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(54) Ink-jet recording medium containing a vanadyl salt

(57) A recording medium for ink-jet printing which comprises a transparent or an opaque support having on at least one surface thereof an ink-receptive layer that can be imaged by the application of liquid ink droplets applied thereto which comprises at least one ink-absorbent polymer or resin and from 0.001 to 5.0 percent by weight, based on the total weight of the ink-receptive layer, of a vanadyl salt of the formula:

$$n[V{=}O]^{+2}\ mX^{-a}$$

wherein X is an acid anion, a is 1, 2 or 3 and n and m satisfy the relationship 2n = am.

The ink-receptive layer substantially reduces or prevents images formed thereon with inks containing triarylmethane dyes from fading and/or distorting.

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Description

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to image-recording media or elements that contain ink-receptive layers that can be imaged by the application of liquid ink droplets by means of an automated printing assembly, such as a computer-driven ink-jet printer, or a graphic plotting device, such as a pen plotter. More particularly, the present invention relates to image-recording media in which the ink-receptive layers thereof yield images formed thereon with inks containing triarylmethane dyes that exhibit decreased image fading and/or color distortion

Description of the Related Art

Ink-jet recording is rapidly gaining acceptance by the public as a recording process because it generates little noise and permits economical multicolor printing.

The ink-jet recording process is a process for performing recording on a recording medium in which droplets of a recording liquid (i.e., an ink) are ejected or propelled from a print head having one or more orifices onto the recording medium.

The recording liquid, or ink, generally comprises a recording agent such as a dye or a pigment and a solvent. The solvent or carrier liquid typically is either water, an organic material such as a monohydric or a polyhydric alcohol or a mixed solvent of water and other water miscible solvents such as monohydric or polyhydric alcohols.

In ink-jet recording, numerous schemes are utilized to control the deposition of the ink droplets onto the image-recording medium to yield the desired image. In one process, known as continuous ink-jet recording, a continuous stream of droplets is charged and deflected in an image-wise manner onto the surface of the image-recording medium, while unimaged droplets are caught and returned to an ink sump. In another process, known as drop-on-demand ink-jet recording, individual ink droplets are projected as needed onto the image-recording medium to form the desired image. Common methods of controlling the projection of ink droplets in drop-on-demand printing include piezoelectric transducers and thermal bubble formation.

Pen plotter assemblies also are used quite extensively for printing valuable information with ink on a recording medium and are particularly useful in the generation of computer aided graphics.

The recording media used in such recording processes typically comprise an ink-receiving or ink-receptive layer provided on a support. The recording media include those which are intended for reflection viewing, which usually have an opaque support, and those which are intended for viewing by transmitted light, which usually have a transparent or translucent support.

A wide variety of different types of ink-receiving layers have been proposed heretofore. For example, U.S. Pat. Nos. 4,868,581 and 4,956,223 describe ink-receiving layers consisting of albumin, gelatin, caesin, starch, cationic starch, gum arabic, sodium alginate, poly(vinyl alcohol), poly(amide), poly(acrylamide), poly(vinylpyrrolidone), a quaternized poly(vinylpyrrolidone), poly(ethyleneimine), poly(vinylpyridinium halide), melamine resins, poly(urethanes), polyesters, carboxymethyl cellulose, a SBR latex, an NBR latex, poly(vinyl formal), poly(vinyl acetate), a phenolic resin, an alkyd resin, poly(methyl methacrylate), and the like.

In general, when such media are imaged with inks, good quality text and graphic images can be generated.

One problem associated with use of such ink-receptive layers, however, is that the images made from certain inks using pen plotters and ink-jet printers are not storage stable when imaged onto the ink-receptive layers. That is, dark fading and other distortions of the image color occur after imaging, especially after a period of time has elapsed. Particularly troublesome inks are those inks which contain triarylmethane dyes. When they are imaged onto an ink-receptive layer, they appear to react with species derived from oxygen, the oxygen having been absorbed into the ink-receptive layer from the surrounding atmosphere, either as a reactive species such as singlet oxygen or as a peroxide or peroxy radical derived from oxygen attack upon another species. Such reactive species present in the polymeric ink-receptive layers are believed to add to specific sites on the triarylmethane dye molecule, specifically the triarylmethane carbon, and disrupt the dye chromophore. This causes the image to fade, bleach-out or undergo color distortion over time, rendering the image unacceptable for viewing.

