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3:00-CV-00386 SAWGRASS SYS INC V. CORPORATE COPY

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BY: B. Reed DEPUTY

UNITED STATES DISTRICT COURT

SOUTHERN DISTRICT OF CALIFORNIA

SAWGRASS SYSTEMS, INC., a South Carolina corporation,

Plaintiff,

v.

CORPORATE COPY, a Tennessee Corporation; TOM PEASE, an individual; PERSONAL DESIGN CONCEPTS a Washington Corporation; and DON BURNETT, an individual,

Defendants.

CASE NO. '00 CV 0386 L (LAB)

COMPLAINT FOR:

1. PATENT INFRINGEMENT
2. INDUCEMENT OF PATENT INFRINGEMENT
3. CONTRIBUTORY PATENT INFRINGEMENT
4. CONSTRUCTIVE TRUST
5. ACCOUNTING

DEMAND FOR JURY TRIAL

Plaintiff SAWGRASS SYSTEMS, INC., ("SAWGRASS") alleges as follows for its complaint ("Complaint"):

JURISDICTION AND VENUE

1. This is a civil action of which this Court has original jurisdiction under 28 U.S.C. § 1332 (diversity of citizenship), 28 U.S. C. §§ 1331, 1338(a) (federal question - patents), and 28 U.S. C. §1367(a) (supplemental) as alleged herein. SAWGRASS and defendants are citizens of different states and the amount in controversy exceeds $75,000.00.

2. Venue is proper in this Court under 28 U.S.C. §§ 1391 and 1400 because all of the defendants have committed within this judicial district actionable conduct as alleged

ORIGINAL

herein, and a substantial part of the events or omissions giving rise to the claim occurred within this judicial district.

PARTIES

3. SAWGRASS is, and at all times herein mentioned was, a corporation organized and existing under the laws of the State of South Carolina. SAWGRASS maintains its principal place of business in Mount Pleasant, South Carolina.

4. Defendant CORPORATE COPY is and at all times herein mentioned was, a corporation organized and existing under the laws of the State of Tennessee. CORPORATE COPY maintains its principal place of business in Memphis, Tennessee.

5. Defendant TOM PEASE is one of the individuals who controls CORPORATE COPY. SAWGRASS is informed and believes and based thereon alleges that TOM PEASE is a principal shareholder, officer and director of CORPORATE COPY. SAWGRASS is informed and believes and on that basis alleges that TOM PEASE aided and abetted the wrongful conduct of CORPORATE COPY as alleged herein.

6. Defendant PERSONAL DESIGN CONCEPTS is, and at all times mentioned herein was, a corporation organized and existing under the laws of the State of Washington. PERSONAL DESIGN CONCEPTS maintains its principal place of business in Pierce County, Washington.

7. SAWGRASS is informed and believes and based thereon alleges that defendant DON BURNETT is one of the individuals who controls PERSONAL DESIGN CONCEPTS and aided and abetted the wrongful conduct of PERSONAL DESIGN CONCEPTS as alleged herein. SAWGRASS is informed and believes and based thereon alleges that DON BURNETT resides in Pierce County, Washington. SAWGRASS is informed and believes and on that basis alleges that TOM PEASE aided and abetted the wrongful conduct of CORPORATE COPY as alleged herein.

8. CORPORATE COPY, TOM PEASE, PERSONAL DESIGN CONCEPTS and DON BURNETT may sometimes each be referred to herein individually as a "Defendant" or collectively as "Defendants".

9. SAWGRASS is informed and believes and based thereon alleges that in doing the things hereafter alleged, Defendants, and each of them, acted as the agents, servants, employees, representatives, and/or alter egos of the other Defendants, acting within the course and scope of their agency, employment and/or representation, and with the knowledge, consent and approval of the other defendants; their conduct was fully ratified by the other Defendants, and each of them, and was performed at their express or implied direction. As a result, each Defendant is jointly and severally liable for the damages alleged herein.

COMMON FACTUAL ALLEGATIONS

10. SAWGRASS is engaged in the research, development and manufacture of inks -- known in the art as "sublimation inks" -- used to affix color graphics to various materials. Sublimation inks are activated by the application of heat and pressure, and exhibit an affinity to polymers and polyester, making it possible to imprint items such as uniforms, T-shirts, caps, mugs, tiles, plaques, sporting good products and many other surfaces with high resolution, full-color images. The image is first printed on a transfer medium, such as a sheet of paper, from which it is transferred to the surface, or substrate, imprinted by means of a press. The imprinted transfer medium is known in the trade as a "sublimation transfer."

11. Prior to SAWGRASS' innovations in the field, various means of printing were employed to create sublimation transfers, such as off-set printing presses or silk-screen. These means were not economical in many applications, especially where mass production was undesirable. Other problems existed, including poor transferred resolution (grainy or chalky appearance of the image on the finished product) and poor color transfer (colors of the transferred image would not match the initial image colors). Attempts to improve resolution by using ink jet printers failed due to problems associated with using sublimation inks through ink jet nozzles. Thus, prior to SAWGRASS' innovations, the business of transferring images to textiles was commercially limited either to mass production, poor resolution-customized transfers, or problematic printing/transfer

processes.

12. In the early 1990's, SAWGRASS contributed several innovations to the state of the art, which enable graphics to be economically imprinted and transferred with high quality resolution, using a personal computer, color printer and heat transfer unit. SAWGRASS principals Nathan S. Hale and Ming Xu (either individually or jointly), have been issued sixteen (16) U.S. patents for innovations in adapting sublimation inks to the demands of high quality transfer needs using popular full-color computer printers. All of these patents have been assigned to SAWGRASS by the inventors, which assignments have been duly recorded with the U.S. Patent & Trademark Office. Seven (7) of the SAWGRASS patents are specifically directed to use of ink jet printers (hereinafter the "SAWGRASS Patents"). Such patents teach a process which allows a color ink jet printer, connected to a personal computer, to print a full color image on a medium for subsequent transfer of the image to another object.

13. U.S. Patent No. 5,487,614 (hereinafter the "'614 Patent") issued on January 30, 1996, teaches, inter-alia, a method of printing using a color thermal ink jet printer to print sublimation dyes on a transfer medium to form a full color printed image. The heat sensitive sublimation dyes are not activated, even though they are printed by a means of a thermal printer. The method yields a very high resolution image after the dyes are activated by applying heat and pressure to the medium to transfer the image onto an object, such as a T-shirt. A true and correct copy of the '614 Patent is attached hereto as Exhibit "A". SAWGRASS is the owner of record of the '614 Patent.

14. U.S. Patent No. 5,488,907 (hereinafter the "'907 Patent") issued on February 6, 1996, teaches, inter-alia, a process of printing a design by means of an ink jet printer using heat activated dye solids. A liquid ink is prepared which comprises heat activated, or sublimation, dye solids, at least one emulsifying enforcing agent for shielding the heat activated dye solids, and at least one solvent in which the emulsifying enforcing agent is in solution. An ink jet printer, which may be a thermal or non-thermal ink jet printer, prints the ink formulation onto the medium, without activating the ink formulation. The process

yields a very high resolution -printed image when the dyes are activated by applying heat and pressure to the medium, and the printed image is transferred onto an object, such as a T-shirt. A true and correct copy of the '907 Patent is attached hereto as Exhibit "B". SAWGRASS is the owner of record of the '907 Patent.

15. The '907 Patent overcomes challenges of compatibility between sublimation inks, which are not soluble, and ink jet printers, which utilize water as the only practical carrier for the ink to be ejected through the very small ink jet nozzles. Because sublimation dyes are insoluble in water, they will not function effectively in ink jet printers without preparation as taught by the '907 Patent, due to clogging of the ink jet nozzle and agglomeration of dye particles within the ink. The '907 Patent teaches preparation of the sublimation dyes by finely dividing them to a maximum diameter of 0.1 microns, to prevent clogging, and then suspending them with an emulsifying enforcing agent, to prevent agglomeration.

16. U.S. Patent No. 5,601,023 (hereinafter the "'023 Patent') issued on February 11, 1997 teaches, inter alia, a method of printing heat activated dye solids, including sublimation dyes, by preparing and printing a liquid ink. The liquid ink comprises a heat activated dye, a liquid carrier and an emulsifying enforcing agent which has an affinity for the sublimation dye, and shields the heat activated dye both prior to, and during, printing by the printer. Printing is performed by a printer, such as a piezo electric printer. The dye is not activated during the printing process, but is activated by the application of heat and pressure during the process of transferring the image from the medium to the object on which the image is to appear. The process yields a very high resolution image. A true and correct copy of the '023 Patent is attached hereto as Exhibit "C". SAWGRASS is the owner of record of the '023 Patent.

17. U.S. Patent No. 5,640,180 (hereinafter the "'180 Patent") issued on June 17, 1997 teaches, inter alia, a method of printing using a liquid ink comprised of heat activated dyes, such as sublimation dyes, which are present in a liquid carrier. A sulfonated lignin disperses the heat activated dye into the liquid carrier. The sulfonated lignin acts as the

emulsifying agent of the '023 Patent, and does not materially increase the amount of heat or time which is required to effect the transfer during the transfer step. A true and correct copy of the '180 Patent is attached hereto as Exhibit "D". SAWGRASS is the owner of record of the '180 Patent.

18. U.S. Patent No. 5,642, 141 (hereinafter the "'141 Patent") issued on June 24, 1997, teaches, inter-alia, a method of printing which is similar to the '180 Patent, in that the method involves the printing of a liquid ink formulation for use in a printer which comprises a heat activated dye, including sublimation dye, a liquid carrier, and at least one agent which disperses the heat activated dye. The dye activates an activation energy of not more than 400°F applied for not more than 210 seconds. When the invention is activated upon transfer, it yields an optical density of 1.0 or greater when measured. This method produces a very high resolution image when the dyes are activated by applying heat and pressure to the medium after printing. A true and correct copy of the '141 Patent is attached hereto as Exhibit "E". SAWGRASS is the owner of record of the '141 Patent.

19. U.S. Patent No. 5,734,396 (hereinafter the "'396 Patent") issued on March 31, 1998, teaches, inter alia, a method of printing heat activated dye solids, including sublimation dye solids, by combining the dye solids with a liquid carrier and an emulsifying enforcing agent, which is soluble in the liquid carrier, and which has an affinity for the dye and protects the dye. The liquid ink is printed by computer-driven printer onto the medium. The process produces an image having very high resolution when the dyes are activated by applying heat and pressure to the medium. A true and correct copy of the '396 Patent is attached hereto as Exhibit "F". SAWGRASS is the owner of record of the '396 Patent.

20. Patent No. 5,830,263 (hereinafter the "'263 Patent") issued on November 3, 1998, teaches, inter alia, a means of suspending the sublimation dyes within a formulation which is compatible with ink jet printers. A true and correct copy of the '263 Patent is attached hereto as Exhibit "G". SAWGRASS is the owner of record of the '263 Patent.

21. Since at least early 1999 and continuing, Defendants CORPORATE COPY

and TOM PEASE (hereinafter "THE CORPORATE COPY Defendants") have sold and continue to sell liquid sublimation inks which infringe the Sawgrass Patents.

22. Sawgrass informed CORPORATE COPY that its sale of the inks infringes the Sawgrass patents in three separate letters dated February 2nd and April 30th, 1999 and January 27th, 2000. In addition, these letters informed TOM PEASE that his actions rendered him personally liable for patent infringement.

23. Sublimation inks are commercially used in ink jet printers only to practice the methods patented in the Sawgrass Patents, and not for any other purpose.

24. SAWGRASS is informed and believes and based thereon alleges that THE CORPORATE COPY Defendants are marketing their liquid sublimation inks under the trade name SUBLIBRITE, with explicit instructions as to how purchasers can practice SAWGRASS' patented processes. SAWGRASS is further informed and believes and based thereon alleges that THE CORPORATE COPY Defendants encourage their customers to infringe the Sawgrass Patents described herein.

25. Defendants PERSONAL DESIGN CONCEPTS and DON BURNETT (hereinafter "The PERSONAL DESIGN CONCEPTS Defendants") use a large amount of sublimation ink in their business. The majority of this use occurs during the winter holiday season. For the past several years, The PERSONAL DESIGN CONCEPTS Defendants have purchased the sublimation ink used during the winter holiday season from one of Sawgrass' distributors in or about the month of October. Typically, The PERSONAL DESIGN CONCEPTS Defendants purchase approximately $10,000 worth of sublimation ink in or about the month of October.

26. During October 1999, SAWGRASS was informed that The PERSONAL DESIGN CONCEPTS Defendants had not placed their customary order for sublimation inks with Sawgrass' distributor. Nathan Hale, a principal of SAWGRASS, spoke with DON BURNETT. Mr. Hale learned that The PERSONAL DESIGN CONCEPTS Defendants were planning to purchase their required sublimation ink from a company located in San Diego, California called Sublimation Resources, Inc. ("Sublimation

Resources"). Sublimation Resources is a defendant in a separate patent infringement lawsuit currently pending in this judicial district which alleges, inter alia, that Sublimation Resources infringed and continues to infringe the Sawgrass Patents.

27. Mr. Hale had several subsequent conversations with DON BURNETT. During these conversations, Mr. Hale informed The PERSONAL DESIGN CONCEPTS Defendants that they would be infringing patent rights held by SAWGRASS if they purchased sublimation inks from Sublimation Resources and used such inks.

28. Despite this information, SAWGRASS is informed and believes, and based thereon alleges that The PERSONAL DESIGN CONCEPTS Defendants purchased sublimation inks from Sublimation Resources and used the inks it purchased.

29. SAWGRASS has been, is being, and will continue to be, damaged by the conduct of Defendants, and each of them. SAWGRASS' harm resulting from Defendants' conduct is irreparable and cannot be remedied in its entirety by the recovery of money damages and SAWGRASS has no adequate remedy at law.

30. All causes of action in this Complaint are pleaded in the alternative.

FIRST CAUSE OF ACTION

PATENT INFRINGEMENT

(Against All Defendants)

31. SAWGRASS realleges and incorporates herein paragraphs 1 through 30 of this Complaint.

32. Defendants, and each of them, have infringed and continue to infringe the claims of the Sawgrass Patents described herein by making, using, selling, offering to sell, and/or distributing products including but not limited to liquid sublimation inks which infringe said patents.

33. Such acts of infringement are occurring, have occurred in the past, and will continue to occur, without the authority or license of SAWGRASS unless this Court permanently enjoins the infringing conduct of Defendants, and each of them.

34. SAWGRASS has been, is being, and will continue to be, damaged by the

infringing conduct of Defendants, and each of them in an amount to be established according to proof at trial.

35. SAWGRASS is informed and believes and based thereon alleges that Defendants, and each of them, have willfully and deliberately conducted the infringing activities described herein, thereby warranting the assessment of enhanced damages pursuant to 35 U.S.C. § 284.

SECOND CAUSE OF ACTION

INDUCING PATENT INFRINGEMENT

(Against THE CORPORATE COPY Defendants)

36. SAWGRASS realleges and incorporates herein paragraphs 1 through 35 of this Complaint, as though set forth in full.

37. THE CORPORATE COPY Defendants have actively encouraged and instructed persons and entities to purchase products (including but not limited to liquid sublimation inks) in order that said persons or entities may practice SAWGRASS' process taught by the claims of the Sawgrass Patents.

38. THE CORPORATE COPY Defendants have engaged in such conduct with knowledge that the inks will be utilized by said consumers to practice SAWGRASS' patented process without authorization or license from SAWGRASS.

39. As alleged herein, THE CORPORATE COPY Defendants are liable for inducing patent infringement under 35 U.S.C. § 271(b).

40. The acts of infringement alleged herein are occurring, have occurred in the past, and will continue to occur, without the authority or license of SAWGRASS unless this Court permanently enjoins the infringing conduct of THE CORPORATE COPY Defendants, and each of them.

41. SAWGRASS has been, is being, and will continue to be, damaged by the infringing conduct of THE CORPORATE COPY Defendants in an amount to be established according to proof at trial.

42. SAWGRASS is informed and believes and based thereon alleges that THE

CORPORATE COPY Defendants have willfully and deliberately conducted the infringing activities described herein, thereby warranting the assessment of enhanced damages pursuant to 35 U.S.C. § 284.

THIRD CAUSE OF ACTION

CONTRIBUTORY PATENT INFRINGEMENT

(Against THE CORPORATE COPY Defendants)

43. SAWGRASS realleges and incorporates herein Paragraphs 1 through 42 of this Complaint as though fully set forth in full.

44. THE CORPORATE COPY Defendants have sold, and continue to sell, liquid sublimation inks which are components required to practice SAWGRASS' methods as taught by the Sawgrass Patents.

45. Such components constitute material parts of SAWGRASS' inventions, and THE CORPORATE COPY Defendants knew, or should have known, that they were especially made, formulated and adapted for use in an infringement of SAWGRASS' patented method and were not a staple article or commodity of commerce suitable for substantial noninfringing use.

46. As alleged herein, THE CORPORATE COPY Defendants are liable as contributory infringers under 35 U.S.C. § 271(c). Such acts of infringement are occurring, have occurred in the past, and will continue to occur, without the authority or license of SAWGRASS unless this Court permanently enjoins the infringing conduct of THE CORPORATE COPY Defendants.

47. SAWGRASS has been, is being, and will continue to be, damaged by the infringing conduct of THE CORPORATE COPY Defendants in an amount to be established according to proof at trial.

48. SAWGRASS is informed and believes and thereon alleges that THE CORPORATE COPY Defendants have willfully and deliberately conducted the infringing activities described herein, thereby warranting the assessment of enhanced damages pursuant to 35 U.S.C. § 284.

FOURTH CAUSE OF ACTION

CONSTRUCTIVE TRUST

(Against All Defendants)

49. SAWGRASS realleges and incorporates herein paragraphs 1 through 48 of this Complaint as set forth in full.

50. Continuing for an unknown time, THE CORPORATE COPY Defendants have been wrongfully infringing upon the Sawgrass Patents and have been profiting therefrom. Such profits rightfully belong to SAWGRASS.

51. Continuing from about October 1999, the PERSONAL DESIGN CONCEPTS Defendants have been infringing upon the Sawgrass Patents and have been profiting therefrom. Such profits rightfully belong to SAWGRASS.

52. Unless an involuntary trust is imposed by the court upon the proceeds from this wrongful conduct, as alleged herein, said revenue is in danger of being lost, removed, or materially destroyed, or encumbered by Defendants, and each of them.

FIFTH CAUSE OF ACTION

ACCOUNTING

(Against All Defendants)

53. SAWGRASS realleges and incorporates herein Paragraphs 1 through 52 of this Complaint as though set forth in full.

54. The exact nature and extent of the financial advantage gained by Defendants, and each of them, as a consequence of the wrongful conduct alleged is so complicated and subject to deception that an ordinary legal action demanding a fixed sum is impracticable and the exact measure of SAWGRASS' damages cannot be determined without an accounting.

55. SAWGRASS has demanded that Defendants, and each of them, account for the revenue attributable to the sale of the liquid sublimation inks being sold and/or distributed by Defendants, and each of them. Defendants, and each of them have failed and refused, and continue to fail and refuse, to render such an accounting.

WHEREFORE, SAWGRASS prays for judgment against Defendants, and each of them, as follows:

As to the First, Second and Third Causes of Action:

1. That, pursuant to 35 U.S.C. § 283, an injunction be issued preliminarily and permanently enjoining Defendants, and each of them, their principals, officers, directors, agents, servants, employees and all those persons in active concert or participation with Defendants from further infringement, inducing infringement and/or contributory infringement;

2. That, pursuant to 35 U.S.C. § 284, judgment be entered against Defendants, and each of them, for damages for infringement, in an amount to be proven at trial, including treble damages and attorneys' fees because of the willful nature of such infringement.

As to the Fourth Cause of Action:

3. For the imposition of an involuntary trust and/or equitable lien upon all proceeds earned by Defendants, and each of them, as a consequence of their tortious conduct;

As to the Fifth Cause of Action:

4. That an accounting of the financial dealings of Defendants, and each of them, arising from the tortious conduct alleged herein be conducted and that SAWGRASS have judgment against Defendants, and each of them, for such sums as may be found due and owing to SAWGRASS under such accounting;

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As to All Causes of Action:

5. For attorneys' fees and costs as provided by law;

6. For pre-judgment interest; and

7. For such other and further relief as the Court may deem proper.

Dated: February 24, 2000

BARNHORST SCHREINER & GOONAN
a professional corporation

By: ______________________
Gregory P. Goonan
Attorneys for Plaintiff,
SAWGRASS SYSTEMS, INC.

DEMAND FOR JURY TRIAL

Plaintiff, Sawgrass Systems, Inc., hereby demands a trial by jury.

Dated: February 24, 2000

BARNHORST SCHREINER & GOONAN
a professional corporation

By: ______________________
Gregory P. Goonan
Attorneys for Plaintiff SAWGRASS SYSTEMS, INC.

US005487614A

United States Patent [19]

Hale

[11] **Patent Number: 5,487,614**

[45] **Date of Patent: * Jan. 30, 1996**

[54] **METHOD OF PRINTING A MULTIPLE COLOR IMAGE USING HEAT SENSITIVE INKS**

[75] Inventor: **Nathan S. Hale**, Mt. Pleasant, S.C.

[73] Assignee: **Sawgrass Systems, Inc., a South Carolina Corporation**, Mt. Pleasant, S.C.

[*] Notice: The portion of the term of this patent subsequent to Sep. 21, 2010, has been disclaimed.

[21] Appl. No.: **207,756**

[22] Filed: **Mar. 8, 1994**

Related U.S. Application Data

[63] Continuation of Ser. No. 195,851, Feb. 10, 1994, Pat. No. 5,431,501, which is a continuation-in-part of Ser. No. 724,610, Jul. 2, 1991, Pat. No. 5,302,223, which is a continuation-in-part of Ser. No. 549,600, Jul. 9, 1990, abandoned.

[51] **Int. Cl.**^{6} **B41J 2/315**

[52] **U.S. Cl.** **400/120.02**; 156/240

[58] **Field of Search** .... 400/120.01, 240, 400/241.1; 156/230, 240, 583.1; 8/471; 346/76 PH, 120.02, 120.08

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,844,770	7/1989	Shiraishi et al.	156/387
4,882,593	11/1989	Touma et al.	346/111
4,930,417	6/1990	Isobe	101/465
5,010,352	4/1991	Takei et al.	346/76 PH
5,246,518	9/1993	Hale	156/230
5,263,781	11/1993	Mima et al.	400/120
5,350,929	9/1994	Meyer et al.	250/573

FOREIGN PATENT DOCUMENTS

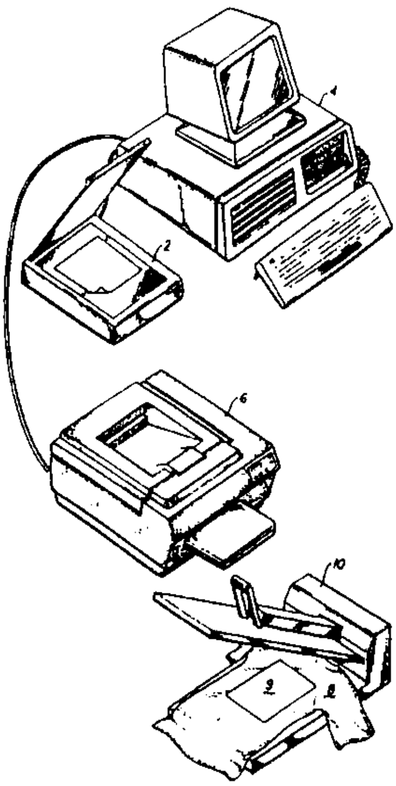
102390 6/1982 Japan .

Primary Examiner—Ren Yan
Attorney, Agent, or Firm—B. Craig Killough

[57] **ABSTRACT**

An image is permanently transferred to a substrate having a cotton component, or other component which is absorbent or porous, from a medium printed with the image by a thermal printer using heat activated ink. A polymer surface preparation material and the ink are transferred by the thermal printer to the medium from a ribbon containing the ink and the surface preparation material, without activating the ink or the surface preparation material. The image is transferred from the medium to the substrate by applying sufficient heat and pressure to the medium to activate and transfer the ink and the surface preparation material, with the surface preparation material bonding the ink to the substrate.

