du deuxième revêtement, et le premier et le deuxième revêtement sont appliqués à partir de formulations à base d'eau ou riches en eau.

2. Support de transfert thermique suivant la revendication 1, dans lequel la viscosité à l'état fondu du deuxième revêtement (24) est au moins 25 fois plus grande que celle du premier revêtement (26).

3. Support de transfert thermique suivant la revendication 2, dans lequel la résine formant liant et sa quantité au sein du premier et du deuxième revêtement (26, 24) sont sélectionnées de manière à donner des propriétés de pégosité à chaud à la deuxième couche plus grandes que les propriétés de pégosité à chaud de la première couche, les propriétés de pégosité à chaud étant quantifiées par des valeurs de résistance au pelage en grammes/centimètres, et les valeurs de résistance au pelage du premier revêtement étant au moins 10 fois plus petites que celles du deuxième revêtement.

4. Support de transfert thermique suivant la revendication 1, dans lequel la viscosité à l'état fondu du deuxième revêtement (24) est de 25 à 100 fois plus grande que celle du premier revêtement (26).

5. Support de transfert thermique suivant l'une quelconques des revendications précédentes qui provient d'émulsions aqueuses et qui est exempt de solvants organiques.

6. Ruban (20) de transfert thermique comprenant :

un substrat (22) en polyester ;
un premier revêtement (26) thermosensible placé sur le substrat de polyester et comprenant de 75 à 97 % du

poids des matières sèches d'une cire dispersible dans l'eau ou d'un mélange de cires dispersibles dans l'eau et de 3 à 25 % du poids des matières sèches d'une résine formant liant ;
un deuxième revêtement (24) thermosensible placé sur le premier revêtement et comprenant par rapport aux matières sèches de 5 à 26 % en poids d'agents colorants, environ de 20 à 75 % en poids d'une résine hydrosoluble, dispersible ou pouvant être émulsionnée formant liant, et ayant de bonnes propriétés de pégosité à chaud et une cire dispersible dans l'eau ou un mélange de cires dispersibles dans l'eau, et **caractérisé en ce que**
le premier revêtement a une viscosité à l'état fondu de l'ordre de 25 à 1500 mPa.s à 150°C à une vitesse de cisaillement de 100 s^{-1} et le deuxième revêtement a une viscosité à l'état fondu de l'ordre de 5000 à 30 000 mPa.s à 150°C à une vitesse de cisaillement de 100 s^{-1} et le premier et le deuxième revêtement sont appliqués à partir de formulations à base d'eau ou riches en eau.

7. Imprimante à transfert thermique comprenant un ruban (20) de transfert thermique tel que revendiqué à la revendication 6.