It has now been found that fading and/or color distortion due to the degradation of triarylmethane dyes can be substantially reduced by the addition of certain water and/or organic-solvent soluble antioxidative materials to the ink-receptive layers of various recording media while maintaining the other required characteristics of the ink-receptive layers intact such as their quick drying capacity, their physical durability and dimensional stability, their low-tack, and the like. Specifically, it has been found that the addition of certain vanadyl salts to the formulations of the ink-receptive layers substantially reduces or eliminates fading and/or color distortion of the images formed thereon by the use of triarylmeth-

ane dyes. It is believed that the vanadyl salts function as scavengers for singlet oxygen and/or peroxides or peroxy radicals present in the ink-receptive formulations so that there are no oxygen or oxygen derivatives present in the ink-receptive layers which are available for the triarylmethane dyes to react with and cause image fading, color distortion or loss of image density.

Summary of the Invention

Thus, in accordance with the present invention there is provided a recording medium which comprises a transparent or an opaque support having on at least one surface thereof an ink-receptive layer that can be imaged by the application of liquid ink droplets applied thereto in which the ink-receptive layer comprises at least one ink-absorbent polymer or resin and from 0.001 to 5.0 percent by weight, based on the total weight of the ink-receptive layer, of a vanadyl salt of the formula:

$$n[V{=}O]^{+2}mX^{-a}$$

wherein X is an acid anion, a is 1, 2 or 3 and n and m satisfy the relationship 2n = am, whereby said ink-receptive layer yields images formed thereon from inks containing triarylmethane dyes which exhibit decreased image fading and color distortion.

Description of Preferred Embodiments

The recording media of the present invention are characterized primarily by their ink-receptive layers which comprise, as a major component, at least one suitable hydrophilic or hydrophobic ink-absorbent polymer or resin, or a blend of such polymers or resins, which can be coated onto a support material to yield an absorbent layer capable of being imaged by an ink-jet or pen plotter printing device and, as a minor component, a vanadyl salt of the formula:

$$n[V{=}O]^{+2}\ mX^{-a}$$

wherein X is an acid anion, a is 1, 2 or 3 and n and m satisfy the relationship 2n = am.

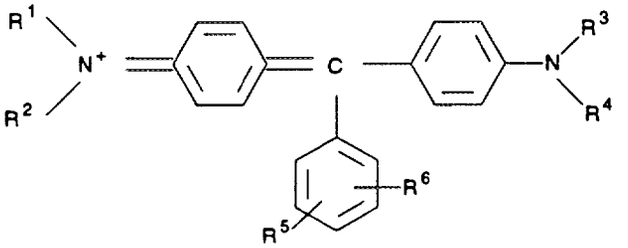
The ink-receptive layers exhibit decreased fading and/or color distortion when imaged with inks containing triarylmethane dyes.

The term "hydrophilic", as used herein, is used to describe materials that are capable of absorbing significant quantities of water, including those that are water-soluble.

The term "hydrophobic", as used herein, is used to describe materials that are substantially insoluble and non-swellable in water or an aqueous fluid.

The recording media generally comprise a substrate or a support, as a supporting member, and a recording face provided on a surface of the substrate or support, namely the ink-receptive layer. When the image generated by the ink-jet recording device or pen plotter is desired to be in the form of a reflection print for surface image observation, the support is opaque. When the image generated by the ink-jet recording device or pen plotter is desired to be viewed in a transmission mode with transmitted light, e.g., in association with an overhead projector, the support is transparent. In this application, the ink-receptive layer also must be transparent or substantially transparent. In either case, the ink-receptive layer comprises or contains at least one hydrophilic or hydrophobic ink-receptive polymer or resin or a blend of such polymers or resins which can be coated onto the support material to yield an ink-absorbent layer capable of being imaged by an ink-jet printing device or a pen plotter.