4 Claims, 3 Drawing Sheets



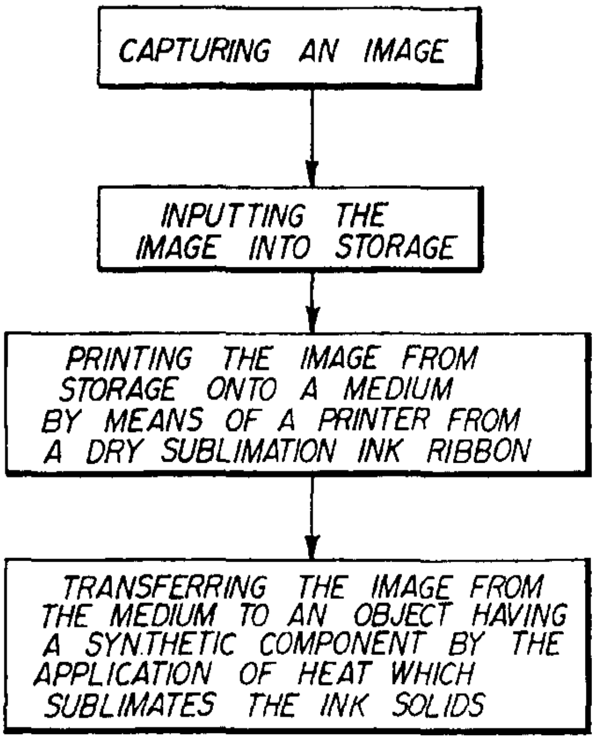

CAPTURING AN IMAGE
INPUTTING THE IMAGE INTO STORAGE
PRINTING THE IMAGE FROM STORAGE ONTO A MEDIUM BY MEANS OF A PRINTER FROM A DRY SUBLIMATION INK RIBBON
TRANSFERRING THE IMAGE FROM THE MEDIUM TO AN OBJECT HAVING A SYNTHETIC COMPONENT BY THE APPLICATION OF HEAT WHICH SUBLIMATES THE INK SOLIDS

FIG 1

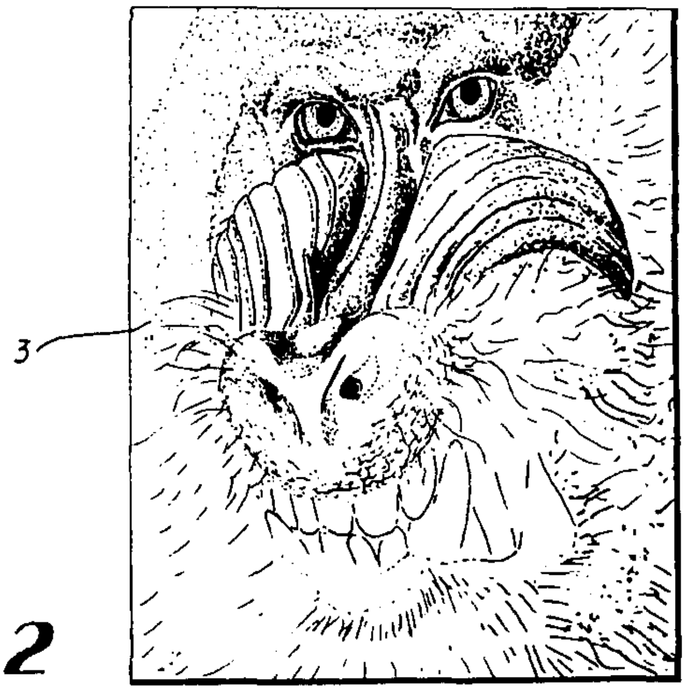

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FIG 2

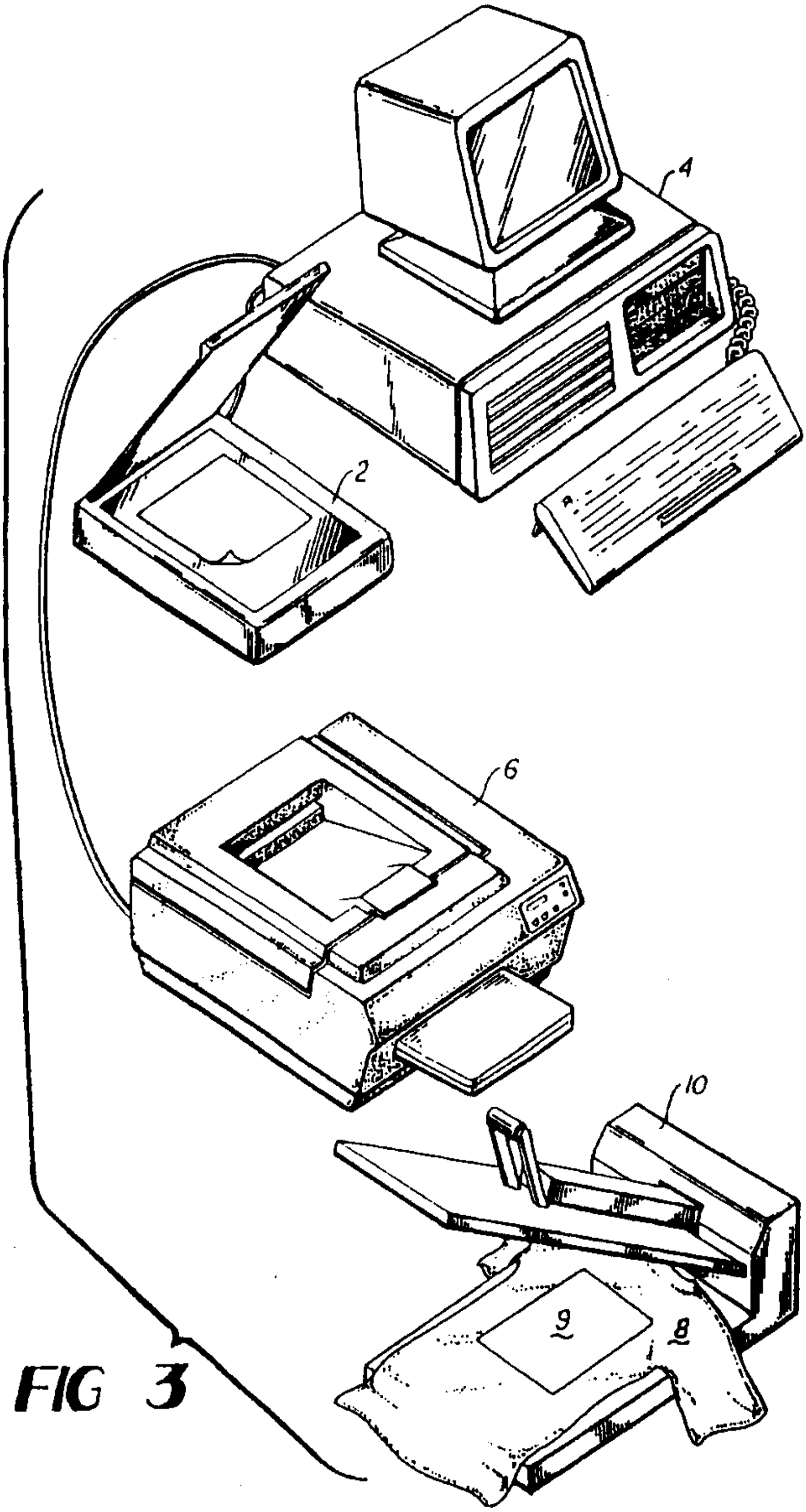

FIG 3

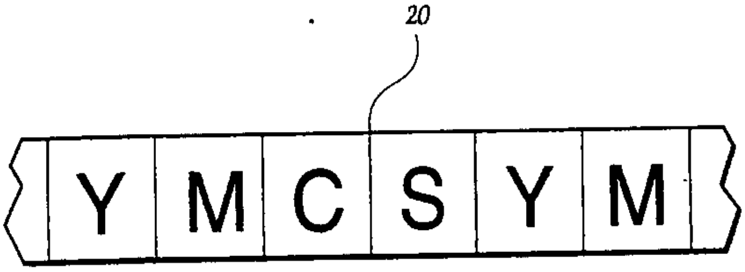

Fig. 4

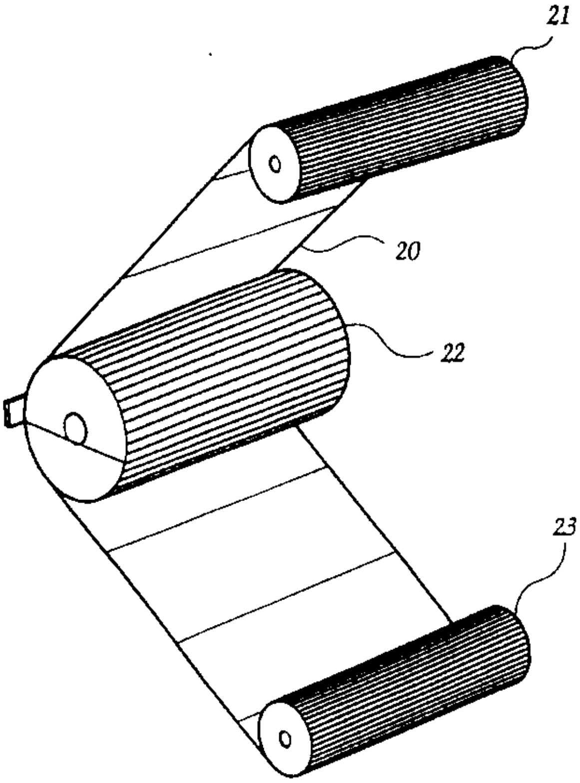

Fig. 5

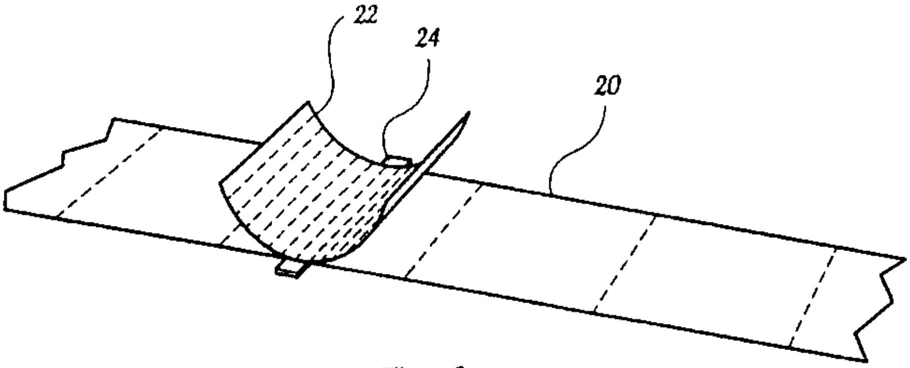

Fig. 6

METHOD OF PRINTING A MULTIPLE COLOR IMAGE USING HEAT SENSITIVE INKS

This is a continuation of application Ser. No. 08/195,851 filed Feb. 10, 1994, now U.S. Pat. No. 5,431,501, which is a continuation in part of application Ser. No. 07/724,610 filed Jul. 2, 1991, now U.S. Pat. No. 5,302, which is a continuation in part of application Ser. No. 07/549,600, filed Jul. 9, 1990, now abandoned.

FIELD OF THE INVENTION

This invention relates to printing generally and is more specifically directed to a method of thermally printing heat activated ink and thermally printing a surface preparation material onto paper or other printable material as a medium, and subsequently heat activating the ink and surface preparation material, thereby transferring the design formed by the ink from the medium to a substrate on which the design is to permanently appear.

BACKGROUND OF THE INVENTION

Words and designs are frequently printed onto clothing and other textile materials, and other objects. Common means of applying such designs to objects include the use of silk screens, and mechanically bonded thermal transfers. Silk screen process is well known in the art, and a mechanical thermal process to textile materials is described in Hare, U.S. Pat. No. 4,244,358.

The use of computer technology allows a virtually instantaneous printing of images. For example, video cameras or scanning may be used to capture an image to a computer. The image may then be printed by any suitable printing means, including mechanical thermal printers, wet printed (inkjet) heat sensitive transfers and laser printers. These printers will print in multiple colors.

The process of thermal transfers by mechanical means is described in Hare, U.S. Pat. No. 4,773,953. The resulting mechanical image, as transferred, is a surface bonded image with a raised plastic like feel to the touch. The resulting printed image is stiff to the feel, has poor dimensional stability when stretched and poor color range.

Heat activated transfer ink solids change to a gas at about 400° F., and have a high affinity for polyester at the activation temperature and a limited affinity for most other materials. Once the gassification bonding takes place, the ink is permanently printed and highly resistant to change or fading caused by laundry products.

Images produced by heat activated inks, such as sublimation inks, which are transferred onto textile materials having a cotton component do not yield the high quality image experienced when images formed by such inks are printed onto a polyester substrate. Images which are printed using sublimation inks applied by heat and pressure onto substrates of cotton or cotton and polyester blends yield relatively poor results. The natural tendency of the cotton fiber to absorb the ink causes the image to lose its resolution and become distorted.

To improve the quality of images transferred onto substrates having a cotton component, such substrates are surface coated with materials, such as the polymeric coating described in DeVries et. al., U.S. Pat. No. 4,021,591. Application of the surface coating to the substrate allows the surface coating material to bond the ink layer to the substrate, reducing the absorbency of the ink by the cotton and improving the image quality.

In the prior art, coverage of the surface coating material has not been matched to the image. The, surface coating material is applied to the substrate over the general area to which the image layer formed by the inks is to be applied, such as by spraying the material or applying the material with heat and pressure from manufactured transfer sheets, which are usually rectangular in shape. The area coated with the surface coating material is therefore larger than the area covered by the ink layer. The surface coating may be seen extending from the margins of the image. The excess surface coating reduces the aesthetic quality of the printed image on the substrate. Further, the surface coating tends to turn yellow with age, which is undesirable on white and other light colored substrates.

Hale, U.S. Pat. No. 5,246,518 and 5,248,363 disclose the use of thermal printers to produce an image on a medium or transfer sheet wherein the image is comprised of sublimation or other heat activated inks. The method described in Hale does not activate the ink during the printing of the medium or transfer sheet.

Color ink formulations for color ink jet printers comprising sublimation pigment solids mixed with water were sold briefly in 1989. The ink formulations were not stable, since the solid pigments settled from the water carrier, and clogged the jets of ink jet printers.

SUMMARY OF THE PRESENT INVENTION

The present invention uses a heat activated ink solids. The ink solids are transferred in the desired design by means of a printer onto a medium, which will most commonly be paper. The printer incorporates a thermal process, but operates at a temperature which is below the temperature which will activate the ink solids. Heat activation of the ink solids does not take place at the time of printing of the image by the printer from the ribbon to the medium, but rather takes place at the time of the transfer of the image from the medium to the substrate on which the image is permanently applied.

Sufficient temperature is applied to the medium and the substrate to transfer the image from the medium to the substrate. The heat activates, or sublimates, the ink solids during this transfer from the medium to the substrate. The image is then permanently bonded to the substrate.

The ribbon used with thermal color printers in this process has alternate color panels of cyan, yellow and magenta, respectively. The heat activated ink solids as used do not have an affinity for highly absorbent fibers such as cotton. The present invention introduces a ribbon panel having a polymeric coating thereon, which acts as a surface coating for the cotton component of the substrate.

After the printer makes its third pass to print the image in the desired colors onto the medium, the printer then prints the surface preparation material from the ribbon. The surface preparation material is printed over the entire image, but does not exceed the boundaries of the image. The image is then transferred from the medium to the substrate by the application of heat and pressure, with the surface preparation material permanently bonding the ink solids to the substrate.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a block diagram showing the printing process.

FIG. 2 illustrates an example of a design printed by a printer using the printing process.

FIG. 3 is a diagrammatic illustration showing exemplary elements of computer and printing systems which could be used to achieve the printing process.

FIG. 4 is a section of a ribbon used with a color thermal printer demonstrating the three color panels of yellow, magenta and cyan respectively, and a fourth panel having surface preparation material thereon, in a repeating pattern.

FIG. 5 demonstrates a ribbon on a roll as the ribbon is transported in a thermal printer.

FIG. 6 shows a section of the ribbon as it comes in contact with the print head of the thermal printer.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In the preferred embodiment, a video camera or scanning device 2 is used to capture an image 3. This image is then input into a computer 4. The computer directs a printer 6 to print the image. Any means of inputting an image into a computer may be used, including images generated by software. Available computer design graphic software may be used, or still photography may be used. The design may be photographic, graphic artistic, or simply letters or words. Virtually any printer which will print in response to a computer may be used, including impact, laser or thermal printers. In most applications, a printer which will print in multiple colors is desirable. A thermal printer which will print in what is known as "four pass" (four color) or "three pass" (three color) may be most commonly used, but laser printers having the same multiple color capability are available. The ribbon 20 is taken from a roll 21 past a platen 22 and print head 24 on to a take up roll 26. FIGS. 4 and 5. The use of cyan, yellow and magenta panels on the ribbon allow the printer to print in full color or multi-color designs.

In the present invention, heat activated ink solids are used, and are transferred to a medium by the printer without activating the ink solids. In the preferred embodiment, the heat activated transfer ink solids are transferred onto the medium by the printer from a ribbon.

The ribbon substrate as used with the printer may be a plastic or a polyester ribbon. The dry release, heat activated ink solid may be retained on the ribbon by the use of a heat sensitive material which will release the ink upon the application of heat to the ribbon. The printer, such as a thermal transfer printer, will transfer the ink in the desired design and colors from the ribbon to the medium at a temperature of approximately 140° F. This temperature is sufficient to release the heat sensitive material to allow transfer of the ink solids to the medium, without activating the ink solids. The wax aids in holding the heat activated ink solids on the medium in the precise design, eliminating the need for specially coated paper, while also producing an image which has high resolution.

While in the preferred embodiment the binder and heat sensitive material are applied with the ink solids from a ribbon, other means of applying the ink solids with a binder could be used. Since a wax in liquid form tends to have an affinity for paper, the wax will readily bond with the paper medium, holding the ink solids to the medium, until the ink solids are released by the application of heat which is sufficient to heat activated transfer the ink solids. Virtually any material may be used as a medium which can be printed upon by a printer, and which will withstand the heat activated transfer temperature of 400° F., as is described herein. If a thermal printer is used, this medium may be any paper commonly used with thermal printers, however, standard bond paper may be used, or even a sheet of metal, if the metal can be handled by the printer.

A surface preparation material may be applied by the printer to the medium. If a multiple pass thermal printer is used, one panel of the ribbon used with the printer has the surface preparation material thereon.

Color thermal printers print from a ribbon having multiple panels of ink bound to the ribbon. Typically, the panels have recurring sequences of cyan, yellow and magenta ink, from which multiple color or full color images may be produced. An embodiment of the present invention provides an additional panel having a surface preparation material thereon, which is bound to the ribbon.

The surface preparation material may be a polymeric material which is bound to the ribbon by a wax with the heat sensitive material binder which is released by the heat from the printer. The panel having the surface preparation material thereon is introduced into the sequence of panels, so that the sequence includes recurring panels of cyan, yellow, magenta, and surface preparation material.

In use, the thermal printer makes four passes to print the image from the ribbon to the medium. The color image is printed in the desired form and image by means of the three color panels present on the ribbon. The surface preparation material is then printed as the last pass, so that the surface preparation material is applied over the inks as they form the image on the medium.

The surface preparation material is printed only over the inks, but is printed completely over the ink solids. It is desired to have the surface preparation material present on all surfaces of the substrate to which the inks are applied, but an excess of the material on the edges or fringes is not desirable. A problem which the present invention solves is that the gross application of the surface preparation results in yellowing of the fabric, which increases as the fabric is laundered. By applying the surface preparation material only where the ink is applied to the substrate, the surface preparation material is covered by the ink, and no yellowing or discoloration of the substrate by the surface preparation material occurs, and no change in hand or feel of the fabric occurs where the image is not present. The use of the computer controlled printer causes the surface preparation to be completely printed over the image on the medium for complete bonding of the inks, but does not allow the surface preparation material to be applied beyond the edges or margins of the images, excepting for reasonable tolerances.

Once the image and the surface preparation material are printed onto the medium, the image may be permanently transferred onto the substrate presently, or at a later time. Most commonly, the design will be transferred onto a textile substrate, such as a shirt 8, although the image may be transferred onto other materials, such as metal, ceramic, wood, or plastic. The design 3, which is printed onto the medium 9 without activating the ink, is placed against the object 8. A temperature which is sufficient to activate the ink solids is then applied. This temperature will typically be around 400° F. This temperature is applied for a time sufficient to heat activate and transfer the ink solids. A heat transfer machine 10 may be used to accomplish the transfer of the inks from the medium to the substrate. Activation, or sublimation, does not take place at the time of printing the image onto the medium, even though heat may be used to accomplish the printing of the image onto the medium, but occurs during the transfer from the medium to the substrate.

The heat activated ink solid will bond to a synthetic material such as polyester, when sufficient heat is applied for a sufficient time. Accordingly, if the object to which the design is to be applied is a textile material and has a sufficient polyester composition, no surface coating is required, although it may be applied.

Printers other than thermal printers could be used. It is preferred that the surface preparation material be applied antecedent to the printing of the inks to the medium, however, application of the surface preparation material should occur during the printing of the medium. For example, if multiple color ink jet printing is performed by applying cyan, yellow and magenta inks as instructed by the computer, the surface preparation material should then be applied by the printer over the inks so as to cover the inks by the printer.

It is possible to achieve adequate results by mixing or incorporating the surface preparation material into the ink formulation, along with the ink, binder and other components. For example, one or more of the panels of the ribbon of the multiple pass thermal printer could incorporate a polymeric surface preparation material which is printed onto the medium with the ink and the binder.

The surface preparation material is applied to the medium by the printer without activating the surface preparation material. The paper which comprises the medium my have a cotton content or other absorbent material content, and it is not desired for the surface preparation material to treat the medium. The invention takes advantage of the relatively low heat ranges employed by printers which use heat as part of the printing process. The surface preparation material is not activated by the printer in printing the medium, but is activated by the higher heat used to transfer the inks to the substrate.

The ribbon could be comprised of heat sensitive dye, heat sensitive material, binder material and other additives. A general formulation is shown as:

Material	Weight %
Sublimation Dye	5–30
Heat Sensitive Material	30–70
Binder	0–30
Additives	0–30

The sublimation dye could have a sublimation temperature or activation temperature of 120° to 300° C. Examples of such dyes are: C.I. Disperse 3 (cyan), C.I. Disperse 14 (cyan), C.I. Disperse Yellow 54 (Yellow), C.I. Disperse Red 60 (Red), Solvent Red 155 (Diaresin Red K, red), etc. The commercial sources of such dyes including Keystone Aniline's Sublaprint® series, BASF Corporation's Bafixan® Transfer Printing dyes series, Eastman Chemical's Eastman® disperse series and Crompton & Knowles Corporation's Intratherm® disperse dyes series. The beau sensitive material could be wax or water-like polymer materials with melting temperature between 50°–120° C. Examples of such materials are hydrocarbon wax, montan wax, ester wax, carnauba wax, polyethylene wax, high-fatty acid monoglyceride, etc. Commercial sources of such materials include Moore and Munger Marketing's fully-refined paraffin wax series, Petrolite Chemical's Polywax® series, etc. The binder materials could be selected from resin polymer materials having relatively low melting points (<150° C.) and low molecular weights (<500,000). Such materials should have glass transition temperatures higher than 0° C. and low affinity to sublimation dyes of the type used herein. The additives serve to prove dispersion, coating aid, mar, gloss, or other features of the image or the printing and

transfer process. Surfactant materials such as Dow Corning® Additives, or BYK Chemie's DisperBYK® could be used.

The ribbon substrate is coated with the formulation by means of direct gravure or other similar coating technology. The substrate may be heat-resistant plastic film (e.g., PET mylar, nylon, cellulose, polyamide, etc.) of 4–20 micron thickness or paper of 10–50 microns thickness.. Coating may be accomplished by using either solvent coating, or hot-melted, or emulsion form with a resulting dry coating thickness of 2–10 microns. The dry coating on the substrate should have a desired melting temperature as determined by the printer application to achieve proper release of the dry coating during thermal printing.

Formulation Example 1

Material	Weight %
Sublaprint 70069	10
Paraffin Wax R-164[2]	22
Polywax 500[3]	4
Piccolastic A70[4]	3.2
Ultrathene ® UE 649-04[5]	0.75
Dow Corning ® 7 Additive[6]	0.05
Toluene	10
Heptane	50
TOTAL	100%

1. Keystone Aniline, USA; 2. Moore & Munger Marketing, Inc.; 3. Petrolite Chemical, Inc.; 4. Hercules, Inc.; 5. Quantum Chemicals, Inc.; 6. Dow Corning Corporation

The formulation of Example 1 may be coated by reverse gravure coating onto 4.5 micron Mylar (DuPont Corporation) at a temperature of 60°–80° C. to achieve a dry thickness of 3 microns.

Formulation Example 2

Material	Weight %
Bafixan ® Red BF[1]	10
ChemCor ® Emulsion 10135[2]	30
Michem ®Lube 160[3]	20
Mocryl ® 132[4]	10
Lucidene ® 395[5]	5
Dapro ® DF 880[6]	0.1
Arcosolv ® PTB[7]	4.9
Distilled Water	20
TOTAL	100%

1. BASF Corporation; 2. Chemical Corporation of America; 3. Michelman Inc.; 4, 5. Morton International; 6. Daniel Products Company; 7. ARCO Chemical

Formulation 2 may be coated after agitation and dispersion by mechanical means by reverse gravure coating onto 4.5 micron Mylar (DuPont Corporation) at room temperature resulting in a dry thickness of 3 microns.