FIG. 1

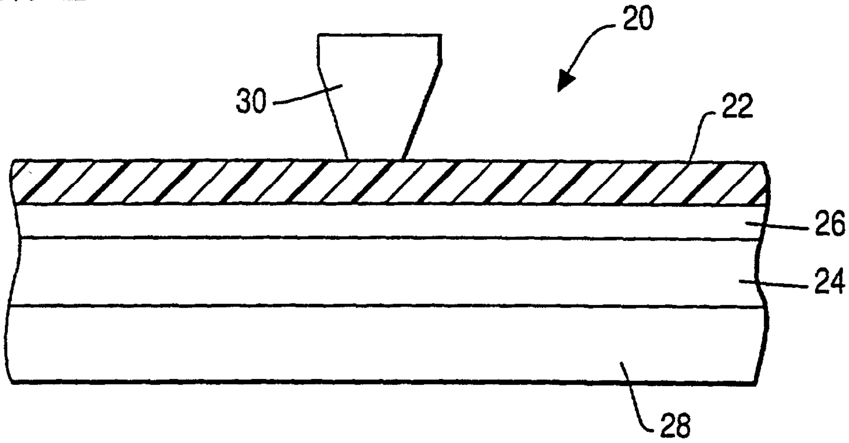


FIG. 2

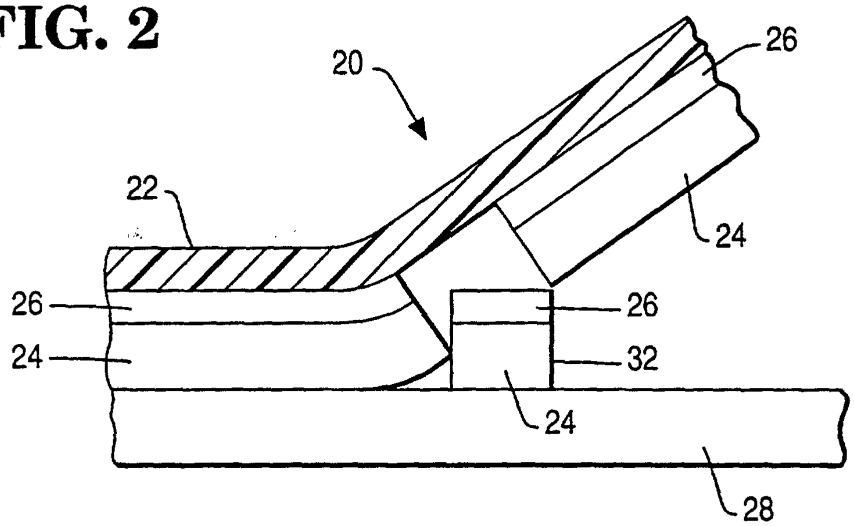


FIG. 3

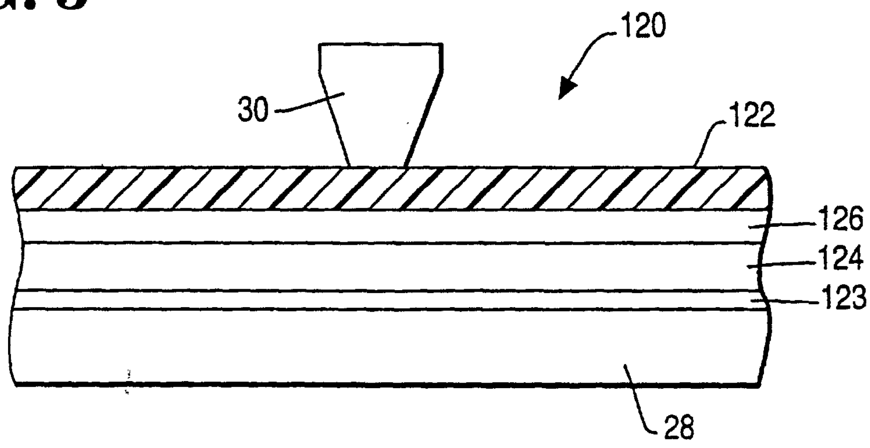
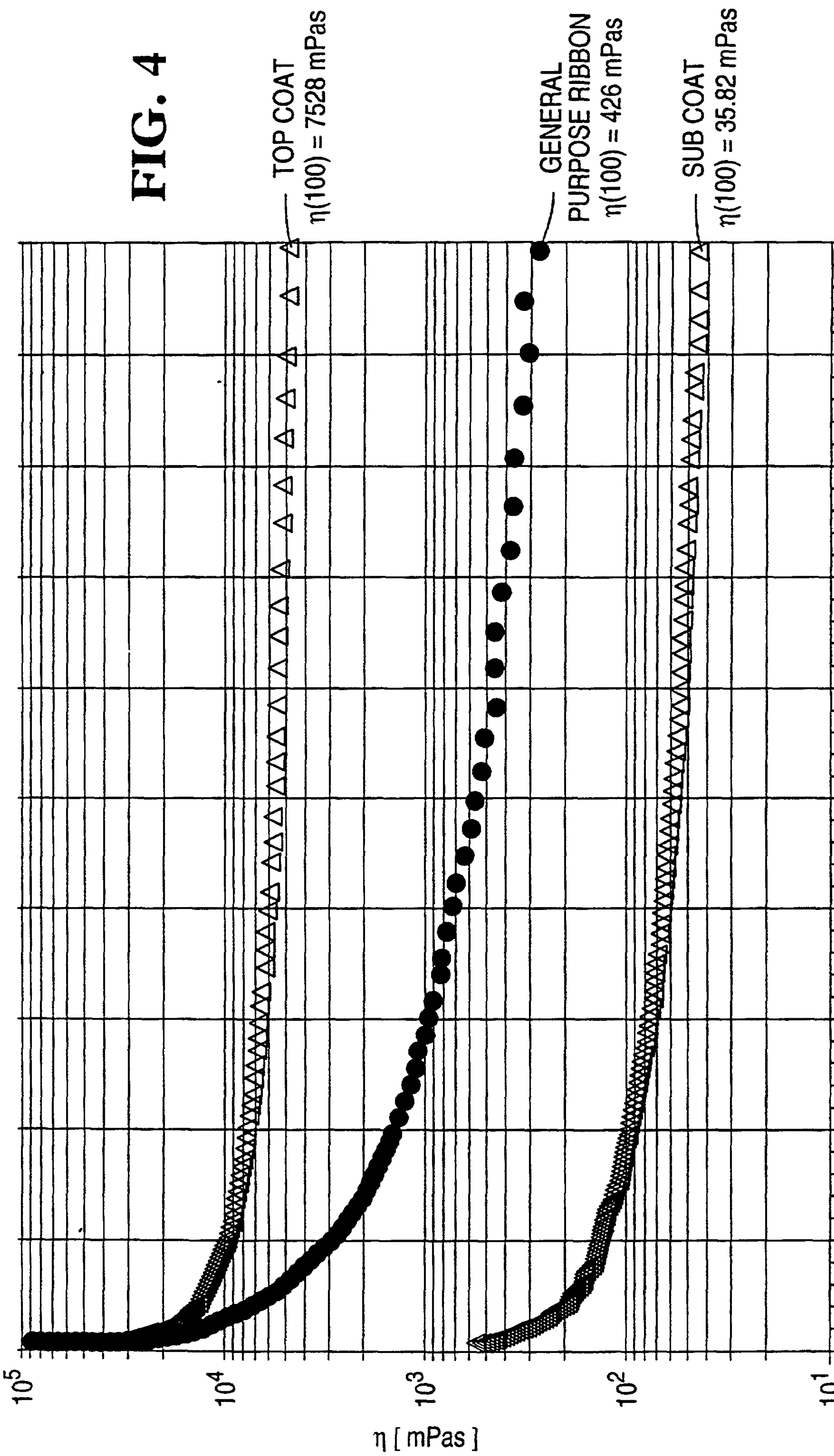


FIG. 4


TOP COAT
η(100) = 7528 mPas
GENERAL
PURPOSE RIBBON
η(100) = 426 mPas
SUB COAT
η(100) = 35.82 mPas
η [mPas]
10^5
10^4
10^3
10^2
10^1
0
50
100
150
200
250
300
350
400
450
500
γ̇ [l / s] AT 150° C