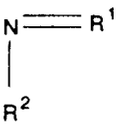
As mentioned previously, many of the commercially available inks for use in ink-jet printing devices and pen plotters contain triarylmethane dyes which appear to react with species derived from oxygen, either as a reactive species such as singlet oxygen or as a peroxide or peroxy radical derived from oxygen attack upon another species and adds to a specific site on the triarylmethane dye molecule to disrupt the dye chromophore. This in turn causes the ink-receptive layer to exhibit image fading and/or color distortion in areas where such dyes comprise a substantial part of the image. Image fading causing more than a 10 per cent decrease in image density is considered unacceptable. The triaylmethane dyes referred to above have the general formula:



wherein

R^1, R^2, R^3, and R^4 may be hydrogen, alkyl groups having from about 1 to about 6 carbon atoms, substituted alkyl groups having constituents selected from sulfonate, halogen, alkoxy, cyano, carboxy, hydroxy, aryl, and substituted aryl wherein the substituent group is sulfonate, alkyl, carboxy or halogen,

R^5 can be hydrogen or



and

R^6 can be R^1 through R^4, sulfonate, halogen, alkoxy, cyano, carboxy or hydroxy.

Specific examples of such dyes include Crystal Violet, Basic Violet 3, Color Index (CI) 42555 and Erioglaucine, Acid Blue 9, CI 42090.

In order to provide the ink-recording media of the present invention with ink-receptive layers that do not exhibit image fading and/or color distortion, the ink-receptive formulations of the ink-receptive layers of the recording media of the invention contain from 0.001 to 5.0 percent by weight, based on the total weight of the ink-receptive layer, of a vanadyl salt of the general formula:

$$n[V{=}O]^{+2}\ mX^{-a}$$

wherein X is an acid anion, a is 1, 2 or 3 and n and m satisfy the relationship 2n = am.
Typically, these additives can reduce the image density loss to less than 10 percent, preferably less than 5 percent.

The salts may either be hydrated or nonhydrated.

Specific examples of such salts include:
vanadyl sulfate, vanadyl acetate, vanadyl chloride, vanadyl phosphate, and the like. A preferred salt is vanadyl sulfate.

Although not wishing to be bound by any particular theory, it is believed that such salts reduce image fading and/or color distortion by functioning as scavengers for singlet oxygen and/or peroxides or peroxy radicals present in the ink-receptive layer so that there are no oxygen or oxygen derivatives present in the ink-receptive layers with which the triarylmethane dyes can react and cause loss of image density, image fading or color distortion.

The hydrophilic or hydrophobic ink-absorbent polymers or resins comprise the major components of the ink-receptive layer. Typically, the resin or polymer comprises at least 40 percent by weight of the ink-receptive layer to insure that an adequate amount of the polymer or resin is present in the ink-receptive layer to achieve a high degree of ink absorbency into the layer.

Examples of suitable naturally occurring water-soluble hydrophilic resins or polymers which can be used to form the ink-receptive layers of the recording media of the present invention which have a high degree of ink-absorbency include naturally occurring water-soluble hydrophilic resins such as albumin, gelatin, ceasin, starch, cationic starch, gum arabic, and sodium alginate. Examples of synthetic water-soluble hydrophilic resins or polymers which can be used in the ink-receptive layers of the recording media of the present invention include poly(vinyl alcohol) poly(amide), poly (acrylimide), poly(vinylpyrrolidone), poly(ethyleneimine), poly(vinylpyridinium halide), melamine resins, poly(urethanes) and polyesters. In addition to the above-described resins, it is possible to include hydrophobic resins such as styrene-butadiene rubbers, acrylonitrile-butadiene rubbers, poly(vinyl butyral), poly(acrylonitrile), poly(vinyl formal), poly (methyl methacrylate), poly(vinyl chloride), poly(vinyl acetate) and the like. Further, polymeric blends containing at least

one water-absorbing hydrophilic polymeric material and at least one hydrophobic polymeric material incorporating acid functional groups such as those blends disclosed in U.S. Pat. No. 5,302,436 to Miller also are suitable for use in forming the ink-receptive layers of the recording media of the present invention. Other hydrophilic and hydrophobic resins or polymers additional to those described above which can be used in the practice of the present invention can easily and readily be determined by those skilled in the art.