The surface preparation material is coated in sequence on a panel of the ribbon. In the preferred embodiment, there are sequential panels of cyan, yellow and magenta, with a fourth panel coated with a surface preparation material. FIG. 4 demonstrates the sequence of the color panels on the-ribbon 20, with Y, M, C, representing yellow, magenta and cyan panels, respectively, and S representing the surface preparation material panel of the ribbon. The surface preparation material is preferred to be a polymer resin (polymer, copolymer and terpolymer) containing polyester, polyvinyl acetate and/or polyurethane, etc. with a relatively low melting temperature (<200° C.). Such materials possess the molecular function group of

$$-O-\overset{\displaystyle O}{\overset{\|}{C}}-R-$$

and achieve satisfactory results as receptor sites for sublimation dyes at the sublimation temperature of the dyes, and possess an hydroxyl function group which bonds with cotton fabric. In order to have satisfactory bonding with the cotton fabric at the fabric swelling stage during thermal process and adequate flexibility of the final product, the surface preparation material should have a glass transition temperature lower than 100° C. Furthermore, to have a "non-sticky" hand or feel of the coated substrate, and fastness of the dye onto the substrate, the polymer resins should have a glass transition temperature which is above −50° C., and preferably above −20° C. The surface preparation materials can be selected from a group comprising poly(methyl methacrylate), poly(vinyl acetate), polyether polyurethane, poly(ethyl methacrylate), poly(methyl acrylate), poly(ethyl acrylate), poly(isobutyl acrylate), poly(isobutyl methacrylate), poly(butyl acrylate), poly(butyl methacrylate), poly(benzyl methacrylate), poly(2-ethylhexyl acrylate), poly(2-ethylhexyl methacrylate), poly(hexyl methacrylate), poly(butylene terephthalate), poly(vinyl butyral), poly (vinyl stearate), poly(octadecyl methacrylate), etc. and the copolymer or terpolymer with other polymer materials with low melting point, low glass transition point poly(vinyl ethyl ether), poly(vinyl chloride), poly(vinylidene fluoride), poly(vinyl methyl ether), etc. Generally, such surface preparation polymers have molecular weights of less than 500,000, and can be coated onto a ribbon in a hot melt, solvent or water-reducible emulsion.

An antioxidant can be added into the polymer component, in order to prevent oxidation of the polymer at elevated temperatures. Without such antioxidant, most polyesters and polyvinyl acetates will turn yellow due to the chemical oxidation process with the oxygen in the air. Approximately 0.1%–5% (by weight) of antioxidant can be added to the formulation during the ribbon manufacturing stage. Examples of such antioxidant materials include Raschig Corporation's Ralox® Antioxidants, Eastman Chemical's Aquastab® Antioxidants and Ethyl Corporation's Ethanox® Antioxidants, etc.

Printers using methods other than the method employed by multiple pass thermal printers as described above may be used. Color inks or toners are printed onto a medium, which may be paper, without activating or sublimating the ink or dye. The surface preparation material is printed over the ink layer. Upon subsequent transfer of the ink layer to the substrate, the surface preparation material will have direct contact with the substrate. As above, activation of the resins of the polymeric surface preparation material occurs during the higher temperature process of transferring the inks from the medium to the substrate. Cross linking and bonding of the surface preparation material to the substrate occurs during this sublimation transfer stage.

The method may be used with ink-jet, bubble jet and phase change ink-jet printing. With these printers, the preparation material is applied in the same manner as the ink material. If three colors are used in the printer, a fourth reservoir and fourth printing nozzle is provided in addition to the reservoirs and nozzles provided for the cyan, yellow, and magenta inks. Viscosity and stability of viscosity, foaming, heat sensitivity, printing filter porosity, and other variables are controlled to ensure proper delivery of the preparation material, in the same manner as the color inks.

Ink used in ink-jet and bubble-jet printing may comprise monomer or polymer materials in either solvent or emulsion form, an initiator or catalyst (which may be compounded into the inks so as to provide separation from the polymer), a corrosion inhibitor, a flow control aid, a viscosity stabilization aid, an evaporation control agent, an anti-foaming chemical, a fusing control agent, fungicities, and anti-oxidants. Formulation Example 3 is an example of an ink composition comprising heat activated inks and a polymeric surface preparation which may be used with ink jet printers.

Phase change ink jet printers use a solid ink which may be in stick form. This "ink stick" comprises heat sensitive inks, wax material, polymer binder and additives such as those used in the ink jet formulation above to control, melting, flow, corrosion and other variables. The ink is changed from solid to liquid by melting the ink stick in a controlled fashion to apply the inks and achieve printing. The inks may be applied in three or more colors, such as cyan, yellow and magenta to achieve multi-color or full color printing. A solid stick comprising a polymeric surface preparation is provided. Wax material, a polymer binder and additives may be included. The surface preparation material is applied from this solid stick over the image printed by the printer onto the medium, for the reasons described above. Alternatively, the surface preparation material could be combined with one or more of the ink sticks containing the inks or dyes, with the surface preparation material applied to the medium along with the ink or dye as the medium is printed. As described above, it is desirable for the surface preparation material to be applied as or from a top layer of the dye layer of the medium so that the surface preparation material contacts the surface of the substrate as the image is applied to the substrate.

Formulation Example 3

Material	Weight %
Sequabond ® 3010AF[1]	25
Sequabond ® 3300[1]	10
Lacidene ® 6452[2]	10
Plyamul40305-00[3]	10
MA-SUL ® corrosion inhibitor[4]	0.25
Nalco ® 2309[5]	0.25
Pentex ® 99[6]	0.05
Kathon ® PFM[7]	0.01
DynaGel ® (100 bloom)[8]	0.30
DPG	4.00
Distilled Water	40.14
TOTAL	100%

1. Sequa Chemicals, Inc; 2. Morton International; 3. Reichhold Chemicals, Inc; 4. King Industries; 5. Nalco Chemical Company, Specialty Chemicals; 6. Rhone-Poulenc, Specialty Chemicals Division; 7. Rohm and Haas Company; 8. Dynagel Inc.

The method may be used with laser printers and color copier machines. The preparation material is compounded with magnetic sensitive material of very fine particle size. The initiating temperature of bonding of the polymeric surface preparation material is adjusted so that it is higher than the fuser temperature used in the laser printer and color copier (i.e., less than 400 degrees F.) so that the surface preparation material does not cause significant bonding to the medium.

The application of inks to absorbent materials such as cotton fiber substrates may be successfully achieved by grafting. By definition, grafting is the permanent attachment and "growth" of a new material onto an existing substrate.

Chemical grafting involves attachment and polymerization of monomers to a substrate to modify or improve the properties of the substrate without any damage of the substrate itself. By using different type of monomers and initiators, chemical grafting provides a purely chemical method of activating bonding sites on a substrate and the compounding and crosslinking of a monomer/polymer with the structure of the substrate under different conditions, such as certain temperature, curing method and catalyst systems.

Grafting has advantages over conventional fabric modification methods such as chemical coating. Chemical grafting is suitable for cotton, nylon, silk, jute, polypropylene, polyester and other fibers to achieve end use purposes, including increasing fabric dying ability. The permanent attachment and extremely thin layer produced by grafting onto substrates generates new applications for certain fibers. For example, polyether polyurethanes can be used to improve the dying ability of cotton fibers through chemical grafting in combination with the use of modified polyethylene glycols. Grafted materials have been proven to possesses much higher resiliency and dying color strength than the fabric itself.

Depending upon the particular substrate and end use of the substrate, chemical grafting can be performed using different grafting materials (i.e. monomer/polymer materials, catalyst, curing method, etc.) such as polyurethane, urea formaldehyde, polyester, polyether, polyvinyl acetate, polyacrylic acetate, and can be accomplished by using UV-curing, catalyst curing or/and thermal curing methods.

What is claimed is:

1. A method of printing a multiple color image using heat sensitive inks printed by a color thermal ink jet printer, comprising the steps of:

a. creating a multiple color image;

b. providing a color thermal ink jet printer;

c. printing, by thermal means and by multiple color process, heat sensitive inks in at least three colors to form said multiple color image on a medium by means of said inks, wherein the printing by thermal means is at a temperature which is below the temperature at which said heat sensitive inks activate, and wherein the thermal means is said color thermal ink jet printer; and

d. transferring said heat sensitive inks from said medium to an object on which the image is to appear by applying heat to said medium at a temperature which is above the temperature at which said heat sensitive inks activate, so as to cause sufficient of said heat sensitive inks to activate and bond to said object to form the multiple color image on said object.

2. A method of printing a multiple color image using heat sensitive inks printed by a color thermal ink jet printer, comprising the steps of:

a. providing a computer driven color thermal ink jet printer;

b. printing, by thermal means, heat sensitive inks of a first color onto a medium, wherein said printing by thermal means occurs at a temperature which is below the temperature at which said heat sensitive inks activate, and wherein said thermal means is said color thermal ink jet printer;

c. printing, by thermal means, heat sensitive inks of a second color onto a medium, wherein at least a portion of said heat sensitive inks of said second color cover at least a portion of said heat sensitive inks of said first color on said medium, and wherein said printing by thermal means occurs at a temperature which is below the temperature at which said heat sensitive inks activate, and wherein said thermal means is said color thermal ink jet printer;

d. printing, by thermal means, heat sensitive inks of a third color onto a medium, wherein at least a portion of said heat sensitive inks of said third color cover at least a portion of said heat sensitive inks of said first color on said medium, and wherein at least a portion of said heat sensitive inks of said third color cover at least a portion of said heat sensitive inks of said second color on said medium, and wherein said printing by thermal means occurs at a temperature which is below the temperature at which said heat sensitive inks activate, and wherein said thermal means is said color thermal ink jet printer, and wherein said printing of said inks of said first color, said printing of said inks of said second color, and said printing of said inks of said third color comprise multiple color process printing, wherein a multiple color image formed by heat sensitive inks printed by means of said multiple color process printing appears on said medium; and

e. transferring said multiple color image formed by heat sensitive inks from said medium to an object on which the multiple color image is to appear by applying heat to said medium at a temperature which will cause sufficient of said heat sensitive inks to activate, so as to cause said heat sensitive inks to bond to said object to form the multiple color image on said object.

3. A method of printing a multiple color image using heat sensitive inks printed by a color thermal ink jet printer, comprising the steps of:

a. providing a computer driven color thermal ink jet printer;

b. printing, by thermal means and by multiple color process, heat sensitive inks of at least three colors, each of which is contained in a separate wax based solid, at a temperature which is above the temperature at which the wax is liquified, but which is below the temperature at which heat sensitive inks activate, so as to cause said wax and said heat sensitive inks to be transferred onto said medium to form a multiple color image, wherein said thermal means is said ink jet printer; and

c. transferring said heat sensitive inks from said medium to an object on which the multiple color image is to appear by applying heat to said medium at a temperature which is above the temperature at which said heat sensitive inks activate, so as to cause sufficient of said heat sensitive inks to activate and transfer onto said object to form said multiple color design on said object.

4. A method of printing a multiple color image using heat sensitive inks printed by a color thermal ink jet printer as described in claim 3, wherein at least three wax based solids are used, with each of said wax based solids comprising at least one color of heat sensitive inks, at least one wax material and at least one polymer binder material.

* * * * *

US005488907A

United States Patent [19]

[11] **Patent Number: 5,488,907**

[45] **Date of Patent: Feb. 6, 1996**

Xu et al.

[54] **PERMANENT HEAT ACTIVATED TRANSFER PRINTING PROCESS AND COMPOSITION**

[75] Inventors: **Ming Xu**; **Nathan Hale**, both of Mt. Pleasant, S.C.

[73] Assignee: **Sawgrass Systems, Inc.**, Mt. Pleasant, S.C.

[21] Appl. No.: **299,736**

[22] Filed: **Sep. 1, 1994**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 195,851, Feb. 10, 1994, which is a continuation-in-part of Ser. No. 724,610, Jul. 2, 1991, Pat. No. 5,302,223, which is a continuation-in-part of Ser. No. 549,600, Jul. 9, 1990.

[51] Int. Cl.[6] **B41L 35/14**

[52] U.S. Cl. **101/488**; 400/120.01

[58] Field of Search .... 400/120.01, 240, 400/241.1; 156/230, 240, 583.1; 8/471; 346/76 PH; 347/88; 101/487, 488

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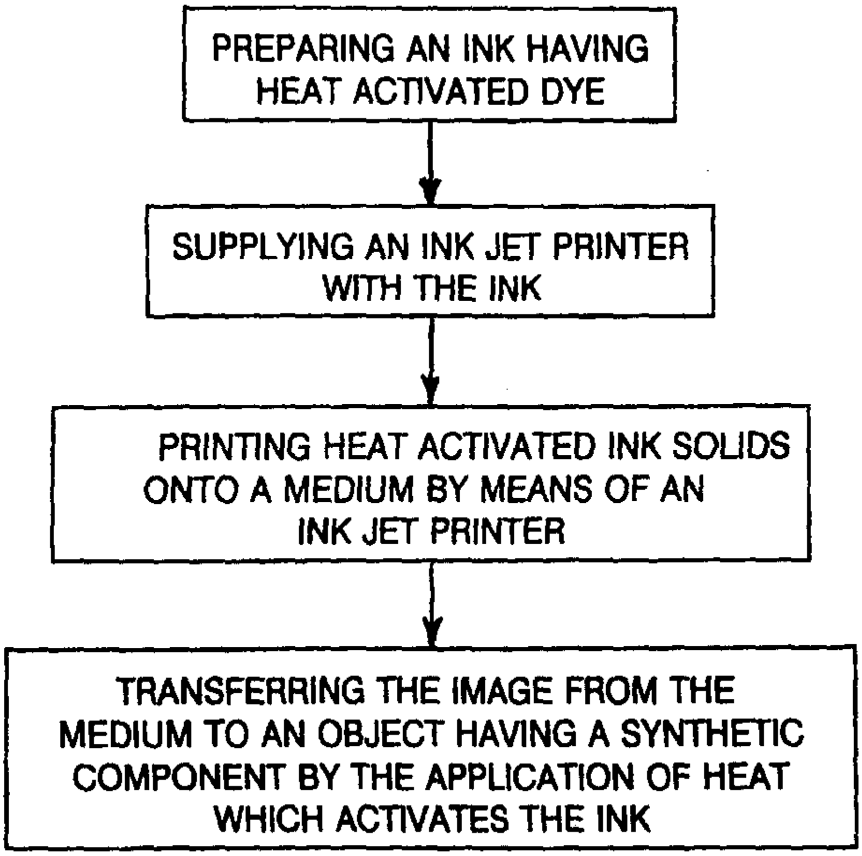
Primary Examiner—Ren Yan
Attorney, Agent, or Firm—B. Craig Killough

[57] **ABSTRACT**

An image is printed on a medium by means of an ink jet printer using an ink composition comprising heat activated ink solids, without activating the ink solids during the process of printing onto the medium. The image is transferred from the medium to the object on which the image is to permanently appear by applying sufficient heat and pressure to the medium to activate and transfer the ink to the object.

6 Claims, 2 Drawing Sheets



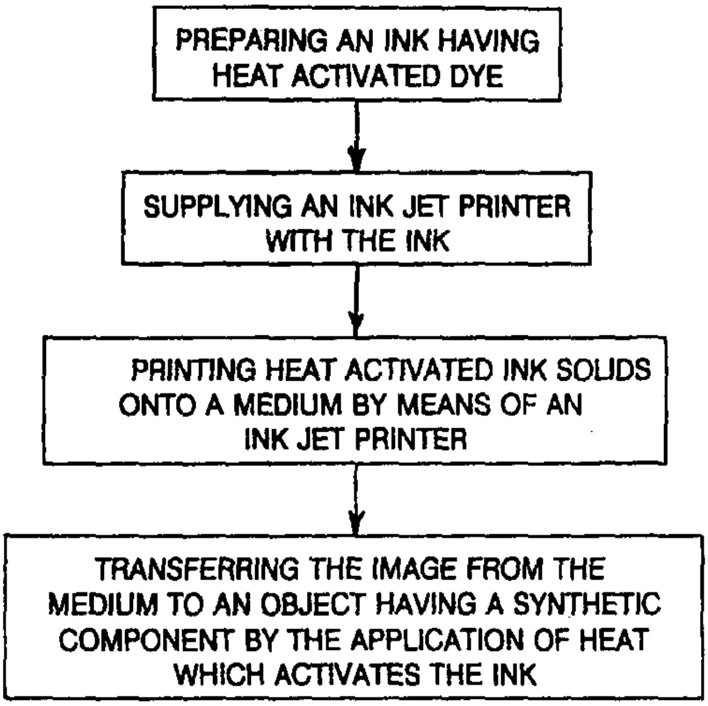

PREPARING AN INK HAVING HEAT ACTIVATED DYE
SUPPLYING AN INK JET PRINTER WITH THE INK
PRINTING HEAT ACTIVATED INK SOLIDS ONTO A MEDIUM BY MEANS OF AN INK JET PRINTER
TRANSFERRING THE IMAGE FROM THE MEDIUM TO AN OBJECT HAVING A SYNTHETIC COMPONENT BY THE APPLICATION OF HEAT WHICH ACTIVATES THE INK

FIG 1

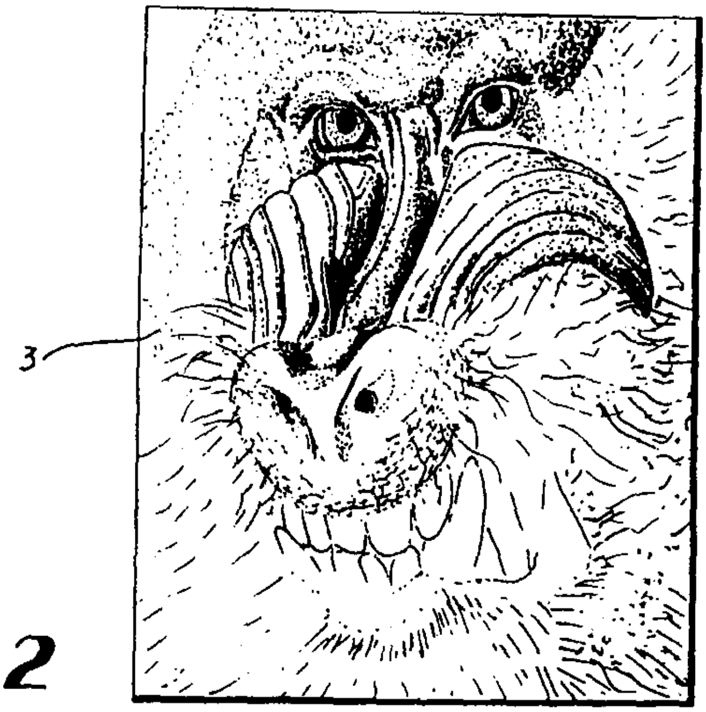

3

FIG 2

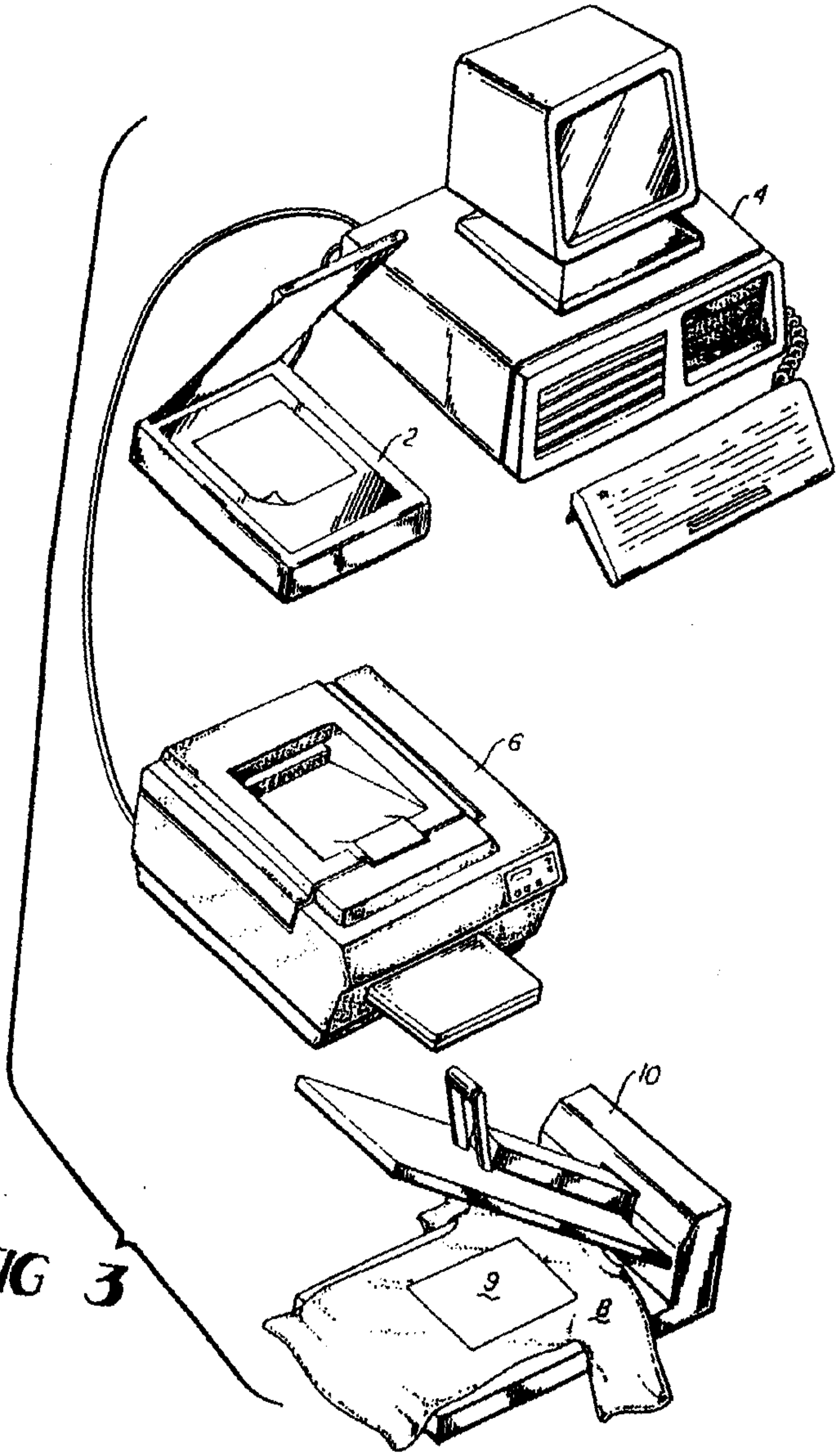


FIG 3

PERMANENT HEAT ACTIVATED TRANSFER PRINTING PROCESS AND COMPOSITION

This application is a continuation in part of application Ser. No. 08/195,851, filed Feb. 10, 1994, which is a continuation in part of application Ser. No. 07/724,610, filed Jul. 2, 1 Patent No. 5,302,223, which is a continuation in part of application Ser. No. 07/549,600, filed Jul. 9, 1990, now abandoned.

FIELD OF THE INVENTION

This invention relates to printing generally, and is more specifically directed to a method of printing heat activated ink by means of an ink jet printer onto paper or other printable substrate as a medium, and subsequently heat activating the ink, thereby transferring the design formed by the ink from the medium to a substrate on which the design is to permanently appear.

BACKGROUND OF THE INVENTION

Words and designs are frequently printed onto clothing and other textile materials, and other objects. Common means of applying such designs to objects include the use of silk screens, and mechanically bonded thermal transfers.

The use of computer technology allows substantially instantaneous printing of images. For example, video cameras or scanning may be used to capture an image to a computer. The image may then be printed by any suitable printing means, including mechanical thermal printers, ink jet printers and laser printers. These printers will print in multiple colors.

Color ink jet printers are in common use. Color ink jet printers use combinations of cyan, yellow and magenta inks or dyes to produce multi-color images.

The primary types of ink jet printers currently in use fall into three categories: phase change, free flow, and bubble jet. The inks or dyes used in phase change ink jet printing are contained in a solid compound which changes state by the application of heat to liquify the solid, whereupon the ink composition is printed. Free flow and bubble jet printers use liquid inks, although the actual printing process of free flow ink jet printers differs from bubble jet printers.

Heat activated transfer ink solids change to a gas at about 400° F., and have a high affinity for polyester at the activation temperature and a limited affinity for most other materials. Once the gassification bonding takes place, the ink is permanently printed and highly resistant to change or fading caused by laundry products.

Hale, U.S. Pat. Nos. 5,246,518, 5,248,363 and 5,302,223 disclose the use of thermal printers to produce an image on a medium or transfer sheet wherein the image is comprised of sublimation or other heat activated inks. The method described in *Hale* does not activate the ink during the printing of the medium or transfer sheet.

The process of printing heat sensitive ink solids such as sublimation inks by means of a phase change ink jet printer is similar to the process described in Hale, U.S. Pat. Nos. 5,246,518, 5,248,363 and 5,302,223. The use of heat by all ink jet printers presents the problem recognized in the Hale patents of printing heat activated inks in a non activated form by means of such printers, since the ink is exposed to high temperatures by the printer. Bubble jet printers, for example, heat the ink during the printing process to around the boiling point of the ink solvent, which is typically water.

Free flow ink jet printers use heat to form pressure which transports the ink during the printing process.

The use of liquid inks, as required by free flow and bubble jet printers, presents a new set of problems when trying to print ink solids. The orifices or nozzles of free flow and bubble jet printers are not designed for the dispensing of solids contained within a liquid material. The orifices of these printers are typically 5–10 microns in diameter, and clogging of the orifice will occur when ink solids of large particle size or in high volume are transferred through the orifice.

Further, when the ink solids are placed into the liquid, the ink solids tend to separate from the liquid over time and fall to the bottom of the ink container. The ink composition is typically sealed in a container at a manufacturing facility, for subsequent mounting of the container within the ink jet printer, meaning that a substantial storage time for the ink composition exists prior to use. Separation of the liquid and solids within the ink formulation presents problems with regard to the mechanical operation of the printer and the print quality achieved from use of the ink formulation.

Color ink formulations for color ink jet printers comprising sublimation dye solids mixed with water were sold briefly in 1989. The ink formulations were not stable, since the solid dye particles settled from the water carrier, and clogged the jets of ink jet printers.

SUMMARY OF THE PRESENT INVENTION

The present invention is a method of printing heat activated ink solids in a non activated form onto a medium in a desired image by means of an ink jet printer, for subsequent transfer of the image from the medium by heat activation of the ink solids. The invention includes ink or dye compositions comprising heat activated ink or dye solids for use with the method. The ink compositions presented include solid compositions at ambient temperature for use with phase change ink jet printers, and emulsions or colloids for use with free flow and bubble jet printers.

The ink solids are transferred in the desired design by means of a printer onto a substrate, which acts as a medium. The substrate may be paper, or it may be other material which will facilitate and withstand the transfer temperature, and which facilitates bonding of the ink layer to the substrate.

The ink jet printer incorporates a thermal process, but the ink solids of the invention do not activate at the operational temperatures of the printer. Heat activation of the ink solids does not take place at the time of printing of the image by the printer, but rather, takes place at the time of the transfer of the image from the medium to the substrate on which the image is permanently applied. The non activated ink solids produce a printed image on the medium which is recognizable, but the colors are dull and are not acceptable for most applications.

Sufficient temperature is then applied to the image to transfer the image from the medium to the substrate on which the image is to permanently appear. The heat activates, or sublimates, the ink solids during this transfer from the medium to the substrate. The image is then permanently bonded to the substrate. The permanent image is sharp, with vivid colors forming the image.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a block diagram showing the printing process.

FIG. 2 illustrates an example of a design printed by a printer using the printing process.

FIG. 3 is a diagrammatic illustration showing exemplary elements of computer and printing systems which could be used to achieve the printing process.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In the preferred embodiment, a video camera or scanning device **2** is used to capture an image **3**. The image is then input into a computer **4**. The computer directs an ink jet printer **6** to print the image. Any means of forming the an image which may be printed from a computer may be used, including images generated by software. Available computer design graphic software may be used, or still photography may be used. The design may be photographic, graphic artistic, or simply letters or words. The use of cyan, yellow and magenta ink compositions allow the printer to print in full color or multi-color designs.

In the present invention, heat activated ink solids are used, and are transferred to a medium by the printer without activating the ink solids. The heat activated ink solids are transferred onto the medium by the printer.

Virtually any material may be used as a medium which can be printed upon by a printer, and which will withstand the heat activated transfer temperature of approximately 400° F., as described herein. This medium may be any paper commonly used with color ink jet printers, however, standard bond paper may be used, or even a sheet of metal, if the metal can be handled by the printer.

Once the image is printed onto the medium, the image may be permanently transferred onto the substrate presently, or at a later time. Most commonly, the design will be transferred onto a textile substrate, such as a shirt **8**, although the image may be transferred onto other materials which act as a substrate, such as metal, ceramic, wood, or plastic. The design **3**, which is printed onto the medium **9** without activating the ink, is placed against the object **8**. A temperature which is sufficient to activate the ink solids is then applied. This temperature will typically be around 400° F. This temperature is applied for a time sufficient to heat activate and transfer the ink solids. A heat transfer machine **10** may be used to accomplish the transfer of the inks from the medium to the substrate. Activation, or sublimation, does not take place at the time of printing the image onto the medium, even though heat may be used to accomplish the printing of the image onto the medium, but occurs during the transfer from the medium to the substrate.

Phase change ink jet printers use an ink composition which is solid at ambient temperature. The ink composition may be in a solid stick form. This "ink stick" comprises heat activated inks, and a phase change material, or transfer vehicle, which will liquify upon the application of heat to the ink composition. A polymer binder and additives may be added to the ink composition. The additives may be used to control melting, flow, drying, corrosion and other variables. The composition is changed from solid to liquid by melting the ink stick in a controlled fashion, to apply the ink solids to the medium, and achieve printing. The melted ink composition is contained in a liquid form in a reservoir at the necessary elevated temperature to maintain the ink composition in liquid form. The liquified ink composition is then taken from the reservoir and printed on demand. The ink composition may be present in the printer in three or more colors, such as cyan, yellow and magenta, and applied by the printer in combination to achieve multiple color or full color printing.

The transfer vehicle may be a wax or wax like material, such as a certain polymers having a low molecular weight and low melting point. Since wax and wax like materials in liquid form tend to have an affinity for paper, the transfer vehicle will readily bond with the paper medium, holding the ink solids to the medium, until the ink solids are released by the application of heat which is sufficient to activate and transfer the ink solids.

The formulation for an ink composition used with a phase change ink jet printer is as follows:

Material	Weight %
Heat Activated Dye/Ink Solid	5–30
Transfer Vehicle	20–70
Emulsifying Enforcing Agent	1–20
Binder	0–30
Plasticizer	0–15
Foam Control Agent	0–10
Viscosity Control Agent	0–10
Surface Tension Control Agent	0–10
Diffusion Control Agent	0–10
Flow Control Agent	0–15
Corrosion Control Agent	0–10
Antioxidant	0–5
TOTAL	100%

The heat sensitive or heat activated dye or ink solid may be a sublimation ink which is finely divided. It is preferred that the solid particle have a diameter which is no larger than 0.1 micron. The transfer material is a wax or wax like material which liquifies at a temperature of 70° to 120 degrees C. to allow printing of the ink onto the medium.

The emulsifying enforcing agent acts as a dispersing agent through which the ink solids are distributed. The emulsifying enforcing agent may be one or more polymers or surfactants, which should be anionic. The binder may be a polymer which strengthens the ink stick when the ink stick is in solid form. The plasticizer increases the solubility of the ink for formulation of the ink stick. The foam control agent and viscosity control agent aid in formulating the ink stick.

The surface tension control agent may be a surfactant. This agent aids in printing of the ink formulation. The diffusion control agent helps control the diffusion of the ink as it is applied to the medium. The flow control agent helps control the melting temperature and rate of the ink during the printing process.

Material	Weight %
Subliprint ® Blue 70014[1]	10.0
Polywax ® PE500[2]	10.0
Exxon FN ® 3505[3]	58.0
DisperByk ® 182[4]	0.5
Vinnapas ® B1.5[5]	1.5
Piccolastic ® A25[6]	10.0
Polygard ®[7]	5.0
Dibutyl Phthalate	5.0
Total:	100.0

[1]Keystone Aniline Corporation
[2]Petrolite Corp.
[3]Exxon Chemical Co.
[4]BYK-Chemie, USA
[5]Wacker Chemicals (USA)
[6]Hercules Inc.
[7]Uniroyal Chemical Co.

Polywax PE500 is a transfer vehicle. This transfer vehicle is a wax-like polymer material. Exxon FN 3505 is a hydrocarbon wax used as part of the transfer vehicle. Other waxes or combinations could be used as the transfer vehicle depending on the printer, its operation temperature, the ink to be printed and the medium to be printed.

DisperByk 182 is an emulsifying enforcing agent. An anionic emulsifying enforcing agent should be used. DispersByk is a polymer type surfactant. Vinnapas B1.5 and Piccolastic are used as binders. Polygard is an antioxidant which is used for corrosion control. Dibutyl phthalate is a plasticizer.

Free flow ink jet printers and bubble jet ink jet printers use inks which are in a liquid form. Free flow ink jet printers dispense ink through an orifice in an ink container. The printer commands and controls the flow of ink through the orifice to print in the desired manner.

Bubble jet printers also use inks which are in a liquid form, and which are held in a container. Bubble jet printers use a different orifice or nozzle system than free flow printers. A channel and heating system is used to form a bubble. The formation of the bubble is controlled by the printer by the application of heat to the ink to print as desired.

The heat activated inks or dyes are solid particles. Free flow and bubble jet printers are designed to be used with liquid inks, but not with inks having solid particulate within the liquid. The presence of solid material clogs the orifice or nozzle of the printer. Further, liquid ink compositions into which a solid particulate is placed or dissolved are not homogenous over time. The solid ink particles in the mixture settle from the liquid toward the bottom of the ink container. This settling increases the clogging of the orifice. Further, print quality is affected if the ink is not consistent.

The liquid ink composition of the present invention is an emulsion comprised of finely divided heat activated ink solids which are placed in an emulsion by means of an emulsifying enforcing agent which is present in a solvent. Humectants, corrosion inhibitors, surfactants, and anti-foaming agents may also be included in the composition.

The formulation of an emulsion comprising heat activated ink solids which is used with ink jet printers requiring liquid inks is as follows:

Material	Weight %
Heat Activated Dye/Ink Solid	5–30
Emulsifying Enforcing Agent	1–20
Binder	0–30
Humectants	0–40
Foam Control Agent	0–10
Fungicide	0–2
Viscosity Control Agent	0–10
Surface Tension Control Agent	0–10
Diffusion Control Agent	0–10
Flow Control Agent	0–15
Evaporation Control Agent	0–20
Corrosion Control Agent	0–10
Cosolvent	0–30
Solvent	30–90
TOTAL	100%

The heat activated dye or ink solid is finely divided and placed into an emulsion by means of the emulsifying agent and the solvent, which may be water. The remaining agents may be added to facilitate formulation, storage and/or printing of the liquid ink composition.

FORMULATION EXAMPLE #2- Yellow Ink-Jet Formula:

Material	Weight %
Bafixan ® Yellow 3FE[8]	2.0
Dipropylene Glycol	4.5
DMSO	1.5
Cobratec ®[9]	0.45
NaOH (10N)	3.0
Distilled H_2O	88.55
Total:	100

[8]BASF Corporation
[9]PMC Specialties Group

Formulation Example 2 comprises a heat activated yellow ink solid or dye. Dipropylene glycol and DMSO are co-solvents. Sodium Hydroxide is an inorganic emulsifying enforcing agent, which also acts as a fungicide. Distilled water acts as a solvent. Cobratec® acts as a corrosion inhibitor.

In this formulation, a particular ink solid is finely divided to yield a small particle size. The particular ink solid of Example 2 will tend to substantially dissolve within sodium hydroxide, which is used as the emulsifying enforcing agent. The combination of the sodium hydroxide and the solvent, which is the formulation example is distilled water, yield an emulsion which may be used in bubble jet and free flow ink jet printers.

Generically, a "humectant" is a moisturizing agent. In the relevant art, the term "humectant" is used to describe agents which are included in ink formulations to regulate the rate at which the ink dries and to control the viscosity of the ink. In addition to these properties, the present invention may comprise one or more humectants which will prevent clogging of the orifice or nozzle. With certain inks, the humectants will regulate the sublimation rate of the inks or dyes as they are transferred from the medium to the object on which the printed design is to permanently appear. The humectant in formulation example 2 is dipropylene glycol, which acts as a co-solvent and humectant.

FORMULATION EXAMPLE #3; Cyan Ink-Jet Formula:

Material	Weight %
Sublaprint ® Blue 70013[10]	1.0
Lignosol ® FTA[11]	3.5
ME ® 39235[12]	10.0
Diethylene Glycol	9.5
DMSO	1.0
Distilled H_2O	75.0
Total:	100.00

[10]Keystone Aniline Corporation
[11]Lignotech (U.S.) Inc.
[12]Michelman, Inc.

Sublaprint® Blue 70013 is a heat activated ink or dye solid. Lignosol® FTA and ME® 39235 are emulsifying enforcing agents. Lignosol® FTA also acts as a fungicide. ME® 39235 is a polymer, and more specifically, it is a polyethylene binder. Diethylene Glycol and DMSO act as humectants. The solvent is distilled water.

Sublaprint® Blue 70013 is more difficult to sublimate than Bifaxan® Yellow 3GE, and is less soluble in the emulsifying enforcing agent. Diethylene glycol is used as a humectant to facilitate sublimation of the Sublaprint® Blue ink solid.

The heat activated ink solid is finely divided to a small particle size. The finely divided ink solid is combined with one or more emulsifying enforcing agents, which are in turn combined with the solvent.

Formulation Example #4: Magenta Ink-Jet Ink Formula:

Material	Weight %
Intratherm ® Brill Red P-31NT[13]	1.5
Lignosol ® FTA[14]	3.0
ME ® 39235[15]	11.0
NA-SUL ®[16]	1.0
DeeFo ® 806-102[17]	0.2
Sorbitol	0.5
Dipropylene Glycol	3.5
Distilled H_2O	79.3
Total:	100

[13]Crompton & Knowles Corporation
[14]Lignotech (U.S.) Inc.
[15]Michelman, Inc.
[16]King Industries
[17]Ultra Additives

Formulation Example #4 comprises a heat activated ink solid or dye which is finely divided and combined in an emulsifying enforcing agent. The emulsifying enforcing agent or medium is, as with Example #3, Lignosol® FTA and ME® 39235. Distilled water is used as a solvent. Dipropylene Glycol is used as a humectant.

Formulation Example #4 further comprises an anti-foaming or foaming control agent, DeeFo® 806-102 to retard foaming of the liquid ink composition. Formulation Example #4 further comprises a surfactant, which may be Sorbitol®, and a corrosion inhibitor, which, in this example, is NA-SUL®.

Formulation Examples 2, 3 and 4 are emulsions. In Example 2, the particular dye has a tendency to dissolve in the emulsifying enforcing agent. Formulation Examples 3 and 4 may also be described as colloids, having finely divided ink particles of not larger than 0.1 microns in diameter present within the disperse medium.

The invention provides an emulsion or colloid which will work within free flow ink jet printers and bubble jet printers, without experiencing problems relating to orifice clogging which results from the use of an ink solid. Further, the use of an emulsion or colloid prevents the separation of the ink solids from the liquid components, rendering an ink composition which is stable over time.

Typically, the liquid ink formulations are present within the printers in containers. Three or more colors of liquid ink are present. The containers may be factory sealed, and as such, the ink formulation may be held within the container for a long period of time.

The bubble jet printer forms the bubble which is used to print the ink at approximately the boiling point of the ink solvent. In most formulations, water will be used as the solvent, so that the ink is exposed to temperatures of 100 degrees C. or higher as the ink is printed. Comparable temperatures may be used in free flow ink jet printers to create pressure for the purpose of transporting the ink for printing. As with the phase change ink jet printer, the ink is exposed to temperatures which will activate or sublimate some heat activated inks or dyes. The inks or dyes used in the ink compositions herein will not activate or sublimate at the operational temperatures of the printer.

What is claimed is:

1. A method of printing a design by means of an ink jet printer using heat activated dye solids, comprising the steps of:

a. preparing an ink formulation comprising heat activated dye solids, at least one emulsifying enforcing agent for shielding the heat activated dye solids and at least one solvent;

b. supplying an ink jet printer with said ink formulation;

c. printing said ink formulation in a desired image by means of said ink jet printer onto a medium at a temperature which is below the temperature at which said heat activated dye solids activate; and

d. transferring said image from said medium to an object on which the image is to appear by thermal means at a temperature which is above the temperature at which said heat activated dye solids activate, so as to cause said heat activated dye solids to transfer onto said object.

2. A method of printing a design by means of an ink jet printer using heat activated dye solids as described in claim 1, further comprising the step of finely dividing said heat activated dye solids prior to performing the step of preparing said ink formulation.

3. A method of printing a design by means of an ink jet printer using heat activated dye solids as described in claim 1, wherein the emulsifying enforcing agent is a polymeric dispersing agent.

4. A method of printing a design by means of an ink jet printer using heat activated dye solids as described in claim 3, further comprising the step of finely dividing said heat activated dye solids prior to performing the step of preparing said ink formulation.

5. A method of printing a design by means of an ink jet printer using heat activated dye solids as described in claim 1, wherein the step of preparing an ink formulation comprises the combining of heat activated dye solids with Lignosol as an emulsifying enforcing agent and at least one solvent.

6. A method of printing a design by means of an ink jet printer using heat activated dye solids as described in claim 5, further comprising the step of finely dividing said heat activated dye solids prior to performing the step of combining said heat activated dye solids with said emulsifying enforcing agent and said solvent.

* * * * *

US005601023A

United States Patent [19]

Hale et al.

[11] **Patent Number: 5,601,023**

[45] **Date of Patent: *Feb. 11, 1997**

[54] **PERMANENT HEAT ACTIVATED TRANSFER PRINTING PROCESS AND COMPOSITION**

[75] Inventors: **Nathan S. Hale; Ming Xu**, both of Mt. Pleasant, S.C.

[73] Assignee: **Sawgrass Systems, Inc.**, Mt. Pleasant, S.C.

[*] Notice: The term of this patent shall not extend beyond the expiration date of Pat. No. 5,488,907.

[21] Appl. No.: **565,999**

[22] Filed: **Dec. 1, 1995**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 506,894, Jul. 25, 1995, and Ser. No. 207,756, Mar. 8, 1994, Pat. No. 5,487,614, which is a continuation of Ser. No. 195,851, Feb. 10, 1994, Pat. No. 5,431,501, said Ser. No. 506,894, is a continuation-in-part of Ser. No. 299,736, Sep. 1, 1994, Pat. No 5,488,907, which is a continuation-in-part of Ser. No. 195,851, which is a continuation-in-part of Ser. No. 724,610, Jul. 2, 1991, Pat. No. 5,302,223, which is a continuation-in-part of Ser. No. 549,600, Jul. 9, 1990, abandoned.

[51] **Int. Cl.**[6] **B41L 35/14**

[52] **U.S. Cl.** **101/488**; 400/120.01

[58] **Field of Search** .... 400/120.01, 120.02, 400/240, 241.1; 156/230, 240, 583.1; 8/471; 346/76 PH; 347/88; 101/487, 488

[56] **References Cited**

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5,246,518	9/1993	Hale	156/230
5,263,781	11/1993	Mima et al.	400/120
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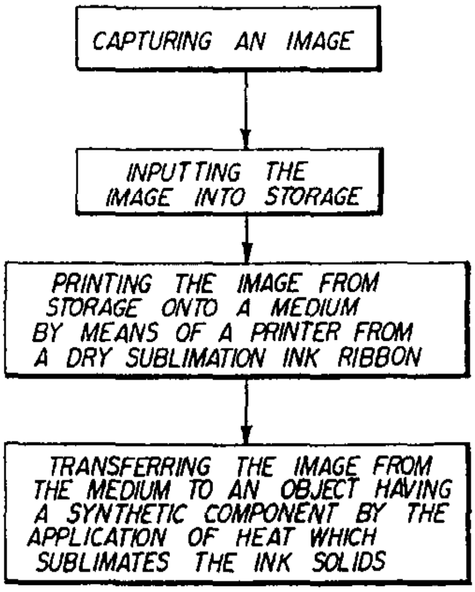
Primary Examiner—Ren Yan

Attorney, Agent, or Firm—B. Craig Killough

[57] **ABSTRACT**

An image is printed on a medium by means of a computer driven printer using an ink composition comprising heat activated dye solids, without activating the dye solids during the process of printing onto the medium. The image is transferred from the medium to the object on which the image is to permanently appear by applying sufficient heat and pressure to the medium to activate the dye and transfer the image to the object. The liquid form of the ink composition uses a liquid carrier and an emulsifying enforcing agent which has an affinity for the dye. The emulsifying enforcing agent shields the heat activated dye both prior to, and during, the printing process.

10 Claims, 2 Drawing Sheets



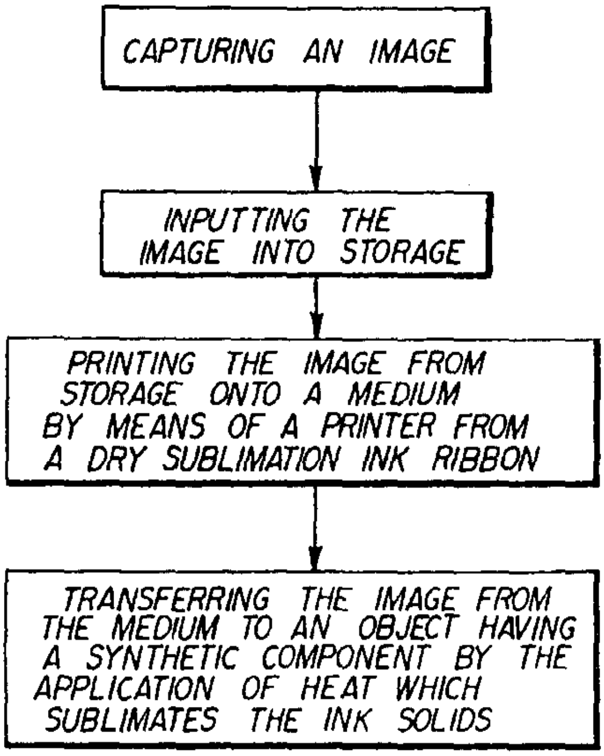

CAPTURING AN IMAGE
INPUTTING THE IMAGE INTO STORAGE
PRINTING THE IMAGE FROM STORAGE ONTO A MEDIUM BY MEANS OF A PRINTER FROM A DRY SUBLIMATION INK RIBBON
TRANSFERRING THE IMAGE FROM THE MEDIUM TO AN OBJECT HAVING A SYNTHETIC COMPONENT BY THE APPLICATION OF HEAT WHICH SUBLIMATES THE INK SOLIDS

FIG 1

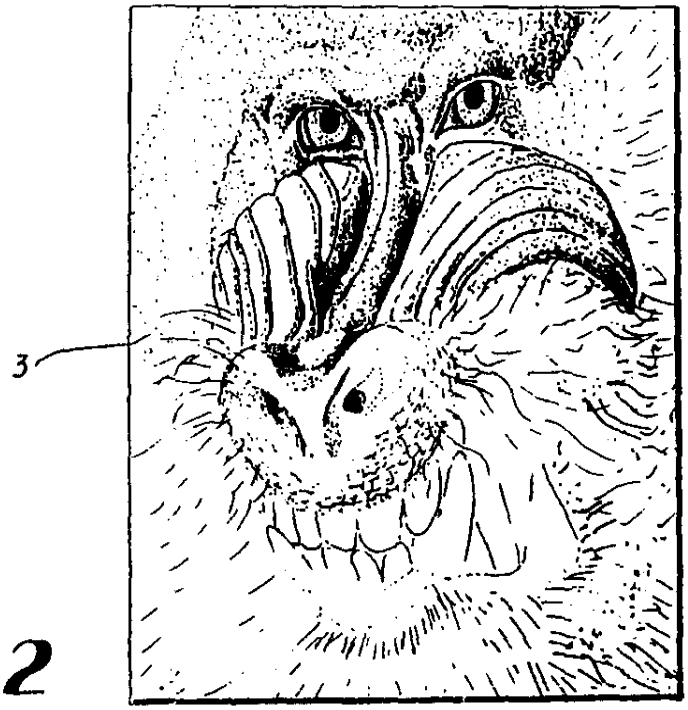

3

FIG 2

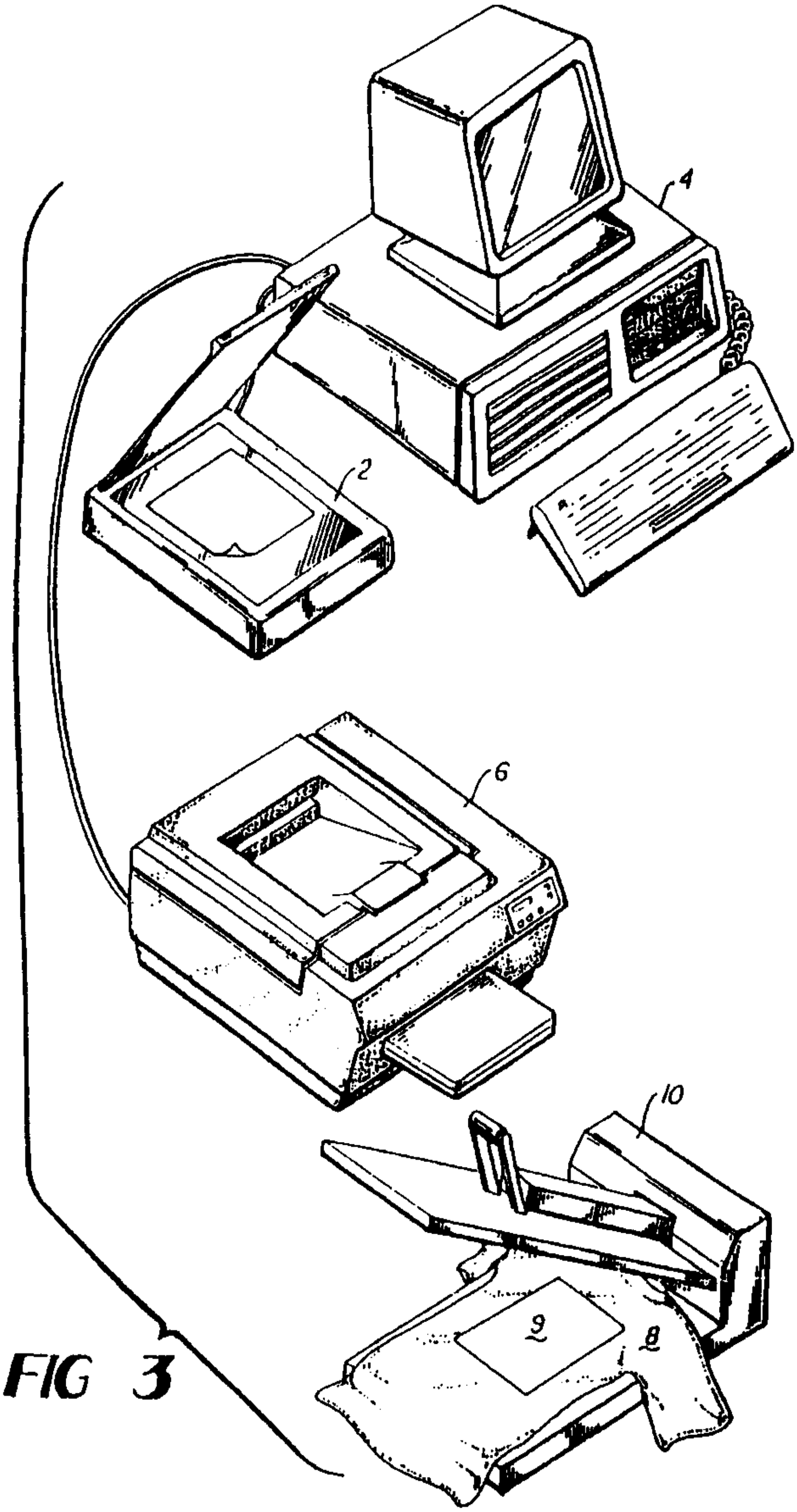


FIG 3

PERMANENT HEAT ACTIVATED TRANSFER PRINTING PROCESS AND COMPOSITION

This application is a continuation-in-part of application Ser. No. 08/506,894, Jul. 25, 1995, which is a continuation-in-part of Ser. No. 08/299,736, Sept. 1, 1994, Pat. No. 5,488,907, which is a continuation-in-part of Ser. No. 08/195,851, Feb. 10, 1994, U.S. Pat. No. 5,431,501, which is a continuation-in-part of Ser. No. 724,610, Jul. 2, 1991, U.S. Pat. No. 5,302,223, which is a continuation-in-part of Ser. No. 549,600, Jul. 9, 1990, abandoned. This application is also a continuation-in-part of Ser. No. 08/207,756, Mar. 8, 1994, U.S. Pat. No. 5,487,614, which is a continuation of Ser. No. 08/195,851, Feb. 10, 1994, U.S. Pat. No. 5,431,501.