The ink-receptive formulations which form the ink-receptive layers of the recording media of the present invention can be prepared by dissolving the components in a common solvent. Well known methods for selecting a common solvent make use of Hansen parameters as described in U.S. Pat No. 4,935,307.

The ink-receptive layer can be applied to the support by conventional coating techniques, e.g., deposition from a solution or a dispersion of the polymers or resins in a solvent or aqueous medium, or blends thereof, by means of such processes as Meyer bar coating, knife coating, reverse roll coating, rotograuve coating, and the like.

Drying of the ink-receptive layer or coating can be effected by conventional drying techniques, e,g., by heating in a hot air oven at a temperature appropriate for the specific support chosen.

In a particularly preferred embodiment, a polymer or resin having a high degree of ink-absorbency is used for forming the ink-receptive layer and since an ink-jet or pen plotter recording method generally employs an aqueous ink, it is preferable to use a polymer or resin having good ink absorbency with respect to an aqueous ink, for example, one of the water-soluble or hydrophilic polymers or resins in the above-described polymers.

A particularly suitable ink-receptive layer for use in the recording media of the present invention is a layer which is coated onto a support as an aqueous dispersion of particles of a polyester ionomer, namely, a poly(cyclohexylenedimethylene isopthalate-cosodiosulfobenzenedicarboxylate) dispersed in a vinyl pyrrolidone polymer as disclosed in U.S. Pat. No. 4,903, 040.

Another particularly suitable ink-receptive layer for use in the recording media of the present invention is a layer which is coated onto a support as an aqueous dispersion of particles of a polyester ionomer, namely a poly(cyclohexylenedimethylene-co-oxydiethylene isophthalate-cosodiosulfobenzenedicarboxylate), dispersed in a vinyl pyrrolidone polymer as disclosed in U.S. Pat. No. 4,903,039.

Still another particularly suitable ink-receptive layer for use in the recording media of the present invention is a layer which is coated onto a support as an aqueous dispersion of particles of a polyester ionomer, namely a poly[cyclohexylenedimethylene-co-xylylene terephthalate-co-malonate-cosodioiminobis(sulfonylbenzoate)] dispersed in a vinyl pyrrolidone polymer as disclosed in U.S. Pat. No. 4, 903, 041.

The particles of polyester generally have a diameter of up to about 1 micrometer, often about 0.001 to 0.1 and typically 0.01 to 0.08 micrometer. The ratio, by weight of polyester to vinyl pyrrolidone polymer in the ink-receptive layer typically is at least 1:1 and generally is in the range of about 1:1 to 6:1.

The ink-receptive layers used in the recording media of the present invention also can incorporate various known additives, including matting agents such as titanium dioxide, zinc oxide, silica and polymeric beads such as crosslinked poly(methyl methacrylate) or polystyrene for the purposes of contributing to the non-blocking characteristics of the recording media of the present invention and to control the smudge resistance thereof; surfactants such as nonionic, hydrocarbon or fluorocarbon surfactants or cationic surfactants, such as quaternary ammonium salts for the purpose of improving the aging behavior of the ink-absorbent resin or layer, promoting the absorption and drying of a subsequently applied ink thereto, enhancing the surface uniformity of the ink-receptive layer and adjusting the surface tension of the dried coating; fluorescent dyes; pH controllers; anti-foaming agents; lubricants; preservatives, viscosity modifiers; dye-fixing agents; waterproofing agents; dispersing agents; UV absorbing agents; mildew-proofing agents; antistatic agents, and the like. Such additives can be selected from known compounds or materials in accordance with the objects to be achieved. It should be noted however that when the image generated by the recording process is desired to be viewed with transmitted light where the support is transparent, the type and amount of additives chosen must be such that the ink-receptive layer itself remains light transmissive or transparent, i.e., substantially non-light-scattering. In this case, therefore, care must be exercised in the selection and amounts of additives which are included in the ink-receptive layers so that the ink-receptive layers remain clear and transparent and are not rendered cloudy or hazy.