FIELD OF THE INVENTION

This invention relates to printing generally, and is more specifically directed to a method of printing heat activated ink by means of an ink jet printer onto paper or other printable substrate as a medium, and subsequently heat activating the ink, thereby transferring the design formed by the ink from the medium to a substrate on which the design is to permanently appear.

BACKGROUND OF THE INVENTION

Words and designs are frequently printed onto clothing and other textile materials, and other objects. Common means of applying such designs to objects include the use of silk screens, and mechanically bonded thermal transfers.

The use of computer technology allows substantially instantaneous printing of images. For example, video cameras or scanning may be used to capture an image to a computer. The image may then be printed by any suitable printing means, including mechanical thermal printers, ink jet printers and laser printers. These printers will print in multiple colors.

Color ink jet printers are in common use. Color ink jet printers use combinations of cyan, yellow and magenta inks or dyes to produce multi-color images.

The primary types of ink jet printers currently in use fall into three categories: phase change, free flow, and bubble jet. The inks or dyes used in phase change ink jet printing are contained in a solid compound which changes state by the application of heat to liquify the solid, whereupon the ink composition is printed. Free flow and bubble jet printers use liquid inks, although the actual printing process of free flow ink jet printers differs from bubble jet printers.

Heat activated transfer ink solids change to a gas at about 400° F., and have a high affinity for polyester at the activation temperature and a limited affinity for most other materials. Once the gassification bonding takes place, the ink is permanently printed and highly resistant to change or fading caused by laundry products.

Hale, U.S. Pat. Nos. 5,246,518, 5,248,363 and 5,302,223 disclose the use of thermal printers to produce an image on a medium or transfer sheet wherein the image is comprised of sublimation or other heat activated inks. The method described in Hale does not activate the ink during the printing of the medium or transfer sheet.

The process of printing heat sensitive ink solids such as sublimation inks by means of a phase change ink jet printer is similar to the process described in Hale, U.S. Pat. Nos. 5,246,518, 5,248,363 and 5,302,223. The use of heat by all ink jet printers presents the problem recognized in the Hale patents of printing heat activated inks in a non activated form by means of such printers, since the ink is exposed to high temperatures by the printer. Bubble jet printers, for example, heat the ink during the printing process to around the boiling point of the ink solvent, which is typically water. Free flow ink jet printers use heat to form pressure which transports the ink during the printing process.

The use of liquid inks, as required by free flow and bubble jet printers, presents a new set of problems when trying to print ink solids. The orifices or nozzles of free flow and bubble jet printers are not designed for the dispensing of solids contained within a liquid material. The orifices of these printers are typically 5–10 microns in diameter, and clogging of the orifice will occur when ink solids of large particle size or in high volume are transferred through the orifice.

Further, when the ink solids are placed into the liquid, the ink solids tend to separate from the liquid over time and fall to the bottom of the ink container. The ink composition is typically sealed in a container at a manufacturing facility, for subsequent mounting of the container within the ink jet printer, meaning that a substantial storage time for the ink composition exists prior to use. Separation of the liquid and solids within the ink formulation presents problems with regard to the mechanical operation of the printer and the print quality achieved from use of the ink formulation. Materials which inhibit separation must also inhibit agglomeration of the solid dye particles, while allowing, and not preventing due to insulation or otherwise, activation of the ink or dye during the final printing at elevated temperatures.

SUMMARY OF THE PRESENT INVENTION

The present invention is a method of printing heat activated ink solids in a non activated form onto a medium in a desired image by means of an ink jet printer, for subsequent transfer of the image from the medium by heat activation of the ink solids. The invention includes ink or dye compositions comprising heat activated ink or dye solids for use with the method. The ink compositions presented include solid compositions at ambient temperature for use with phase change ink jet printers, and emulsions or colloids for use with free flow and bubble jet printers.

The ink solids are transferred in the desired design by means of a printer onto a substrate, which acts as a medium. The substrate may be paper, or it may be other material which will facilitate and withstand the transfer temperature, and which facilitates bonding of the ink layer to the substrate.

The ink jet printer incorporates a thermal process, but the ink solids of the invention do not activate at the operational temperatures of the printer. Heat activation of the ink solids does not take place at the time of printing of the image by the printer, but rather, takes place at the time of the transfer of the image from the medium to the substrate on which the image is permanently applied. The non activated ink solids produce a printed image on the medium which is recognizable, but the colors are dull and are not acceptable for most applications.

Sufficient temperature is then applied to the image to transfer the image from the medium to the substrate on which the image is to permanently appear. The heat activates, or sublimates, the ink solids during this transfer from the medium to the substrate. The image is then permanently bonded to the substrate. The permanent image is sharp, with vivid colors forming the image.

When the ink formulation prepared according to the invention is a liquid, finely divided dye solids are present in a liquid carrier, in a colloidal or emulsion form. An emulsifying enforcing agent, which has characteristics of a surfactant, surrounds and shields the dye particles to prevent undesired activation at low heat and to prevent agglomeration of the dye particles. However, the emulsifying enforcing agent allows activation of the dye at higher temperatures.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a block diagram showing the printing process.

FIG. 2 illustrates an example of a design printed by a printer using the printing process.

FIG. 3 is a diagrammatic illustration showing exemplary elements of computer and printing systems which could be used to achieve the printing process.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In the preferred embodiment, a video camera or scanning device 2 is used to capture an image 3. The image is then input into a computer 4. The computer directs a printer 6 to print the image. Any means of forming the an image which may be printed from a computer may be used, including images generated by software. Available computer design graphic software may be used, or still photography may be used. The design may be photographic, graphic artistic, or simply letters or words. The use of cyan, yellow and magenta ink compositions allow the printer to print in full color or multi-color designs.

In the present invention, heat activated ink solids are used, and are transferred to a medium by the printer without activating the ink solids. The heat activated ink solids are transferred onto the medium by the printer.

Virtually any material may be used as a medium which can be printed upon by a printer, and which will withstand the heat activated transfer temperature of approximately 400° F., as described herein. This medium may be any paper commonly used with color ink jet printers, however, standard bond paper may be used, or even a sheet of metal, if the metal can be handled by the printer.

Once the image is printed onto the medium, the image may be permanently transferred onto the substrate presently, or at a later time. Most commonly, the design will be transferred onto a textile substrate, such as a shirt 8, although the image may be transferred onto other materials which act as a substrate, such as metal, ceramic, wood, or plastic. The design 3, which is printed onto the medium 9 without activating the ink, is placed against the object 8. A temperature which is sufficient to activate the ink solids is then applied. This temperature will typically be around 400° F. This temperature is applied for a time sufficient to heat activate and transfer the ink solids. A heat transfer machine 10 may be used to accomplish the transfer of the inks from the medium to the substrate. Activation, or sublimation, does not take place at the time of printing the image onto the medium, even though heat may be used to accomplish the printing of the image onto the medium, but occurs during the transfer from the medium to the substrate.

Phase change ink jet printers use an ink composition which is solid at ambient temperature. The ink composition may be in a solid stick form. This "ink stick" comprises heat activated inks, and a phase change material, or transfer vehicle, which will liquify upon the application of heat to the

ink composition. A polymer binder and additives may be added to the ink composition. The additives may be used to control melting, flow, drying, corrosion and other variables. The composition is changed from solid to liquid by melting the ink stick in a controlled fashion, to apply the ink solids to the medium, and achieve printing. The melted ink composition is contained in a liquid form in a reservoir at the necessary elevated temperature to maintain the ink composition in liquid form. The liquified ink composition is then taken from the reservoir and printed on demand. The ink composition may be present in the printer in three or more colors, such as cyan, yellow and magenta, and applied by the printer in combination to achieve multiple color or full color printing.

The transfer vehicle may be a wax or wax like material, such as a certain polymers having a low molecular weight and low melting point. Since wax and wax like materials in liquid form tend to have an affinity for paper, the transfer vehicle will readily bond with the paper medium, holding the ink solids to the medium, until the ink solids are released by the application of heat which is sufficient to activate and transfer the ink solids.

The formulation for an ink composition used with a phase change ink jet printer is as follows:

Material	Weight %
Heat Activated Dye/Ink Solid	5–30
Transfer Vehicle	20–70
Emulsifying Enforcing Agent	1–20
Binder	0–30
Plasticizer	0–15
Foam Control Agent	0–10
Viscosity Control Agent	0–10
Surface Tension Control Agent	0–10
Diffusion Control Agent	0–10
Flow Control Agent	0–15
Corrosion Control Agent	0–10
Antioxidant	0–5
TOTAL	100%

The heat sensitive or heat activated dye or ink solid may be a sublimation ink which is finely divided. It is preferred that the solid particle have a diameter which is no larger than 0.1 micron. The transfer material is a wax or wax like material which liquifies at a temperature of 70 to 120 degrees C to allow printing of the ink onto the medium.

The emulsifying enforcing agent acts as a dispersing agent through which the ink solids are distributed. The emulsifying enforcing agent may be one or more polymers or surfactants, which should be anionic. The binder may be a polymer which strengthens the ink stick when the ink stick is in solid form. The plasticizer increases the solubility of the ink for formulation of the ink stick. The foam control agent and viscosity control agent aid in formulating the ink stick.

The surface tension control agent may be a surfactant. This agent aids in printing of the ink formulation. The diffusion control agent helps control the diffusion of the ink as it is applied to the medium. The flow control agent helps control the melting temperature and rate of the ink during the printing process.

FORMULATION EXAMPLE#1: Cyan phase-change ink-Jet Ink Formula

Material	Weight %
Sublaprint ® Blue 70014[1]	10.0
Polywax ® PE500[2]	10.0
Exxon FN ® 3505[3]	58.0
DisperByk ® 182[4]	0.5
Vinnapas ® B1.5[5]	1.5
Piccolastic ® A25[6]	10.0
Polygard ®[7]	5.0
Dibutyl Phthalate	5.0
Total:	100.0

[1]Keystone Aniline Corporation
[2]Petrolite Corp.
[3]Exxon Chemical Co.
[4]BYK-Chemie, USA
[5]Wacker Chemicals (USA)
[6]Hercules Inc.
[7]Uniroyal Chemical Co.

Polywax PE500 is a transfer vehicle. This transfer vehicle is a wax-like polymer material. Exxon FN 3505 is a hydrocarbon wax used as part of the transfer vehicle. Other waxes or combinations could be used as the transfer vehicle depending on the printer, its operation temperature, the ink to be printed and the medium to be printed.

DisperByk 182 is an emulsifying enforcing agent. An anionic emulsifying enforcing agent should be used. DispersByk is a polymer type surfactant. Vinnapas B1.5 and Piccolastic are used as binders. Polygard is an antioxidant which is used for corrosion control. Dibutyl phthalate is a plasticizer.

Free flow ink jet printers and bubble jet ink jet printers use inks which are in a liquid form. Free flow ink jet printers dispense ink through an orifice in an ink container. The printer commands and controls the flow of ink through the orifice to print in the desired manner.

Bubble jet printers also use inks which are in a liquid form, and which are held in a container. Bubble jet printers use a different orifice or nozzle system than free flow printers. A channel and heating system is used to form a bubble. The formation of the bubble is controlled by the printer by the application of heat to the ink to print as desired.

The heat activated inks or dyes are solid particles. Free flow and bubble jet printers are designed to be used with liquid inks, but not with inks having solid particulate within the liquid. The presence of solid material clogs the orifice or nozzle of the printer. Further, liquid ink compositions into which a solid particulate is placed or dissolved are not homogenous over time. The solid ink particles in the mixture settle from the liquid toward the bottom of the ink container. This settling increases the clogging of the orifice. Further, print quality is affected if the ink is not consistent.

The liquid ink composition of the present invention is an emulsion comprised of finely divided heat activated ink solids which are placed in an emulsion by means of an emulsifying enforcing agent which is present in a solvent. Humectants, corrosion inhibitors, surfactants, and anti-foaming agents may also be included in the composition.

The formulation of an emulsion comprising heat activated ink solids which is used with ink jet printers requiring liquid inks is as follows:

Material	Weight %
Heat Activated Dye/Ink Solid	5–30
Emulsifying Enforcing Agent	1–20
Binder	0–30
Humectants	0–40
Foam Control Agent	0–10
Fungicide	0–2
Viscosity Control Agent	0–10
Surface Tension Control Agent	0–10
Diffusion Control Agent	0–10
Flow Control Agent	0–15
Evaporation Control Agent	0–20
Corrosion Control Agent	0–10
Cosolvent	0–30
Solvent	30–90
TOTAL	100%

The heat activated dye or ink solid is finely divided and placed into an emulsion by means of the emulsifying agent and the solvent, which may be water. The remaining agents may be added to facilitate formulation, storage and/or printing of the liquid ink composition.

FORMULATION EXAMPLE#2-Yellow Ink-Jet Formula

Material	Weight %
Bafixan ® Yellow 3FE[8]	2.0
Dipropylene Glycol	4.5
DMSO	1.5
Cobratec ®[9]	0.45
NaOH (10N)	3.0
Distilled H_2O	88.55
Total:	100

[8]BASF Corporation
[9]PMC Specialties Group

Formulation Example 2 comprises a heat activated yellow ink solid or dye. Dipropylene glycol and DMSO are co-solvents. Sodium Hydroxide is an inorganic emulsifying enforcing agent, which also acts as a fungicide. Distilled water acts as a solvent. Cobratec® acts as a corrosion inhibitor.

In this formulation, a particular ink solid is finely divided to yield a small particle size. The particular ink solid of Example 2 will tend to substantially dissolve within sodium hydroxide, which is used as the emulsifying enforcing agent. The combination of the sodium hydroxide and the solvent, which is the formulation example is distilled water, yield an emulsion which may be used in bubble jet and free flow ink jet printers.

Generically, a "humectant" is a moisturizing agent. In the relevant art, the term "humectant" is used to describe agents which are included in ink formulations to regulate the rate at which the ink dries and to control the viscosity of the ink. In addition to these properties, the present invention may comprise one or more humectants which will prevent clogging of the orifice or nozzle. With certain inks, the humectants will regulate the sublimation rate of the inks or dyes as they are transferred from the medium to the object on which the printed design is to permanently appear. The humectant in formulation example 2 is dipropylene glycol, which acts as a co-solvent and humectant.

FORMULATION EXAMPLE#3; Cyan Ink-Jet Formula

Material	Weight %
Sublaprint ® Blue 70013[10]	1.0
Lignosol ® FTA[11]	3.5
ME ® 39235[12]	10.0
Diethylene Glycol	9.5
DMSO	1.0
Distilled H_2O	75.0
Total:	100.00

[10]Keystone Aniline Corporation
[11]Lignotech (U.S.) Inc.
[12]Michelman, Inc.

Sublaprint® Blue 70013 is a heat activated ink or dye solid. Lignosol® FTA and ME®39235 are emulsifying enforcing agents. Lignosol® FTA also acts as a fungicide. ME®39235 is a polymer, and more specifically, it is a polyethylene binder. Diethylene Glycol and DMSO act as humectants. The solvent is distilled water.

Sublaprint® Blue 70013 is more difficult to sublimate than Bifaxan® Yellow 3GE, and is less soluble in the emulsifying enforcing agent. Diethylene glycol is used as a humectant to facilitate sublimation of the Sublaprint® Blue ink solid.

The heat activated ink solid is finely divided to a small particle size. The finely divided ink solid is combined with one or more emulsifying enforcing agents, which are in turn combined with the solvent.

Formulation Example#4: Magenta Ink-Jet Ink Formula

Material	Weight %
Intratherm ® Brill Red P-31NT[13]	.5
Lignosol ® FTA[14]	3.0
ME ® 39235[15]	11.0
NA-SUL ®[16]	1.0
DeeFo ® 806-102[17]	0.2
Sorbitol	0.5
Dipropylene Glycol	3.5
Distilled H_2O	79.3
Total:	100

[13]*Crompton & Knowles Corporation*
[14]Lignotech (U.S.) Inc.
[15]Michelman, Inc.
[16]King Industries
[17]Ultra Additives

Formulation Example#4 comprises a heat activated ink solid or dye which is finely divided and combined in an emulsifying enforcing agent. The emulsifying enforcing *agent or medium is, as with Example#3, Lignosol® FTA and* ME® 39235. Distilled water is used as a solvent. Dipropylene Glycol is used as a humectant.

Formulation Example#4 further comprises an anti-foaming or foaming control agent, DeeFo® 806-102 to retard foaming of the liquid ink composition. Formulation Example#4 further comprises a surfactant, which may be Sorbitol®, and a corrosion inhibitor, which, in this example, is NA-SUL®.

Formulation Examples 2, 3 and 4 are emulsions. In Example 2, the particular dye has a tendency to dissolve in the emulsifying enforcing agent. Formulation Examples 3 and 4 may also be described as colloids, having finely divided ink particles of not larger than 0.1 microns in diameter present within the disperse medium.

The invention provides an emulsion or colloid which will work within free flow ink jet printers, piezio electric printers, and bubble jet printers, without experiencing problems relating to orifice clogging which results from the use of an ink solid. Further, the use of an emulsion or colloid prevents the separation of the ink solids from the liquid components, rendering an ink composition which is stable over time. Typically, the liquid ink formulations are present within the printers in containers. Three or more colors of liquid ink are present. The containers may be factory sealed, and as such, the ink formulation may be held within the container for a long period of time.

The bubble jet printer forms the bubble which is used to print the ink at approximately the boiling point of the ink solvent. In most formulations, water will be used as the solvent, so that the ink is exposed to temperatures of 100 degrees C or higher as the ink is printed. Comparable temperatures may be used in free flow ink jet printers to create pressure for the purpose of transporting the ink for printing. As with the phase change ink jet printer, the ink is exposed to temperatures which will activate or sublimate some heat activated inks or dyes. The inks or dyes used in the ink compositions herein will not activate or sublimate at the operational temperatures of the printer.

The liquid ink formulation comprises a liquid carrier. The liquid carrier, or solvent, may be water. An emulsifying enforcing agent, which is soluable in the liquid carrier, forms an emulsion or a colloid in the liquid carrier. The emulsifying enforcing agent has an affinity for the heat activated dye, and attaches to, or may surround, all or part of individual particles of the dye particles.

The heat activated dye as used is a finely divided solid which is substantially insoluable in the liquid carrier. The dye particles, when placed in a liquid, will tend to agglomerate, vastly reducing, and practically eliminating, the efficacy of the ink formulation. The emulsifying enforcing agent is used to form an emulsion or a colloid, and in the present invention, also surrounds and shields, and thereby separates, the individual dye particles from the liquid carrier and from each other, preventing agglomeration of the dye particles, and thereby preventing the ink formulation from clogging the orifices of the printer, such as the ink jets. The emulsifying enforcing agent shields and insulates the dye particles, preventing activation or sublimation of the dye due to exposure to heat present in the printer and the printer processes. The emulsifying enforcing agent shields the dye particles, and improves the shelf life of the ink formulation. The adverse effects of heat, chemical reactions, light, time, and other factors that may be present in the packaging environment, or any environment within or surrounding the printer, or printing processes are eliminated or reduced by the emulsifying enforcing agent. However, while the emulsifying enforcing agent shields the dye particles, the insulation properties of the emulsifying enforcing agent are such that heat activation of the heat activated dye is achieved during final transfer of the image from the medium, which is performed at, or above, the temperature at which the dye activates, and the required optical density of the dye after final transfer by heat activation is attained.

An example of an emulsifying enforcing agent which will achieve the objects of the invention, when used with water as a liquid carrier, is a metallic sulfonate salt known as lignin sulfonate. Lignin sulfonates are sold under various brand names, including Lignosol and Raykrome. Other lignin products which may be used as the emulsifying enforcing agent to produce stable dispersion/emulsion systems include kraft lignin products and oxylignins.

Generally, lignin materials may be categorized by the two main processes in manufacturing lignins: kraft pulping and sulfite pulping. Each of the processes produce lignin materials with different structures and molecular weights, and therefore, they exhibit different performance properties in dye dispersing, stablizing and emulsification. Other than these two groups, there is a group of lignin products called oxylignins which are derived from lignins that have been oxidized and have a reduced number of sulphonic and methoxyl gruops and increased number of functional phenolic, hydroxyl and carboxylic groups.

Lignin products can be further modified through processes or reverse processes of sulphoncation, methylation, carboxylation and fractionation, etc. in order to change their chemical and physical properties, such as water solubilities in different pH ranges, molecular weight, heat stability and emulsification ability.

Lignin sulphonates, kraft lignins, or oxylignins can be used as dye dispersant/emulsifying enforcing agents in the invention to generate stable sublimation or heat sensitive dye emulsion/colloid systems, with proper adjustment of solvent and usage level. Lignosulfonate products such as Maprasperse CBA-1 (Lignotech), Marasperse 52CP (Lignotech), Lignosol FTA (Lignotech), Lignosol SFX-65 (Lignotech), Temsperse S002 (Temfibre, Inc.) Stepsperse DF series (Stephan Co.), and Weschem NA-4 (Wesco Technologies, LTD) may be used. Kraft lignin products such as Diwatex XP (Lignotech), and Reax 85 (Westvaco), and oxylignin products such as Marasperse CBOS-6 and Vanisperse CB are suitable for use as the emulsifying enforcing agent in the ink formulation of the present invention. The resulting aqueous system forms a double-layer structure, with a dye particle in the center surrounded by lignin molecules and another hydrated layer on the outer layer, to shield the dye particles from reagglomerating, and from the effects of chemical and physical changes introduced during storage or printing of the ink formulation.

Other materials can be used as either emulsifying enforcing agents or as additives to improve the emulsion/colloid stability, and thereby enchance the printing quality, by eliminating clogging and kogation at the print head. These materials may comprise a concentration from 0.1% to 15% by weight of the total formulation without damaging the sublimation heat transfer quality of the heat-sensitive dye at the heat transfer stage. These materials can be added into the system during the process of reducing the particle size of the dyes, or after the dye particles have been dispersed into the aqueous solution. These materials function also as emulsion/colloid stablizers, leveling agents, wetting agents, or foam control agents.

The materials which can be used for this purpose incude alkylaryl polyether alcohol nonionic surfactants, such as Triton X series (Octylphenoxy-polyethoxyethanol); alkylamine ethoxylates nonionic surfactants such as Triton FW series, Triton CF-10, and Tergitol (Union Carbide Chemicals); polysorbate products such as Tween (ICI Chemicals and Polymers); polyalkylene and polyalkylene modified surfactants, such as Silwet surfactants (polydimethylsioxane copolymers) and CoatOSil surfactants from OSI Specialties; alcohol alkoxylates nonionic surfactants, such as Renex, BRIJ, and Ukanil; Sorbitan ester products such as Span and Arlacel; alkoxylated esters/PEG products, such as Tween, Atlas, Myrj and Cirrasol surfactants from ICI Chemicals and Polymers; unsaturated alcohol products such as surfynol series surfactants from Air Products Co., alkyl phosphoric acid ester surfactant products, such as amyl acid phosphate, Chemphos TR-421; alkyl amine oxide such as Chemoxide series from Chemron Corporation; anionic sarcosinate surfactants such as Hamposyl series from Hampshire Chemical corporation; glycerol esters or polyglycol ester nonionic surfactants such Hodag series from Calgene Chemical, Alphenate (Henkel-Nopco), Solegal W (Hoechst AG), Emultex (Auschem SPA); and polyethylene glycol ether surfactants such as Newkalgen from Takemoto Oil and Fat Co.

The solid dyes which are used in the ink formulation and in the printing process have a particle size which is too large for use in ink jet printers, as such dyes are currently commercially available. The particle size and nonsolubility in water also presents other problems previously discussed. The dye must be finely divided, which may be accomplished using mills, grinders, homogenizers or micronizers. One or more different emulsion enforcing agents including surfactants dispersants, emulsifying agents, wetting agents, defoamers or anti-foamers, or corrosion inhibitors may be used in the process to improve and facilitate the process of finely dividing the dye. Examples of grinding devices to finely divide the dye include microfluidizers, roller mills, vertical mills, horizontal mills, jet mills, ball mills, attrition mills, and ultrasonic micronizer/homogenizing mills.

For example, the heat sensitive dye is mixed with the emulsifying enforcing agent, and/or other additives and co-solvents, and deionized distilled water. The dry chemicals are mechanically mixed, dispersed into the liquid phase, and then fed into grinding facility. The grinding device is operated while monitoring temperature, pressure, viscosity, interfacial tension, surface tension, pH value and flow speed, without activating the heat sensitive dye, until the mean diameter of the dye particles is between 0.1 to 0.5 microns.

Particles which have a diameter of larger than 0.2–0.5 microns should be eliminated from the composition, such as by filtration or centrifuge. The resulting ink composition has a mean particle size of 0.2 microns or less, with the solid percentage ranging from 0.05% –10% by weight, to produce an ink composition which achieves the objectives of the present invention.

What is claimed is:

1. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, comprising the steps of:

a. preparing a liquid ink formulation comprising a heat activated dye, a liquid carrier, and an emulsifying enforcing agent which is soluble in said liquid carrier and has an affinity for said heat activated dye and surrounds individual particles of said heat activated dye and separates said individual particles from said liquid carrier, and which allows heat activation of said heat activated dye at the temperature at which said heat activated dye activates, and wherein said heat activated dye is a finely divided solid which is substantially insoluble in said liquid carrier;

b. supplying a printer with said liquid ink formulation;

c. printing said liquid ink formulation in a desired image by means of said printer onto a medium at a temperature which is below the temperature at which said heat activated dye activates; and

d. transferring said image from said medium to an object on which the image is to appear by thermal means at a temperature which is sufficient to activate the heat activated dye, so as to cause the heat activated dye to transfer onto said object.

2. A method of printing using heat activated dye solids by means of a printer which uses liquid ink as described in claim 1, wherein said emulsifying enforcing agent is a lignin.

3. A method of printing using heat activated dye solids by means of a printer which uses liquid ink as described in claim 1, wherein said liquid ink formulation further comprises an additive.

4. A method of printing using heat activated dye solids by means of a printer which uses liquid ink as described in claim 3, wherein said additive is a surfactant.

5. A method of printing using heat activated dye solids by means of a printer which uses liquid ink as described in claim 2, wherein the emulsifying enforcing agent is a sulphonated lignin.

6. A method of printing using heat activated dye solids by means of a printer which uses liquid ink as described in claim 1, wherein said printer is a piezo electric printer.

7. A method of printing a design by means of a computer driven printer using heat activated dye solids, comprising the steps of:

a. preparing an ink formulation comprising a heat activated dye, a liquid carrier, and an emulsifying enforcing agent which is soluble in said liquid carrier and has an affinity for said heat activated dye, wherein said emulsifying enforcing agent surrounds and shields

individual particles of said heat activated dye and separates said individual particles from said liquid carrier, and wherein said heat activated dye is a finely divided solid which is substantially insoluble in said liquid carrier;

b. supplying a printer with said ink formulation;

c. printing said ink formulation in a desired image by means of said printer onto a medium at a temperature which is below the temperature at which said heat activated dye activates; and

d. transferring said image from said medium to an object on which the image is to appear by thermal means at a temperature which is sufficient to activate the heat activated dye, so as to cause the heat activated dye to transfer onto said object.

8. A method of printing a design by means of a computer driven printer using heat activated dye solids as described in claim 7, wherein the emulsifying enforcing agent is a sulphonated lignin.

9. A method of printing a design by means of a computer driven printer using heat activated dye solids as described in claim 8, wherein the emulsifying enforcing agent is Lignosol.

10. A method of printing a design by means of a computer driven printer using heat activated dye solids as described in claim 7, wherein said printer is a piezo electric printer.

* * * * *

US005640180A

United States Patent [19]

Hale et al.

[11] Patent Number: 5,640,180

[45] Date of Patent: Jun. 17, 1997

[54] **LOW ENERGY HEAT ACTIVATED TRANSFER PRINTING PROCESS**

[75] Inventors: **Nathan Hale; Ming Xu**, both of Mt. Pleasanton, S.C.

[73] Assignee: **Sawgrass Systems, Inc.**, Mt. Pleasant, S.C.

[21] Appl. No.: **710,171**

[22] Filed: **Sep. 12, 1996**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 695,121, Aug. 1, 1996, and Ser. No. 506,894, Jul. 25, 1995, which is a continuation-in-part of Ser. No. 299,736, Sep. 1, 1994, Pat. No. 4,488,907, said Ser. No. 695,121, is a continuation-in-part of Ser. No. 565,999, Dec. 1, 1995, which is a continuation-in-part of Ser. No. 207,756, Mar. 8, 1994, Pat. No. 5,485,614.

[51] **Int. Cl.**[6] **B41J 2/01**

[52] **U.S. Cl.** **347/3**; 347/213

[58] **Field of Search** 347/213, 3; 400/120.02, 400/120.01

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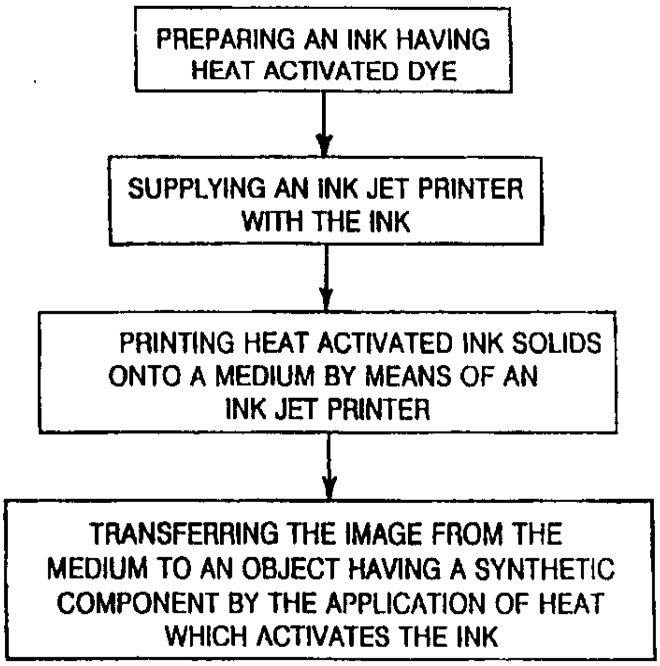
Primary Examiner—Huan H. Tran
Attorney, Agent, or Firm—B. Craig Killough

[57] **ABSTRACT**

A method of printing a liquid ink which is produced from a heat activated dye which is selected from a limited group of dyes which are capable of transfer at low energy. A printer which uses liquid ink, such as an ink jet printer, prints an image onto an intermediate substrate medium. The dyes contained in the ink are not substantially activated during the process of printing on to the medium. The image formed by the printed ink is transferred from the medium to a final substrate by the application of heat and pressure for a short period of time to activate the ink. The dye and dispersing/emulsifying agent(s) are selected from a limited group to produce an ink which permits thermal transfer at low energy, with the resulting image, as deposited on the final substrate, having an optical density of 1.0 or greater.

21 Claims, 2 Drawing Sheets



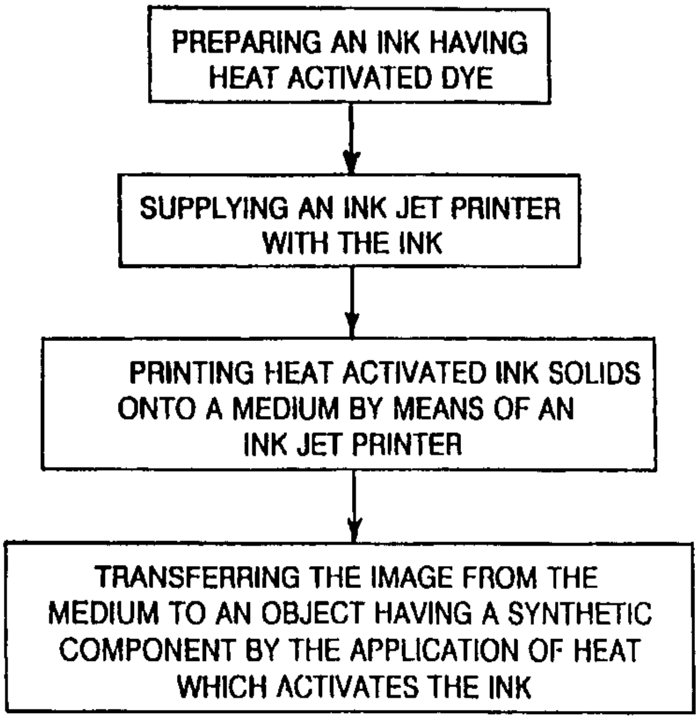

PREPARING AN INK HAVING HEAT ACTIVATED DYE
SUPPLYING AN INK JET PRINTER WITH THE INK
PRINTING HEAT ACTIVATED INK SOLIDS ONTO A MEDIUM BY MEANS OF AN INK JET PRINTER
TRANSFERRING THE IMAGE FROM THE MEDIUM TO AN OBJECT HAVING A SYNTHETIC COMPONENT BY THE APPLICATION OF HEAT WHICH ACTIVATES THE INK

FIG 1

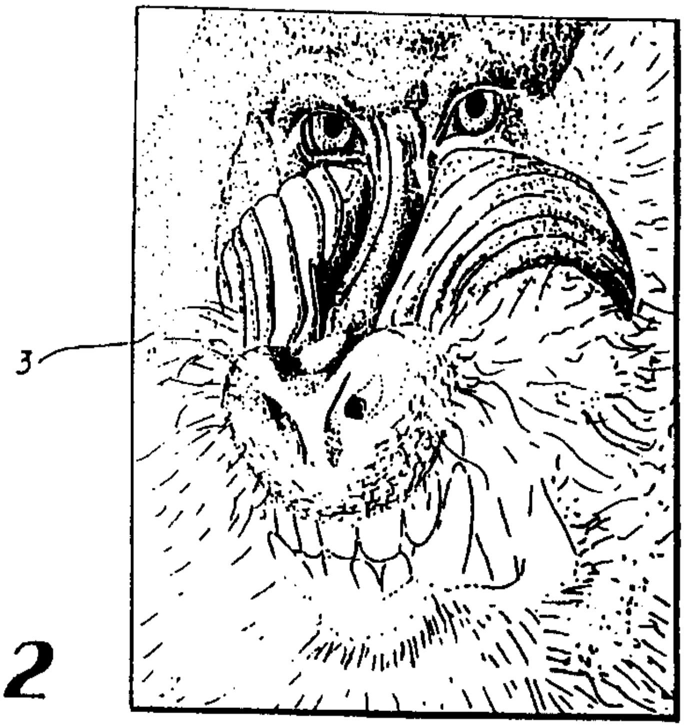

3

FIG 2

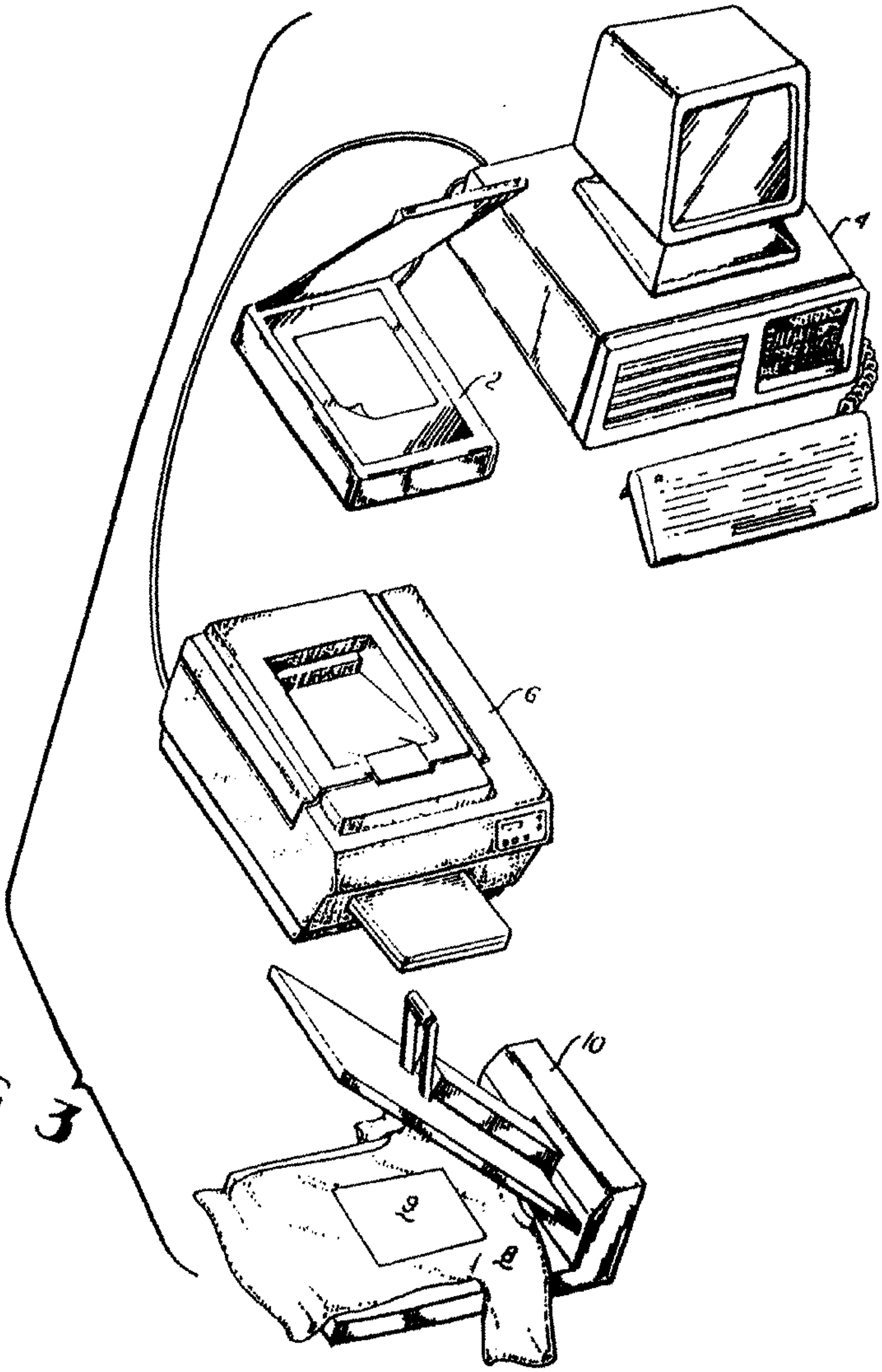


FIG 3

LOW ENERGY HEAT ACTIVATED TRANSFER PRINTING PROCESS

This application is a continuation-in-part of Ser. No. 08/695,121 filed Aug. 1, 1996, which is a continuation-in-part of Ser. No. 08/565,999, filed Dec. 1, 1995, which is a continuation-in-part of application Ser. No. 08/207,756 filed Mar. 8, 1994, U.S. Pat. No. 5,485,614, issued Jan. 30, 1996. This application is a continuation-in-part of Ser. No. 08/506,894, filed Jul. 25, 1995, which is a continuation-in-part of 08/299,736, U.S. Pat. No. 4,488,907.

FIELD OF THE INVENTION

This invention relates to printing heat sensitive, dye diffusion or sublimation inks generally, and is more specifically related to a method of printing liquid inks comprising these dyes onto an intermediate transfer sheet by means of an ink jet printer or other printer which uses liquid inks, and subsequently transferring the printed image from the intermediate sheet by the application of heat and pressure.

BACKGROUND OF THE INVENTION

Words and designs are frequently printed onto clothing and other textile materials, and other objects. The use of computer technology allows substantially instantaneous printing of images. For example, video cameras or scanning may be used to capture an image to a computer. The image may then be printed by any suitable printing means, including mechanical thermal printers, ink jet printers and laser printers. These printers will print multiple color images.

Color ink jet printers are in common use. Color ink jet printers use combinations of cyan, yellow and magenta inks or dyes to produce multiple color images. Most ink jet printers in common use employ inks which are in liquid form.

Heat activated, dye diffusion and sublimation ink solids change to a gas at about 400° F., and have a high affinity for polyester and other synthetic materials at the activation temperature, and a limited affinity for most other materials. Once the bonding from gassification and condensation takes place, the ink is permanently printed, and is resistant to change or fading caused by laundry products, heat or light.

Hale, U.S. Pat. Nos. 5,246,518, 5,248,363, 5,302,223, and 5,485,614 and Hale et al., U.S. Pat. No. 5,488,907, disclose the use of printers to produce an image on a medium or transfer sheet wherein the image is comprised of sublimation, dye diffusion or other heat activated inks. The ink is not activated during the printing of the medium or transfer sheet.

Problems are associated with liquid inks prepared from insoluble dye solids. The orifices or nozzles of most ink jet printers are not designed for the dispensing of dye solids contained within a liquid material. The orifices of these printers are typically 5–30 microns in diameter, and clogging of the orifice will occur when ink solids of large particle size or in high volume are transferred through the orifice.

Further, when the ink solids are placed into a liquid carrier, the ink solids tend to separate from the liquid over time and fall to the bottom of the ink container. The ink is typically packaged in a container at a manufacturing facility for subsequent mounting of the container within the ink jet printer, meaning that a substantial storage time for the ink composition exists prior to use. Separation of the liquid and solids comprising the ink formulation presents problems with regard to the mechanical operation of the printer and

the print quality achieved from use of the ink formulation. Agents which are included within the ink formulation to inhibit separation must also inhibit agglomeration of the solid dye particles, but the agents must not inhibit activation of the dye during the final transfer at elevated temperatures, by insulating the dye or reacting with the dye, or otherwise.

Accordingly, the production of stable liquid inks from dyes which are not water soluble is difficult to achieve without destroying or reducing the properties of the dye which are required for practicing the process of the invention. In the prior art, liquid inks have been produced from dyes that initially have properties suitable for practicing the process. However, the production of liquid inks from these dyes changes or masks the required properties, and therefore, the resulting inks cannot be satisfactorily used to practice the process. For example, additives which will inhibit the dye particles from settling out of the liquid carrier, or which will inhibit agglomeration, tend to insulate the dye particles, meaning that the energy required for sublimation, diffusion or activation of the dye is elevated to unacceptable levels for practicing the process. Other additives which are used in the prior art to produce a liquid ink from the solid dyes are reactive with the dye, and modify or eliminate required properties of the dyes. Other "side effects" of using these additives include undesired color modification or contamination, bonding with the intermediate substrate, or optical density on the final substrate which is inadequate.

While certain solvents will dissolve the dyes, the requirements of the process makes the use of these solvents impractical. Dye materials solubilized to the molecular level have a tendency to bond with fibers, both synthetic and natural. Accordingly, the dyes cannot be effectively transferred from a substrate used as an intermediate transfer sheet by the application of heat and pressure as required by the process of the present invention.

SUMMARY OF THE PRESENT INVENTION

This invention is a method of printing a liquid ink which is produced from sublimation, dye diffusion, or heat sensitive dyes. A printer which uses liquid ink, such as an ink jet printer, prints the image onto a medium, or intermediate substrate, which may be paper. The sublimation, dye diffusion, or heat sensitive dyes (hereinafter collectively referred to as "heat activated dyes") contained in the ink are not substantially sublimated or activated during the process of printing on to the medium. The image formed by the printed ink is transferred from the medium to a final substrate by the application of heat and pressure which sublimates or activate the ink. This thermal transfer step is achieved at low energy when compared to other sublimation or activation processes known and used in the art. One of the goals of the process requires that the thermal transfer occur by applying heat and pressure for no more than three and one-half minutes, and preferably less time. In the prior art, heat at the activation temperature is applied for up to thirty minutes. Accordingly, as used herein, a low energy transfer is a thermal transfer of the image from the intermediate sheet to the final substrate by applying a temperature which is not higher than 450° F., for no more than three and one-half minutes, with the resulting image, as deposited on the final substrate, having an optical density of 1.0 or greater, as measured by an X-Rite 418 densitometer in the density operation mode with background corrections.

The dyes, or perhaps pigments, which are suitable for practicing the invention are dyes which are capable of low energy transfer from the medium onto the final substrate to produce an image on the final substrate which is waterfast and colorfast. After transfer, the dyes are no longer substantially heat sensitive. Dyes which have these characteristics are found in various classifications of dyes, including disperse dyes, solvent dyes, basic dyes, acid dyes and vat dyes. However, none of the dyes which are currently available and which are suitable for producing a liquid ink for practicing the invention are soluble in water.

Accordingly, only a relatively small range of dyes in combination with a relatively small range of dispersing/emulsifying agents will produce a stable liquid ink which will allow the printing method to be practiced. Characteristics of acceptable dyes and dispersing/emulsifying agents which will produce a liquid ink with which to practice the printing method are disclosed herein.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a block diagram showing the printing process.

FIG. 2 illustrates an example of a design printed by a printer using the printing process.

FIG. 3 is a diagrammatic illustration showing exemplary elements of computer and printing systems which could be used to achieve the printing process.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

An image is input into a computer 4. The computer directs a printer 6 to print the image. Any means of forming the an image which may be printed from a computer may be used, including images generated by software. Available computer design graphic software may be used, or still photography may be used. The design may be photographic, graphic artistic, or simply letters or words. The use of cyan, yellow and magenta ink compositions allow the printer to print in full color or multi-color designs.

After the image is printed onto the medium, the image may be permanently transferred by thermal means. Most commonly, the design will be transferred onto a textile substrate, such as a shirt 8, although the image may be transferred onto other materials which act as a substrate, such as metal, ceramic, wood, or plastic. The design 3, which is printed onto the medium 9 without activating the ink, is placed against the object 8. A temperature which is sufficient to activate the dye is applied. This temperature will typically be around 400° F. This temperature is applied for a time sufficient to heat activate and transfer the ink solids in accordance with the requirements of the invention. A heat transfer machine 10 may be used to accomplish the transfer of the inks from the medium to the substrate. Activation, or sublimation, of the dye does not take place at the time of printing the image onto the medium, but occurs during the transfer from the medium to the substrate. The group of heat activated dyes from which dyes may be selected for use in the invention are dyes which substantially sublimate or activate at low energy to form an image which has an optical density value of no less than 1.0, and which is waterfast and colorfast. Each of the dyes which comprise this group will achieve an optical density of 1.25 or greater after activation, when optical density is measured by an X-Rite 418 densitometer in the density operation mode with background correction.

The invention requires the dyes to be transferred at low energy (as defined above) after the dyes are formulated into a liquid ink as described herein and printed onto the medium

(the "acceptable dyes"). While a larger group of dyes can be sublimated at low energy, dyes which are not acceptable cannot be formulated into a liquid ink which retains the required properties. While most of the acceptable dyes are disperse dyes, certain other dyes which will perform according to the goals of the invention are included in the group of acceptable dyes.

In general, the acceptable dyes are not reactive, and do not have strong polar function groups, such as sulfonate or carboxyl groups. Reacting the dyes with chemical agents added to the formulation in order to form a liquid ink, as is sometimes done in the prior art, tends to inhibit the activation of the dyes at low energy, which is contrary to the present invention. The acceptable dyes have a molecular weight which is less than 600, and is preferably within a range of 200–400. Most of the acceptable dyes are disperse dyes but certain solvent dyes, vat dyes, basic or cationic dyes (such as carbinol base dyes or anthraquinone type dyes having a quarternary amine), acid dyes, direct dyes, mordant dyes and oxidizing colors also fall within the group of acceptable dyes.

The ink formulation prepared according to the invention is a liquid. Dye solids of small particle size are dispersed in a liquid carrier, and one or more agents are used to maintain what may be called, according to various definitions, a colloidal, dispersion or emulsion system. The term "emulsion" is used herein to describe the system, even though the system could, in some forms, be called a colloid or a dispersion.

The heat activated solid dye particles are of small size. It is preferred that the individual solid dye particles have no dimension which is greater than 0.5 microns.

The solid dye particles are dispersed into the liquid carrier. The dispersion is normally achieved by the introduction of a dispersing agent, although mechanical or other physical means could be used. An emulsifying agent is introduced to prevent coagulation or coalescense of the individual dye particles and to stabilize the system.

As set forth in the examples, a single agent may be used as a dispersing and emulsifying agent. Multiple agents may be used in accordance with the goals of the invention. The agent or agents stabilize the system, so that the system remains sufficiently homogenous over time to allow successful printing and transfer of the dye according to the method of the invention. Further, the agent shields the individual particles from the adverse effects of the storage, transportation and printer environments, such as heat, cold and light. While the agent shields the dye particles while they are in the liquid system, it does not inhibit low energy transfer of the dyes in the form of the printed image.

The agents used to disperse and/or emulsify the dye particles include various dispersant materials, surfactants (including cationic, anionic, amphoteric, and nonionic surfactants) and polymeric surfactants. Polymeric materials with dispersing ability, but which are not surfactants, can also be used. Either synthetic or natural materials can be used. The dispersing/emulsifying agents each have a molecular weight which is less than 100,000, and preferably less than 10,000. Thermal stability of the agents is essential to prevent decomposition and/or chemical reaction between the agents and the other components in the systems.

As with the dye, to accomplish the printing method of the invention, the agent(s) do not have active function groups which will react or crosslink with the medium, or which will react or crosslink with the dye or pigment in the system, since such reactions or linkages inhibit the required properties of the dye at the time of activation. The agent(s) must form the emulsion from the finely divided dye particle and the liquid carrier, but must not materially insulate or otherwise materially inhibit the activation of the dye at the time of final transfer.