Particularly preferred ink-receptive layers for use in the recording media used in the present invention are layers which are coated onto a support as an aqueous dispersion of 5 to 7 weight percent of a water-dispersible polyester ionomer of the type disclosed and described in the above-mentioned U.S. Pat. Nos. 4,903,039, 4,903,040 and 4,903,041, 2.5 to 5.0 weight percent of poly(vinyl pyrrolidone), 0 to 0.5 weight percent of poly(vinyl alcohol), 0.05 to 0.3 weight percent poly(methyl methacrylate-codivinylbenezene) particles having an average particle size of 3 to 30 micrometers to enhance the smoothness of the ink-receiving layer, 0.01 to 0.1 weight percent of propylene glycol butyl ether as a surfactant to provide an ink-receiving layer having a uniform thickness, 0.01 to 0.1 weight percent vanadyl sulfate 2-hydrate and 90 weight percent water.

The ink-receptive layer may have a dry thickness sufficient for absorbing and capturing the recording liquid or ink, which may range, though variable depending on the amount of recording liquid, from 1 to 30 micrometers, preferably from 5 to 20 micrometers.

The support materials utilized in the recording media of the present invention may be transparent or opaque materials, as desired. Examples of useful support materials include paper, cloth, wood, metallic sheet materials, plastic film and glass. Most typically, paper is used where an opaque support is desired, and plastic film is used where a transparent support is desired. For the preparation of transparent recording media, the support can be composed of cellulose esters, such as cellulose triacetate, cellulose acetate propionate or cellulose acetate butyrate, polyesters such as poly(ethylene terephthalate), polyamides, polyimides, polycarbonates, polyolefins, poly(vinyl acetates), polyethers, poly(vinyl chloride) resins, polysulfonamides, glass and the like. Polyester supports, and especially poly(ethylene terephthalate), are preferred because of their excellent dimensional stability characteristics. The support must be transparent if used for overhead image projection and, if transparent, may contain known additives including UV light absorbers to filter out ultraviolet light so as to enhance the lightfastness of the recorded image. The UV absorber should be capable of absorbing light mainly in the 250 to 400 nanometer region from the light penetrating the transparent support. The light in this wavelength range is mainly responsible for the decomposition and deterioration of the dyes used as recording agents in recording liquids, thereby discoloring, fading or bleaching the image. The following compounds can be cited as suitable ultraviolet absorbers: 2,2'-dihydroxy-4-dimethoxybenzophenone (Cyasorb UV-24 available from ACC); benzophenone compounds such as 2,2'-dihydroxy-4,4'-dimethoxybenzophenone (Uvinul D-49 available from BASF); 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, (Tinuvin P available from Ciba Geigy); 2-(2'-hydroxy-5'-tert-butylphenyl)benzotriazole (Tinuvin PS available from Ciba Geigy); 2-(2'-hydroxy-3', 5'-di-tert-butylphenyl)benzotriazole (Tinuvin 320 available from Ciba Geigy); 2-(2'-hydroxy-3'-tert-butyl-5' methylphenyl)-5-chlorobenzotriazole (Tinuvin 326 available from Ciba Geigy); phenyl salicylate (Seesorb 201 available from Nisseki Calcium); p-tert-butylphenyl salicylate (Sumisorb 90 available from Sumitomo Chemical) and salicylic acid compounds such as p-octylphenyl salicylate (OPS available from Eastman Chemical).