Agents having the required properties when used with some or all of the acceptable dyes include Lignosulfonate products such as Marasperse 52CP (Lignotech), Lignosol FTA (Lignotech), Lignosol SFX-65 (Lignotech), Maprasperse CBA-1 (Lignotech), Temsperse S002 (Temfibre, Inc.) Stepsperse DF series (Stephan Co.), and Weschem NA-4 (Wesco Technologies, LTD), Kraft lignin products such as Diwatex XP (Lignotech), and Reax 85 (Westvaco), and oxylignin products such as Marasperse CBOS-6 and Vanisperse CB.

Other examples of emulsifying agents and dispersants are alkylaryl polyether alcohol nonionic surfactants, such as Triton X series (Octylphenoxypolyethoxyethanol); alkylamine ethoxylates nonionic surfactants such as Triton FW series, Triton CF-10, and Tergitol (Union Carbide Chemicals); polysorbate products such as Tween (ICI Chemicals and Polymers); polyalkylene and polyalkylene modified surfactants, such as Silwet surfactants (polydimethylsioxane copolymers) and CoatOSil surfactants from OSI Specialties; alcohol alkoxylates nonionic surfactants, such as Renex, BRIJ, and Ukanil; Sorbitan ester products such as Span and Arlacel; alkoxylated esters/PEG products, such as Tween, Atlas, Myrj and Cirrasol surfactants from ICI Chemicals and Polymers; unsaturated alcohol products such as surfynol series surfactants from Air Products Co., alkyl phosphoric acid ester surfactant products, such as amyl acid phosphate, Chemphos TR-421; alkyl amine oxide such as Chemoxide series from Chemron Corporation; anionic sarcosinate surfactants such as Hamposyl series from Hampshire Chemical corporation; glycerol esters or polyglycol ester nonionic surfactants such Hodag series from Calgene Chemical, Alphenate (Henkel-Nopco), Solegal W (Hoechst AG), Emultex (Auschem SPA); and polyethylene glycol ether surfactants such as Newkalgen from Takemoto Oil and Fat Co.

Multiple agents may be used in combination to improve the emulsification of the system and to stabilize the system, as long as the agents are not reactive and do not cause precipitation or otherwise negatively impact upon the emulsification process or the transfer process.

Organic solvents, cosolvents, and/or humectants can also be used as additional additives. Aliphatic and/or aromatic alcohols (thioalcohols), alkoxylated alcohols (thioalcohols), halogenated alcohols (thioalcohols) and carboxylated alcohols (thioalcohols), including mono-alcohol (thioalcohol), diol (thiodialcohol), triol (thiotrialcohol) and polyol (thiopolyalcohol), aminoxide, diamine, triamine material, may be used to improve dye dispersibility, solubility and/or stability in the final ink composition. Examples of solvent materials are diethylene glycol, DMSO and dipropylene glycol.

Other additives can also be introduced into the ink, such as surfactants, corrosion control agents, foam control agents, antioxidants, radiation stabilizers, thermal stabilizers, flame retarding agents, pH control agents, viscosity control agents, or surface (interfacial) tension control agents can be added during or after the emulsification process. Other materials, including dispersants, emulsifying agents, and stabilizers, may be included in the formulation by means of methods known in the art.

EXAMPLES

An example of a liquid ink composition usable in an ink jet printer is as follows:

Material	Weight %
heat sensitive dye(s)	0.05–20%
dispersant/emulsifying agent	0.05–30%
solvent(s)/cosolvent(s)	0–45%
additive(s)	0–15%
water	40–98%
Total	100%

The heat sensitive dye may be a red (magenta), blue (cyan), yellow or brown dye. The dispersant/emulsifying agent may be a sulfonated lignin such as Marasperse CBA-1. The additive(s) may be Tergitol 15-s-9, Triton X-165, Triton X-405 or Surfynol 465. The solvents and/or co-solvents may be diethlene glycol and/or thioglycol and/or 2-pyrrolidone and/or 1-methoxy 2-propanol.

EXAMPLE A

30 grams of finely divided Spirit Blue Base (CAS#68389-46-8) is mixed with 15 grams of Ultrazine NA (Lignotech, USA) and 500 grams of de-ionized water. An ultrasonic pulverizer is used to disperse the dye into the aqueous phase for approximately 30 minutes. Two (2.0) grams of Solsperse 27000 (Zenica Colors, USA) is added into the mixture, which is pulverized for another 10 minutes to achieve a stable emulsion. The mixture is filtered to remove particles larger than 0.25 microns. The printing ink for use in the ink jet printer is formulated from the emulsion as follows:

Material	Weight %
Emulsion	87.0
Glycol	4.0
1-methoxy-2-propanol	7.0
Ammonyx LO (1)	2.0
Total	100%

(1). Stepan Co

The resulting ink is printed by the HP 560 Deskjet printer onto plain copy paper in a dark cyan color, and is transferred from the paper medium or receiver onto a polyester fabric substrate by thermal transfer at 400° F. temperature with 40 lb. pressure applied for 20 seconds. The image as applied to the polyester fabric substrate has an optical density value of 1.4–1.5 for the cyan color as read by an X-Rite 418 densitometer.

EXAMPLE B

Twenty (20) grams of Disperse Yellow 9 (CAS#6373-73-5) is mixed with four (4) grams of Sulfynol 131 (Air Products) and 5.0 grams of glycerol (CAS#56-81-5) and 480 grams of de-ionized water. The pulverizer is used to disperse the dye into the aqueous phase for approximately 25 minutes. One (1.0) gram of Sulfynol 104 E (Air Products) is added to the mixture and pulverized for another 10 minutes to produce an emulsion. The mixture is filtered to remove particles larger than 0.25 microns. The liquid ink for use in the ink jet printer is formulated as follows:

Material	Weight %
Emulsion	78.5
Diethylene Glycol	8.0
Thiodiethanol	5.0
Sulfynol 465	4.0
1-2-Propandiol	4.0
DEA	0.5
Total	100%

The resulting liquid ink is printed by a Canon Bubble Jet 4100 printer onto plain copy paper. The printed image is thermally transferred from the paper medium to a polyester textile substrate at 400° F., while applying 40 lb. pressure for 20 seconds. An intense yellow color having an optical density of 1.4, as measured by an X-Rite 418 densitometer with background correction. appears on the substrate.

EXAMPLE C

Twenty-five (25) grams of finely divided Solvent Red 52 (CAS#81-39-0), is mixed with twenty-two (22) grams of Transferin® N-38 (Boehme Filatex, Inc.) and one hundred and fifty (150) grams of de-ionized water. An ultrasonic pulverizer is used to finely divide the dye and to disperse and micronize the solid dye particles into the aqueous phase by operating the pulverizer for approximately Forty-five (45) minutes. Five (5) grams of Tergitol™ 15-S-15 (Union Carbide, USA). Ten (10) grams of 1,4-butanediol, and two hundred and twenty (220) grams of de-ionized water are then added into the dispersion and pulverized for an additional ten (10) minutes. The dispersion is then filtered to remove solid particulate having a dimension which is larger than 0.25 microns. A liquid ink is formulated using the homogenized emulsion as follows:

Component	Weight %
Emulsion	85.0
Tergitol ™ 15-S-9[1]	3.997
1-pyrrolidinone	2.0
1-ethoxy-2-propanol	6.0
IPA	3.0
Kathon ® PFM[2]	0.003
Total	100

[1]Union Carbide, USA
[2]Rohm & Haas Company

The liquid ink is then printed by an Epson Stylus Color Pro or Epson Stylus Color IIs piezo electric ink jet printer to form an image on plain copy paper. The image is transferred from the paper to a polyester fabric substrate by the application of pressure and heat at a temperature of 400° F. for 25 seconds. The image as transferred has an optical density of 1.45 for the magenta color, as measured by an X-Rite 418 densitometer with background correction.

What is claimed is:

1. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, comprising the steps of:

a. preparing a liquid ink formulation comprising a heat activated dye, a liquid carrier, and a sulfonated lignin agent which disperses said heat activated dye into said liquid carrier, wherein said sulfonated lignin agent does not substantially increase the activation energy required to activate said heat activated dye after said heat activated dye is printed onto a medium;

b. supplying a printer with said liquid ink formulation;

c. printing said liquid ink formulation by means of said printer to form an image on a medium without materially activating the heat activated dye; and

d. transferring said image from said medium to a substrate on which the image is to appear by the application of heat and pressure at a temperature which is sufficient to activate the heat activated dye, so as to cause the heat activated dye to transfer on to said substrate.

2. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, as described in claim 1, wherein said heat activated dye is not reactive with said sulfonated lignin agent or said liquid carrier.

3. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, as described in claim 1, wherein said heat activated dye is substantially insoluble in said liquid carrier.

4. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, as described in claim 1, wherein said ink formulation further comprises at least one solvent.

5. A method of printing using heat activated dye solids by means of a printer which uses liquid ink as described in claim 1, wherein said sulfonated lignin agent shields said heat activated dye but does not substantially increase the activation energy required to activate said heat activated dye after said heat activated dye is printed on to said medium.

6. A method of printing using heat activated dye solids by means of a printer which uses liquid ink as described in claim 1, wherein said heat activated dye has a molecular weight in the range of 200 to 400.

7. A method of printing using heat activated dye solids by means of a printer which uses liquid ink as described in claim 1, wherein said heat activated dye is comprised of individual particles of said heat activated dye, and wherein said individual particles of said heat activated dye do not have a dimension which is greater than 0.5 microns.

8. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, comprising the steps of:

a. preparing a liquid ink formulation comprising a heat activated dye, a liquid carrier, a sulfonated lignin agent and a surfactant, wherein said sulfonated lignin agent and said surfactant disperse said heat activated dye into said liquid carrier and form an emulsion from said heat activated dye and said liquid carrier, and wherein said sulfonated lignin agent and said surfactant do not substantially increase the activation energy required to activate said heat activated dye after said heat activated dye is printed onto a medium;

b. supplying a printer with said liquid ink formulation;

c. printing said liquid ink formulation by means of said printer to form an image on a medium without materially activating the heat activated dye; and

d. transferring said image from said medium to a substrate on which the image is to appear by the application of heat and pressure at a temperature which is sufficient to activate the heat activated dye, so as to cause the heat activated dye to transfer on to said substrate.

9. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, as described in claim 8, wherein said heat activated dye is not reactive with said sulfonated lignin agent or said liquid carrier.

10. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, as described in claim 8, wherein said heat activated dye is substantially insoluble in said liquid carrier.

11. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, as described in claim 8, wherein said ink formulation further comprises at least one solvent.

12. A method of printing using heat activated dye solids by means of a printer which uses liquid ink as described in claim 8, wherein said surfactant shields said heat activated dye but does not substantially increase the activation energy required to activate said heat activated dye after said heat activated dye is printed on to said medium.

13. A method of printing using heat activated dye solids by means of a printer which uses liquid ink as described in claim 8, wherein said heat activated dye has a molecular weight in the range of 200 to 400.

14. A method of printing using heat activated dye solids by means of a printer which uses liquid ink as described in claim 8, wherein said heat activated dye is comprised of individual particles of said heat activated dye, and wherein said individual particles of said heat activated dye do not have a dimension which is greater than 0.5 microns.

15. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, comprising the steps of:

a. preparing a liquid ink formulation comprising a heat activated dye, a liquid carrier, and a sulfonated lignin agent which disperses said heat activated dye into said liquid carrier, wherein said sulfonated lignin agent does not substantially increase the activation energy required to activate said heat activated dye after said heat activated dye is printed onto a medium;

b. supplying a printer with said liquid ink formulation;

c. printing said liquid ink formulation by means of said printer to form an image on a medium without materially activating the heat activated dye; and

d. subsequently activating said heat activated dye by the application of heat and pressure to said heat activated dye at a temperature which is sufficient to activate the heat activated dye.

16. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, as described in claim 15, wherein said heat activated dye is not reactive with said sulfonated lignin agent or said liquid carrier.

17. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, as described in claim 15, wherein said heat activated dye is substantially insoluble in said liquid carrier.

18. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, as described in claim 15, wherein said ink formulation further comprises at least one solvent.

19. A method of printing using heat activated dye solids by means of a printer which uses liquid ink as described in claim 15, wherein said sulfonated lignin agent shields said heat activated dye but does not substantially increase the activation energy required to activate said heat activated dye after said heat activated dye is printed on to said medium.

20. A method of printing using heat activated dye solids by means of a printer which uses liquid ink as described in claim 15, wherein said heat activated dye has a molecular weight in the range of 200 to 400.

21. A method of printing using heat activated dye solids by means of a printer which uses liquid ink as described in claim 15, wherein said heat activated dye is comprised of individual particles of said heat activated dye, and wherein said individual particles of said heat activated dye do not have a dimension which is greater than 0.5 microns.

* * * * *

US005642141A

United States Patent [19]

Hale et al.

[11] Patent Number: 5,642,141

[45] Date of Patent: *Jun. 24, 1997

[54] **LOW ENERGY HEAT ACTIVATED TRANSFER PRINTING PROCESS**

[75] Inventors: **Nathan Hale; Ming Xu**, both of Mt. Pleasant, S.C.

[73] Assignee: **Sawgrass Systems, Inc.**, Mt. Pleasant, S.C.

[*] Notice: The term of this patent shall not extend beyond the expiration date of Pat. No. 5,488,907.

[21] Appl. No.: **695,121**

[22] Filed: **Aug. 5, 1996**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 565,999, Dec. 1, 1995, which is a continuation-in-part of Ser. No. 207,756, Mar. 8, 1994, Pat. No. 5,485,614, and a continuation-in-part of Ser. No. 506,896, Jul. 26, 1995, Pat. No. 5,568,805, which is a continuation-in-part of Ser. No. 299,736, Sep. 1, 1994, Pat. No. 5,488,907.

[51] **Int. Cl.**^{6} **B41J 2/01**

[52] **U.S. Cl.** **347/3**; 347/213

[58] **Field of Search** 347/213, 3; 400/120.2, 400/120.1

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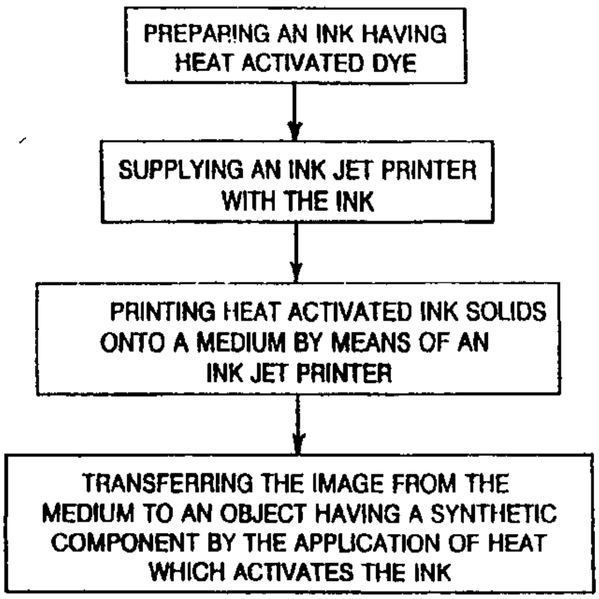
Attorney, Agent, or Firm—B. Craig Killough

[57] **ABSTRACT**

A method of printing a liquid ink which is produced from a heat activated dye which is selected from a limited group of dyes which are capable of transfer at low energy. A printer which uses liquid ink, such as an ink jet printer, prints an image onto an intermediate substrate medium. The dyes contained in the ink are not substantially activated during the process of printing on to the medium. The image formed by the printed ink is transferred from the medium to a final substrate by the application of heat and pressure for a short period of time to activate the ink. The dye and dispersing/emulsifying agent(s) are selected from a limited group to produce an ink which permits thermal transfer at low energy, with the resulting image, as deposited on the final substrate, having an optical density of 1.0 or greater.

23 Claims, 2 Drawing Sheets



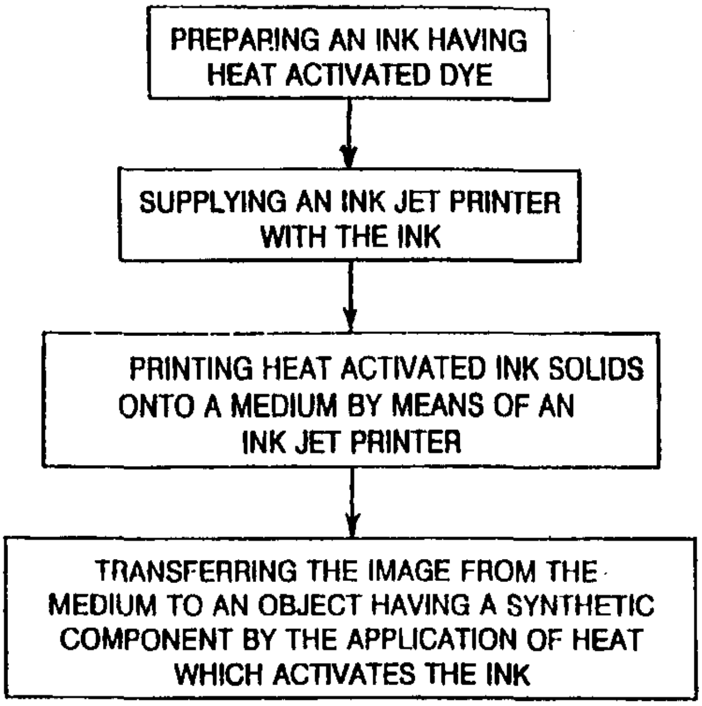

PREPARING AN INK HAVING HEAT ACTIVATED DYE
SUPPLYING AN INK JET PRINTER WITH THE INK
PRINTING HEAT ACTIVATED INK SOLIDS ONTO A MEDIUM BY MEANS OF AN INK JET PRINTER
TRANSFERRING THE IMAGE FROM THE MEDIUM TO AN OBJECT HAVING A SYNTHETIC COMPONENT BY THE APPLICATION OF HEAT WHICH ACTIVATES THE INK

FIG 1

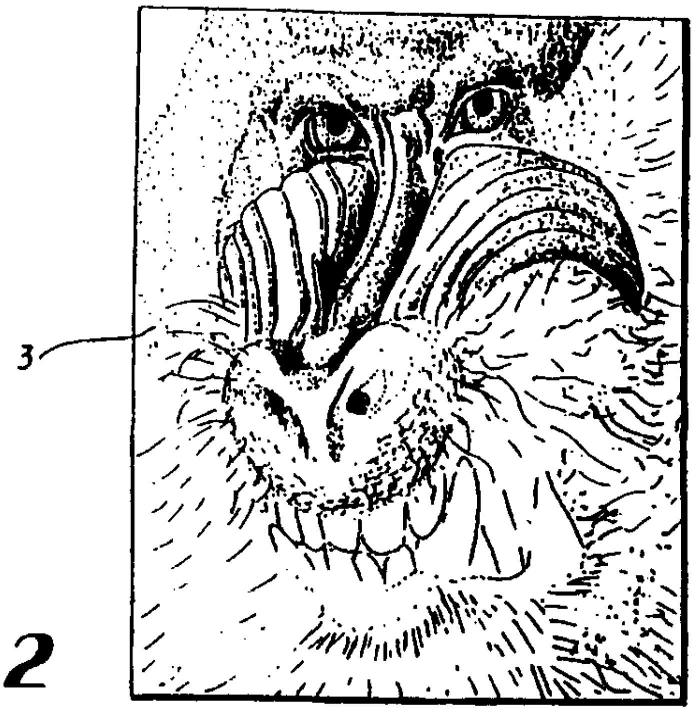

3

FIG 2

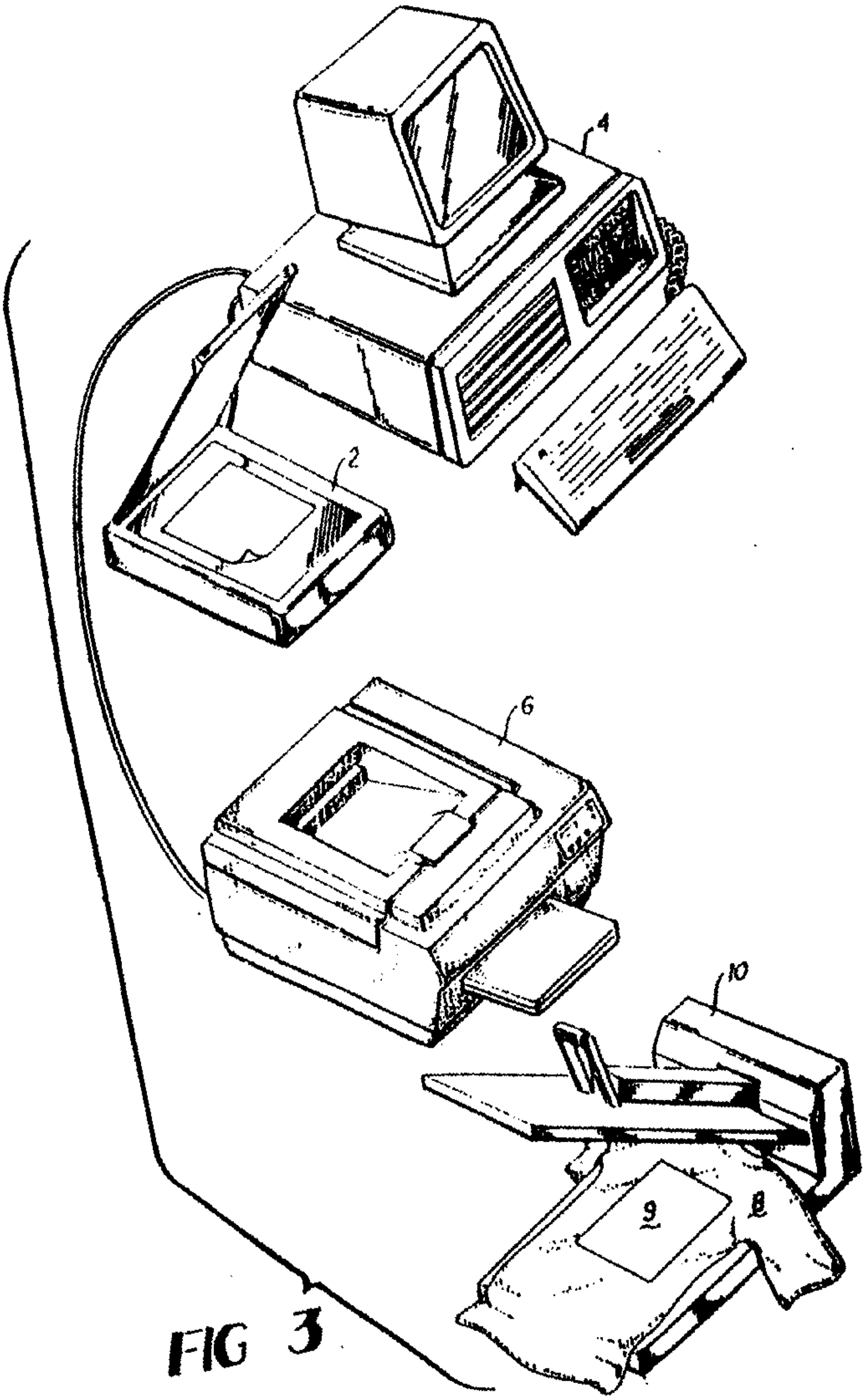


FIG 3

LOW ENERGY HEAT ACTIVATED TRANSFER PRINTING PROCESS

This application is a continuation-in-part of Ser. No. 08/565,999, filed Dec. 1, 1995, which is a continuation-in-part of application Ser. No. 08/207,756 filed Mar. 8, 1994, U.S. Pat. No. 5,485,614, issued Jan. 30, 1996; This application is a continuation-in-part of Ser. No. 08/506,896, filed Jul. 26, 1995, now U.S. Pat. No. 5,568,805 which is a continuation-in-part of Ser. No. 08/299,736, filed Sep. 1, 1994, U.S. Pat. No. 5,499,907.

FIELD OF THE INVENTION

This invention relates to printing heat sensitive, dye diffusion or sublimation inks generally, and is more specifically related to a method of printing liquid inks comprising these dyes onto an intermediate transfer sheet by means of an ink jet printer or other printer which uses liquid inks, and subsequently transferring the printed image from the intermediate sheet by the application of heat and pressure.

BACKGROUND OF THE INVENTION

Words and designs are frequently printed onto clothing and other textile materials, and other objects. The use of computer technology allows substantially instantaneous printing of images. For example, video cameras or scanning may be used to capture an image to a computer. The image may then be printed by any suitable printing means, including mechanical thermal printers, ink jet printers and laser printers. These printers will print multiple color images.

Color ink jet printers are in common use. Color ink jet printers use combinations of cyan, yellow and magenta inks or dyes to produce multiple color images. Most ink jet printers in common use employ inks which are in liquid form.

Heat activated, dye diffusion and sublimation ink solids change to a gas at about 400° F., and have a high affinity for polyester and other synthetic materials at the activation temperature, and a limited affinity for most other materials. Once the bonding from gassification and condensation takes place, the ink is permanently printed, and is resistant to change or fading caused by laundry products, heat or light.

Hale., U.S. Pat. Nos. 5,246,518, 5,248,363, 5,302,223, and 5,485,614 and Hale et al., U.S. Pat. No. 5,488,907, disclose the use of printers to produce an image on a medium or transfer sheet wherein the image is comprised of sublimation, dye diffusion or other heat activated inks. The ink is not activated during the printing of the medium or transfer sheet.