In addition, the support itself must be self-supporting. By "self-supporting" is meant a support material such as a sheet or film that is capable of an independent existence in the absence of a supporting substrate. The support is suitably of a thickness of from about 10 micrometers to about 500 micrometers, preferably from about 25 micrometers to 125 micrometers, when it is transparent and from about 75 micrometers to 300 micrometers, preferably 125 to 300 micrometers when it is opaque. If desired, in order to promote adhesion of the ink-receptive layer to the support, the surface of the support may first be treated with a chemical priming medium as is generally known in the art. Examples of such conventional priming or adhesion promoting agents for forming a priming layer on the surface of the support include halogenated phenols or partially hydrolyzed vinyl chloride-vinyl acetate copolymers. Such a copolymer conveniently contains from 60 to 98 percent of vinyl chloride and from 0.5 to 3 percent of hydroxyl units, by weight, of the copolymer. The molecular weight (number average molecular weight) of the copolymer is in a range of from 10,000 to 30,000 and preferably from 16,500 to 25,000.

The priming agent suitably is applied at a concentration level which will yield a priming layer having a relatively thin dry coat thickness, for example, generally less than 2, and preferably less than 1 micrometer. Alternatively, the support surface may be corona-discharge-treated prior to applying the ink-receptive layer to the support surface in order to promote adhesion of the ink-receptive layer to the support.

If desired, when the ink-receptive layer is to be supported by an opaque support such as paper, a solvent hold-out layer comprising, for example, a poly(olefin) can be coated directly on the front or view surface of the support in order to prevent the solvent from the ink-receptive layer from penetrating the pores and fibers of the paper substrate. This allows for a more uniform, predictable coating of the ink-receptive layer onto the paper. The poly(olefin) layer also prevents the paper from tearing due to the large amounts of water and/or organic solvent it would otherwise absorb without the presence of the poly(olefin) layer or coating positioned between the ink-receptive layer and the paper as taught herein during the coating process of the ink-receptive layer onto the support material. Further, the presence of the poly (olefin) layer prevents the paper from curling and/or cockling due to the large amounts of water and/or organic solvent which it would otherwise absorb during the coating process.

The poly(olefin) used in the coating of the base paper should preferably be of the low density poly(ethylene) (LDPE) and/or the high density poly(ethylene)(HDPE) type. However, other poly(olefins), such as, poly(propylene) also may be utilized. The coating thickness of the poly(olefin) layer, in which other known additives for enhancing its physical and optical properties such as surfactants, optical brighteners, plasticizers, antioxidants, light stabilizers, and the like may be included, should be from 6 to 65 micrometers, preferably 10 to 40 micrometers.

Optionally, an additional backing layer or coating can be applied to the backside (i.e., uncoated) surface of the paper for the purposes of improving the machine-handling properties of the recording medium, controlling friction and resistivity, and the like. Typically, the backing layer comprises a binder and a filler. Typical fillers include amorphous and crystalline silicas, poly(methyl methacrylate), hollow sphere polystyrene beads, micro crystalline cellulose, zinc oxide, talc, and the like. The filler loading in the backing layer is generally less than 2 percent by weight of the binder component and the average particle size of the filler material is in the range of 10 to 30 micrometers and preferably 15 to 20 micrometers. Typical of the binders used in the backing layer are polymers that are not water-absorptive, such as acrylates, methacrylates, polystyrenes and poly(vinyl chloride)-poly(vinyl acetate) copolymers. Additionally, an antistatic agent also can be included in the backing layer to prevent static hindrance of the recording media. Particularly suitable antistatic agents

are compounds such as dodecylbenzenesulfonate sodium salt, octylsulfonate potassium salt, oligostyrenesulfonate sodium salt, dibutylnapthalenesulfonate sodium salt, laurylsulfosuccinate sodium salt, and the like.

The antistatic agent is added to the binder composition in an amount of 0.1 to 15 percent by weight based on the weight of the binder.

The recording media of the present invention can have the ink-receptive layer thereof overcoated with an ink-permeable, anti-tack protective layer, such as, for example, a layer comprising poly(vinyl alcohol), hydroxymethyl cellulose, hydroxyethyl cellulose, hydroxypropylmethyl cellulose, carboxymethyl cellulose, and the like. The overcoat or topcoat layer also can provide surface properties to aid in properly controlling the spread of the ink droplets to improve image quality. The ink-permeable layer having the functions as described above can be accomplished by forming a thin film of about 10 micrometers or less, preferably about 0.01 to 3.0 micrometers, of the protective polymeric material over the ink-receptive layer using conventional coating methods such as those described above. .

In practice, various additives may be employed in the coatings of the overcoat. These additives include surface active agents which control wetting or spreading action of the coating mixture, antistatic agents, suspending agents, and particulates which control the frictional properties or act as spacers for the coated product.

The invention is further illustrated by reference to the examples.

Example 1

An ink-receiving layer comprising 5.66 weight percent poly[1,4-cyclohexylenedimethylene-co-2,2'-oxydiethylene (46/54) isophthalate-co-5-sodiosulfo-1,3-benzenedicarboxylate (82/18) obtained from Eastman Chemical as AQ55, 3.77 weight percent poly(vinyl pyrrolidone) supplied by ISP Corporation under the tradename PVP K-90, 0.4 weight percent poly(vinyl alcohol) sold by Air Products and Chemicals under the tradename AIRVOL 325, 0.05 weight percent Vanadyl Sulfate 2-Hydrate Crystals, 95 percent, obtained from Eastman Fine Chemicals, 0.10 weight percent poly(methyl methacrylate-co-divinylbenzene) particles having an average particle size of 25 micrometers, 0.12 weight percent propylene glycol butyl ether obtained from Union Carbide Corporation under the tradename Propasol-B and 89.9 weight percent distilled water was applied to a transparent support comprising a 4 mil thick film of poly(ethylene terephthalate) at a dry laydown coverage of 0.8 g/ft^2 to form a recording medium of the invention. The support was corona discharge-treated just prior to the application of the coating solution.

Comparative Example 2

An ink-receptive recording medium identical to that described in Example 1 was prepared, except that the vanadyl sulfate was omitted.

Example 3

Samples of the ink-recording medium 8.5 inches (21.59 cm) in width and 11 inches (27.94 cm) in length prepared as described in Example 1 and Comparative Example 2 were imaged with a Hewlett-Packard Desk Write 550C Ink-Jet Printer employing a commercially available ink containing a triarylmethane cyan dye (Acid Blue 9) obtained from Hewlett-Packard. The images comprised a printed area or patch in the form of a square one-inch (2.54 cm) in length and one inch (2.54 cm) in width. The images appeared identical in hue and density immediately after printing. The images were then aged under identical ambient conditions in the dark over a period of 168 days at which time it was observed that the image sample of Example 1 appeared identical to a freshly imaged print, but that the corresponding imaged sample of Comparative Example 2 had changed dramatically. Specifically, the cyan patches of Comparative Example 2 appeared faded. These observations were consistent with the undesired bleaching of the triarylmethene Acid Blue 9.

The invention has been described with reference to certain preferred embodiments, but it will be understood that variations and modifications can be made within the spirit and scope of the invention.

Claims

1. A recording medium which comprises a transparent or an opaque support having on at least one surface thereof an ink-receptive layer that can be imaged by the application of liquid ink droplets applied thereto in which the ink-receptive layer comprises at least one ink-absorbent polymer or resin and from 0.001 to 5.0 percent by weight, based on the total weight of the ink-receptive layer, of a vanadyl salt of the formula:

$$n\,[V{=}O]^{+2}\,mX^{-a}$$

wherein X is an acid anion, a is 1, 2 or 3 and n and m satisfy the relationship 2n = am, whereby said ink-receptive layer yields images formed thereon from inks containing triarylmethane dyes which exhibit decreased image fading and color distortion.

2. A recording medium of claim 1, further comprising an ink-permeable protective layer for said ink-receptive layer.

3. A recording medium of claim 1, further comprising at least one priming layer between said support and said ink-receiving layer.

4. A recording medium of claim 1, wherein said resin is a hydrophilic resin.

5. A recording medium of claim 4, wherein said hydrophilic resin is poly(vinyl alcohol).

6. A recording medium of claim 4, wherein said hydrophilic resin is poly(vinylpyrrolidone).

7. A recording medium of claim 4, wherein said hydrophilic resin comprises a polyester.

8. A recording medium of claim 7, wherein said polyester is a poly(cyclohexylenedimethyelene isopthalate-co-sodiosulfobenzenedicarboxylate).

9. A recording medium of claim 7, wherein said polyester is a poly(cyclohexylenedimethyelene-co-oxydiethylene isopthalate-co-sodiosulfobenzene-dicarboxylate).

10. A recording medium of claim 7, wherein said polyester is a poly[cyclohexylenedimethylene-coxylylene terephthalate-co-malonate-co-sodioiminobis(sulfonylbenzoate)].

11. A recording medium of claim 7, wherein said polyester is poly[1,4-cyclohexylenedimethylene-co-2,2'-oxydiethylene (46/54) isophthalate-co-5-sodiosulfo-1,3-benzenedicarboxylate (82/18)

12. A recording medium of claim 8, wherein said polyester comprises particles of a poly(cyclohexylenedimethyelene isopthalate-co-sodiosulfonbenzenedicarboxylate) dispersed in a vinylpyrrolidone polymer.

13. A recording medium of claim 9, wherein said polyester comprises particles of a poly(cyclohexylenedimethyelene-co-oxydiethylene isopthalate-co-sodiosulfonbenzenedicarboxylate) dispersed in a vinylpyrrolidone polymer.

14. A recording medium of claim 10, wherein said polyester comprises particles of a poly[cyclohexylenedimethylene-co-xylylene terephthalate-co-malonate-co-sodioiminobis(sulfonylbenzoate)] dispersed in a vinylpyrrolidone polymer.

15. A recording medium of claim 11, wherein said polyester comprises particles of poly[1,4-cyclohexylenedimethylene-co-2,2'-oxydiethylene (46/54) isophthalate-co-5-sodiosulfo-1,3-benzenedicarboxylate (82/18) dispersed in a vinylpyrrolidone polymer.

16. A recording medium of claim 1, wherein the ink-receiving layer is coated onto the support as an aqueous dispersion of 5.0 to 7.0 weight percent of poly[1,4-cyclohexylenedimethylene-co-2,2'-oxydiethylene (46/54) isophthalate-co-5-sodiosulfo-1,3-benzenedicarboxylate (82/18), 2.5 to 5.0 weight percent of poly(vinylpyrrolidone), 0 to 0.5 weight percent of poly(vinyl alcohol), 0.05 to 0.3 weight percent poly(methyl methacrylate-co-divinylbenzene) particles, 0.01 to 0.1 weight percent propylene glycol butyl ether, 0.01 to 0.1 weight percent vanadyl sulfate 2-hydrate.

17. A recording medium of claim 1, wherein said support is paper.

18. A recording medium of claim 1, wherein said support is a polyester film.

19. A recording medium of claim 18, wherein said polyester is poly(ethylene terephthalate).

20. A recording medium of claim 1, wherein the dried thickness of said ink-receiving layer is from 1 to 30 micrometers.

21. A recording medium of claim 1, wherein the dried thickness of said support is from 10 to 500 micrometers.

22. A recording medium of claim 1, wherein said vanadyl salt is vanadyl sulfate.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 42 0268

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	PATENT ABSTRACTS OF JAPAN vol. 14 no. 58 (M-930) [4001] ,2 February 1990 & JP-A-01 285376 (TOMOEGAWA PAPER COMPANY LIMITED) 16 November 1989, * abstract *	1-22	B41M5/00
X	DE-A-36 02 437 (SHARP K.K.) * page 2, line 14; claim 1 *	1-22	
X	FR-A-2 238 596 (KORES HOLDING ZUG A.G.) * page 2, line 1 - line 15; claim 1 *	1-22	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B41M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22 November 1995	Bacon, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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