Problems are associated with liquid inks prepared from insoluble dye solids. The orifices or nozzles of most ink jet printers are not designed for the dispensing of dye solids contained within a liquid material. The orifices of these printers are typically 5–30 microns in diameter, and clogging of the orifice will occur when ink solids of large particle size or in high volume are transferred through the orifice.

Further, when the ink solids are placed into a liquid carrier, the ink solids tend to separate from the liquid over time and fall to the bottom of the ink container. The ink is typically packaged in a container at a manufacturing facility for subsequent mounting of the container within the ink jet printer, meaning that a substantial storage time for the ink composition exists prior to use. Separation of the liquid and solids comprising the ink formulation presents problems with regard to the mechanical operation of the printer and

the print quality achieved from use of the ink formulation. Agents which are included within the ink formulation to inhibit separation must also inhibit agglomeration of the solid dye particles, but the agents must not inhibit activation of the dye during the final transfer at elevated temperatures, by insulating the dye or reacting with the dye, or otherwise.

Accordingly, the production of stable liquid inks from dyes which are not water soluble is difficult to achieve without destroying or reducing the properties of the dye which are required for practicing the process of the invention. In the prior art, liquid inks have been produced from dyes that initially have properties suitable for practicing the process. However, the production of liquid inks from these dyes changes or masks the required properties, and therefore, the resulting inks cannot be satisfactorily used to practice the process. For example, additives which will inhibit the dye particles from settling out of the liquid carrier, or which will inhibit agglomeration, tend to insulate the dye particles, meaning that the energy required for sublimation, diffusion or activation of the dye is elevated to unacceptable levels for practicing the process. Other additives which are used in the prior art to produce a liquid ink from the solid dyes are reactive with the dye, and modify or eliminate required properties of the dyes. Other "side effects" of using these additives include undesired color modification or contamination, bonding with the intermediate substrate, or optical density on the final substrate which is inadequate.

While certain solvents will dissolve the dyes, the requirements of the process makes the use of these solvents impractical. Dye materials solubilized to the molecular level have a tendency to bond with fibers, both synthetic and natural. Accordingly, the dyes cannot be effectively transferred from a substrate used as an intermediate transfer sheet by the application of heat and pressure as required by the process of the present invention.

SUMMARY OF THE PRESENT INVENTION

This invention is a method of printing a liquid ink which is produced from sublimation, dye diffusion, or heat sensitive dyes. A printer which uses liquid ink, such as an ink jet printer, prints the image onto a medium, or intermediate substrate, which may be paper. The sublimation, dye diffusion, or heat sensitive dyes (hereinafter collectively referred to as "heat activated dyes") contained in the ink are not substantially sublimated or activated during the process of printing on to the medium. The image formed by the printed ink is transferred from the medium to a final substrate by the application of heat and pressure which sublimates or activate the ink. This thermal transfer step is achieved at low energy when compared to other sublimation or activation processes known and used in the art. One of the goals of the process requires that the thermal transfer occur by applying heat and pressure for no more than three and one-half minutes, and preferably less time. In the prior art, heat at the activation temperature is applied for up to thirty minutes. Accordingly, as used herein, a low energy transfer is a thermal transfer of the image from the intermediate sheet to the final substrate by applying a temperature which is not higher than 450° F., for no more than three and one-half minutes, with the resulting image, as deposited on the final substrate, having an optical density of 1.0 or greater, as measured by an X-Rite 418 densitometer in the density operation mode with background corrections.

The dyes, or perhaps pigments, which are suitable for practicing the invention are dyes which are capable of low energy transfer from the medium onto the final substrate to produce an image on the final substrate which is waterfast and colorfast. After transfer, the dyes are no longer substantially heat sensitive. Dyes which have these characteristics are found in various classifications of dyes, including disperse dyes, solvent dyes, basic dyes, acid dyes and vat dyes. However, none of the dyes which are currently available and which are suitable for producing a liquid ink for practicing the invention are soluble in water.

Accordingly, only a relatively small range of dyes in combination with a relatively small range of dispersing/emulsifying agents will produce a stable liquid ink which will allow the printing method to be practiced. Characteristics of acceptable dyes and dispersing/emulsifying agents which will produce a liquid ink with which to practice the printing method are disclosed herein.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a block diagram showing the printing process.

FIG. 2 illustrates an example of a design printed by a printer using the printing process.

FIG. 3 is a diagrammatic illustration showing exemplary elements of computer and printing systems which could be used to achieve the printing process.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

An image is input into a computer 4. The computer directs a printer 6 to print the image. Any means of forming the an image which may be printed from a computer may be used, including images generated by software. Available computer design graphic software may be used, or still photography may be used. The design may be photographic, graphic artistic, or simply letters or words. The use of cyan, yellow and magenta ink compositions allow the printer to print in full color or multi-color designs.

After the image is printed onto the medium, the image may be permanently transferred by thermal means. Most commonly, the design will be transferred onto a textile substrate, such as a shirt 8, although the image may be transferred onto other materials which act as a substrate, such as metal, ceramic, wood, or plastic. The design 3, which is printed onto the medium 9 without activating the ink, is placed against the object 8. A temperature which is sufficient to activate the dye is applied. This temperature will typically be around 400° F. This temperature is applied for a time sufficient to heat activate and transfer the ink solids in accordance with the requirements of the invention. A heat transfer machine 10 may be used to accomplish the transfer of the inks from the medium to the substrate. Activation, or sublimation, of the dye does not take place at the time of printing the image onto the medium, but occurs during the transfer from the medium to the substrate. The group of heat activated dyes from which dyes may be selected for use in the invention are dyes which substantially sublimate or activate at low energy to form an image which has an optical density value of no less than 1.0, and which is waterfast and colorfast. Each of the dyes which comprise this group will achieve an optical density of 1.25 or greater after activation, when optical density is measured by an X-Rite 418 densitometer in the density operation mode with background correction.

The invention requires the dyes to be transferred at low energy (as defined above) after the dyes are formulated into a liquid ink as described herein and printed onto the medium (the "acceptable dyes"). While a larger group of dyes can be sublimated at low energy, dyes which are not acceptable cannot be formulated into a liquid ink which retains the required properties. While most of the acceptable dyes are disperse dyes, certain other dyes which will perform according to the goals of the invention are included in the group of acceptable dyes.

In general, the acceptable dyes are not reactive, and do not have strong polar function groups, such as sulfonate or carboxyl groups. Reacting the dyes with chemical agents added to the formulation in order to form a liquid ink, as is sometimes done in the prior art, tends to inhibit the activation of the dyes at low energy, which is contrary to the present invention. The acceptable dyes have a molecular weight which is less than 600, and is preferably within a range of 200–400. Most of the acceptable dyes are disperse dyes but certain solvent dyes, vat dyes, basic or cationic dyes (such as carbinol base dyes or anthraquinone type dyes having a quarternary amine), acid dyes, direct dyes, mordant dyes and oxidizing colors also fall within the group of acceptable dyes.

The ink formulation prepared according to the invention is a liquid. Dye solids of small paricle size are dipsersed in a liquid carrier, and one or more agents are used to maintain what may be called, according to various definitions, a collodial, dispersion or emulsion system. The term "emulsion" is used herein to describe the system, even though the system could, in some forms, be called a colloid or a dispersion.

The heat activated solid dye particles are of small size. It is preferred that the individual solid dye particles have no dimension which is greater than 0.5 microns.

The solid dye particles are dispersed into the liquid carrier. The dispersion is normally achieved by the introduction of a dispersing agent, although mechanical or other physical means could be used. An emulsifying agent is introduced to prevent coagulation or coalescense of the individual dye particles and to stabilize the system.

As set forth in the examples, a single agent may be used as a dispersing and emulsifying agent. Multiple agents may be used in accordance with the goals of the invention. The agent or agents stabilize the system, so that the system remains sufficiently homogenous over time to allow successful printing and transfer of the dye according to the method of the invention. Further, the agent shields the individual particles from the adverse effects of the storage, transportation and printer environments, such as heat, cold and light. While the agent shields the dye particles while they are in the liquid system, it does not inhibit low energy transfer of the dyes in the form of the printed image.

The agents used to disperse and or emulsify the dye particles include various dispersant materials, surfactants (including cationic, anionic, amphoteric, and nonionic suffactants) and polymeric surfactants. Polymeric materials with dispersing ability, but which are not surfactants, can also be used. Either synthetic or natural materials can be used. The dispersing/emulsifying agents each have a molecular weight which is less than 100,000, and preferably less than 10,000. Thermal stability of the agents is essential to prevent decomposition and/or chemical reaction between the agents and the other components in the systems.

As with the dye, to accomplish the printing method of the invention, the agent(s) do not have active function groups which will react or crosslink with the medium, or which will react or crosslink with the dye or pigment in the system, since such reactions or linkages inhibit the required properties of the dye at the time of activation. The agent(s) must form the emulsion from the finely divided dye particle and the liquid carrier, but must not materially insulate or otherwise materially inhibit the activation of the dye at the time of final transfer.

Agents having the required properties when used with some or all of the acceptable dyes include Lignosulfonate products such as Marasperse 52CP (Lignotech), Lignosol FTA (Lignotech), Lignosol SFX-65 (Lignotech), Maprasperse CBA-1 (Lignotech), Temsperse S002 (Temfibre, Inc.) Stepsperse DF series (Stephan Co.), and Weschem NA-4 (Wesco Technologies, LTD), Kraft lignin products such as Diwatex XP (Lignotech), and Reax 85 (Westvaco), and oxylignin products such as Marasperse CBOS-6 and Vanisperse CB.

Other examples of emulsifying agents and dispersants are alkylaryl polyether alcohol nonionic surfactants, such as Triton X series (Octylphenoxypolyethoxyethanol); alkylamine ethoxylates nonionic surfactants such as Triton FW series, Triton CF-10, and Tergitol (Union Carbide Chemicals); polysorbate products such as Tween (ICI Chemicals and Polymers); polyalkylene and polyalkylene modified surfactants, such as Silwet surfactants (polydimethylsiloxane copolymers) and CoatOSil surfactants from OSI Specialties; alcohol alkoxylates nonionic surfactants, such as Renex, BRIJ, and Ukanil; Sorbitan ester products such as Span and Arlacel; alkoxylated esters/PEG products, such as Tween, Atlas, Myrj and Cirrasol surfactants from ICI Chemicals and Polymers; unsaturated alcohol products such as surfynol series surfactants from Air Products Co., alkyl phosphoric acid ester surfactant products, such as amyl acid phosphate, Chemphos TR-421; alkyl amine oxide such as Chemoxide series from Chemron Corporation; anionic sarcosinate surfactants such as Hamposyl series from Hampshire Chemical corporation; glycerol esters or polyglycol ester nonionic surfactants such Hodag series from Calgene Chemical, Alphenate (Henkel-Nopco), Solegal W (Hoechst AG), Emultex (Auschem SPA); and polyethylene glycol ether surfactants such as Newkalgen from Takemoto Oil and Fat Co.

Multiple agents may be used in combination to improve the emulsification of the system and to stabilize the system, as long as the agents are not reactive and do not cause precipitation or otherwise negatively impact upon the emulsification process or the transfer process.

Organic solvents, cosolvents, and/or humectants can also be used as additional additives. Aliphatic and/or aromatic alcohols (thioalcohols), alkoxylated alcohols (thioalcohols), halogenated alcohols (thioalcohols) and carboxylated alcohols (thioalcohols), including mono-alcohol (thioalcohol), diol (thiodialcohol), triol (thiotrialcohol) and polyol (thiopolyalcohol), aminoxide, diamine, triamine material, may be used to improve dye dispersibility, solubility and/or stability in the final ink composition. Examples of solvent materials are diethylene glycol, DMSO and dipropylene glycol.

Other additives can also be introduced into the ink, such as surfactants, corrosion control agents, foam control agents, antioxidants, radiation stabilizers, thermal stabilizers, flame retarding agents, pH control agents, viscosity control agents, or surface (interfacial) tension control agents can be added during or after the emulsification process. Other materials, including dispersants, emulsifying agents, and stabilizers, may be included in the formulation by means of methods known in the art.

An example of a liquid ink composition usable in an ink jet printer is as follows:

Material	Weight %
heat sensitive dye(s)	0.05–20%
dispersant/emulsifying agent	0.05–30%
solvent(s)/cosolvent(s)	0–45%
additive(s)	0–15%
water	40–98%
Total	100%

EXAMPLES

Example 1

30 grams of finely divided Spirit Blue Base (CAS# 68389-46-8) is mixed with 15 grams of Ultrazine NA (Lignotech, USA) and 500 grams of de-ionized water. An ultrasonic pulverizer is used to disperse the dye into the aqueous phase for approximately 30 minutes. Two (2.0) grams of Solsperse 27000 (Zenica Colors, USA) is added into the mixture, which is pulverized for another 10 minutes to achieve a stable emulsion. The mixture is filtered to remove particles larger than 0.25 microns. The printing ink for use in the ink jet printer is formulated from the emulsion as follows:

Material	Weight %
Emulsion	87.0
Glycol	4.0
1-methoxy-2-propanol	7.0
Ammonyx LO (1)	2.0
Total	100%

(1). Stepan Co

The resulting ink is printed by the HP 560 Deskjet printer onto plain copy paper in a dark cyan color, and is transferred from the paper medium or receiver onto a polyester fabric substrate by thermal transfer at 400° F. temperature with 40 lb. pressure applied for 20 seconds. The image as applied to the polyester fabric substrate has an optical density value of 1.4–1.5 for the cyan color as read by an X-Rite 418 densitometer.

Example 2

Twenty (20) grams of Disperse Yellow 9 (CAS# 6373-73-5) is mixed with four (4) grams of Sulfynol 131 (Air Products) and 5.0 grams of glycerol (CAS# 56-81-5) and 480 grams of de-ionized water. The pulverizer is used to disperse the dye into the aqueous phase for approximately 25 minutes. One (1.0) gram of Sulfynol 104 E (Air Products) is added to the mixture and pulverized for another 10 minutes to produce an emulsion. The mixture is filtered to remove particles larger than 0.25 microns. The liquid ink for use in the ink jet printer is formulated as follows:

Material	Weight %
Emulsion	78.5
Diethylene Glycol	8.0
Thiodiethanol	5.0
Sulfynol 465	4.0

-continued

Material	Weight %
1-2-Propandiol	4.0
DEA	0.5
Total	100%

The resulting liquid ink is printed by a Canon Bubble Jet 4100 printer onto plain copy paper. The printed image is thermally transferred from the paper medium to a polyester textile substrate at 400° F., while applying 40 lb. pressure for 20 seconds. An intense yellow color having an optical density of 1.4, as measured by an X-Rite 418 densitometer with background correction, appears on the substrate.

Example 3

Twenty-five (25) grams of finely divided Solvent Red 52 (CAS# 81-39-0), is mixed with twenty-two (22) grams of Transferin® N-38 (Boehme Filatex, Inc.) and one hundred and fifty (150) grams of de-ionized water. An ultrasonic pulverizer is used to finely divide the dye and to disperse and micronize the solid dye particles into the aqueous phase by operating the pulverizer for approximately Forty-five (45) minutes. Five (5) grams of Tergitol™ 15-S-15 (Union Carbide, USA), Ten (10) grams of 1,4-butanediol, and two hundred and twenty (220) grams of de-ionized water are then added into the dispersion and pulverized for an additional ten (10) minutes. The dispersion is then filtered to remove solid particulate having a dimension which is larger than 0.25 microns. A liquid ink is formulated using the homogenized emulsion as follows:

Component	Weight %
Emulsion	85.0
Tergitol™ 15-S-9[1]	3.997
1-pyrrolidinone	2.0
1-ethoxy-2-propanol	6.0
IPA	3.0
Kathon ® PFM[2]	0.003
Total	100

[1]Union-Carbide, USA
[2]Rohm & Haas Company

The liquid ink is then printed by an Epson Stylus Color Pro or Epson Stylus Color IIs piezo electric ink jet printer to form an image on plain copy paper. The image is transferred from the paper to a polyester fabric substrate by the application of pressure and heat at a temperature of 400° F. for 25 seconds. The image as transferred has an optical density of 1.45 for the magenta color, as measured by an X-Rite 418 densitometer with background correction.

What is claimed is:

1. A method of printing dye by means of a printer which uses liquid ink, comprising the steps of:

a. preparing a liquid ink formulation comprising a heat activated dye, a liquid carrier, and at least one agent which disperses and emulsifies said heat activated dye, wherein said heat activated dye activates upon the application of heat at or greater than the activation temperature for 210 seconds or less, and wherein said at least one agent does not substantially increase the activation energy required to activate said heat activated dye after said heat activated dye is printed onto a medium;

b. supplying a printer with said liquid ink formulation;

c. printing said liquid ink formulation by means of said printer to form an image on a medium without materially activating the heat activated dye; and

d. transferring said image from said medium to a substrate on which the image is to appear by the application of heat and pressure at a temperature which is sufficient to activate the heat activated dye for 210 seconds or less, so as to cause the heat activated dye to transfer on to said substrate.

2. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, as described in claim 1, wherein said heat activated dye is not reactive with said at least one agent and said liquid carrier.

3. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, as described in claim 1, wherein said heat activated dye is substantially insoluble in said liquid carrier.

4. A method of printing using heat activated dye solids by means of a printer which uses liquid ink as described in claim 1, wherein said at least one agent shields said heat activated dye but does not substantially increase the activation energy required to activate said heat activated dye after said heat activated dye is printed on to said medium.

5. A method of printing using heat activated dye solids by means of a printer which uses liquid ink as described in claim 1, wherein said heat activated dye has a molecular weight in the range of 200 to 400.

6. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, as described in claim 1, wherein said heat activated dye is not reactive with said at least one agent and said liquid carrier.

7. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, as described in claim 1, wherein said at least one agent is not reactive with said heat activated dye and does not react with said medium and does not link with said medium.

8. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, as described in claim 1, wherein said heat activated dye is comprised of individual particles of said heat activated dye, and wherein said individual particles of said heat activated dye do not have a dimension which is greater than 0.5 microns.

9. A method of printing using heat activated dye solids by means of a printer which uses liquid ink according to the method of claim 1, further comprising the steps of: preparing a second liquid ink formulation comprising a heat activated dye of a second color, a liquid carrier, and at least one agent which disperses and emulsifies said heat activated dye of a second color, wherein said heat activated dye of a second color activates upon the application of heat at or greater than the activation temperature for 210 seconds or less, and wherein said at least one agent does not substantially increase the activation energy required to activate said heat activated dye of a second color after said heat activated dye of a second color is printed onto a medium; preparing a third liquid ink formulation comprising a heat activated dye of a third color, a liquid carrier, and at least one agent which disperses and emulsifies said heat activated dye of a third color, wherein said heat activated dye of a third color activates upon the application of heat at or greater than the activation temperature for 210 seconds or less, and wherein said at least one agent does not substantially increase the activation energy required to activate said heat activated dye of a third color after said heat activated dye of a third color is printed onto a medium; supplying said printer with said second liquid ink formulation and said third liquid ink

formulation; printing said second liquid ink formulation and said third liquid ink formulation by means of said printer along with said liquid ink formulation to form said image in multiple colors on said medium without materially activating said heat activated dye, said heat activated dye of a second color or said heat activated dye of a third color.

10. A method of printing a design by means of a computer driven printer using heat activated dye solids, comprising the steps of:

a. preparing an ink formulation comprising a heat activated dye, a liquid carrier, and at least one agent which disperses said heat activated dye in said liquid carrier and forms an emulsion from said heat activated dye and said liquid carrier, wherein said heat activated dye activates at an activation energy of not greater than 450° F. applied for not more than 210 seconds, and wherein said at least one agent does not substantially increase the activation energy required to activate said heat activated dye after said heat activated dye is printed on to a medium, and wherein said heat activated dye is a solid and is substantially insoluble in said liquid carrier;

b. supplying a printer with said liquid ink formulation;

c. printing said liquid ink formulation by means of said printer to form an image on a medium without materially activating the heat activated dye; and

d. transferring said image by thermal means from said medium to a substrate on which the image is to appear at a temperature of not greater than 450° F. applied with pressure for not more than 210 seconds, so as to cause the heat activated dye to transfer onto said substrate.

11. A method of printing using heat activated dye solids by means of a printer which uses liquid ink as described in claim 10, wherein said at least one agent shields said heat activated dye but does not substantially increase the activation energy required to activate said heat activated dye after said heat activated dye is printed on to said medium.

12. A method of printing using heat activated dye solids by means of a printer which uses liquid ink as described in claim 10, wherein said heat activated dye has a molecular weight in the range of 200 to 400.

13. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, as described in claim 10, wherein said heat activated dye is not reactive with said at least one agent and said liquid carrier.

14. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, as described in claim 10, wherein said at least one agent is not reactive with said heat activated dye and does not react with said medium and does not link with said medium.

15. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, as described in claim 10, wherein said heat activated dye is comprised of individual particles of said heat activated dye, and wherein said individual particles of said heat activated dye do not have a dimension which is greater than 0.5 microns.

16. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, according to the method of claim 10, further comprising the steps of: preparing a second liquid ink formulation comprising a heat activated dye of a second color, a liquid carrier, and at least one agent which forms an emulsion from said heat activated dye of a second color and said liquid carrier, wherein said heat activated dye of a second color activates at an activation energy of not greater than 450° F. applied for not more than 210 seconds, and wherein said at least one agent does not substantially increase the activation energy required to activate said heat activated dye of a second color after said heat activated dye of a second color is printed on to a medium, and wherein said heat activated dye of a second color is a solid and is substantially insoluble in said liquid carrier; preparing a third liquid ink formulation comprising a heat activated dye of a third color, a liquid carrier, and at least one agent which forms an emulsion from said heat activated dye of a third color and said liquid carrier, wherein said heat activated dye of a third color activates at an activation energy of not greater than 450° F. applied for not more than 210 seconds, and wherein said at least one agent does not substantially increase the activation energy required to activate said heat activated dye of a third color after said heat activated dye of a third color is printed on to a medium, and wherein said heat activated dye of a third color is a solid and is substantially insoluble in said liquid carrier; supplying said printer with said second liquid ink formulation and said third liquid ink formulation; printing said second liquid ink formulation and said third liquid ink formulation by means of said printer along with said liquid ink formulation to form said image in multiple colors on said medium without materially activating said heat activated dye, said heat activated dye of a second color or said heat activated dye of a third color.

17. A method of printing a design by means of a computer driven printer using heat activated dye solids, comprising the steps of:

a. preparing an ink formulation comprising a heat activated dye, a liquid carrier, and at least one agent which disperses said heat activated dye in said liquid carrier and forms an emulsion from said heat activated dye and said liquid carrier, wherein said heat activated dye activates at an activation energy of not greater than 450° F. applied for not more than 210 seconds, and wherein said at least one agent does not substantially increase the activation energy required to activate said heat activated dye after said heat activated dye is printed onto a medium, and wherein said heat activated dye is a solid and is substantially insoluble in said liquid carrier;

b. supplying a printer with said ink formulation;

c. printing said liquid ink formulation by means of said printer to form an image on a medium without materially activating the heat activated dye; and

d. transferring said image by thermal means from said medium to a substrate on which the image is to appear at a temperature which is not greater than 450° F. applied with pressure for not more than 210 seconds, so as to cause the heat activated dye to transfer onto said substrate in the form of said image, wherein said image as transferred on to the substrate has an optical density of 1.0 or greater, as measured by an X-Rite 418 densitometer in the density operation mode with background corrections.

18. A method of printing using heat activated dye solids by means of a printer which uses liquid ink as described in claim 17, wherein said at least one agent shields said heat activated dye but does not substantially increase the activation energy required to activate said heat activated dye after said heat activated dye is printed on to said medium.

19. A method of printing using heat activated dye solids by means of a printer which uses liquid ink as described in claim 17, wherein said heat activated dye has a molecular weight in the range of 200 to 400.

20. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, as described in claim 17, wherein said heat activated dye is not reactive with said at least one agent and said liquid carrier.

21. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, as described in claim 17, wherein said at least one agent is not reactive with said heat activated dye and does not react with said medium and does not link with said medium.

22. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, as described in claim 17, wherein said heat activated dye is comprised of individual particles of said heat activated dye, and wherein said individual particles of said heat activated dye do not have a dimension which is greater than 0.5 microns.

23. A method of printing using heat activated dye solids by means of a printer which uses liquid ink, according to the method of claim 17, further comprising the steps of: preparing a second liquid ink formulation comprising a heat activated dye of a second color, a liquid carrier, and at least one agent which forms an emulsion from said heat activated dye of a second color and said liquid carrier, wherein said heat activated dye of a second color activates at an activation energy of not greater than 450° F. applied for not more than 210 seconds, and wherein said at least one agent does not substantially increase the activation energy required to activate said heat activated dye of a second color after said heat activated dye of a second color is printed on to a medium, and wherein said heat activated dye of a second color is a solid and is substantially insoluble in said liquid carrier; preparing a third liquid ink formulation comprising a heat activated dye of a third color, a liquid carrier, and at least one agent which forms an emulsion from said heat activated dye of a third color and said liquid carrier, wherein said heat activated dye of a third color activates at an activation energy of not greater than 450° F. applied for not more than 210 seconds, and wherein said at least one agent does not substantially increase the activation energy required to activate said heat activated dye of a third color after said heat activated dye of a third color is printed on to a medium, and wherein said heat activated dye of a third color is a solid and is substantially insoluble in said liquid carrier; supplying said printer with said second liquid ink formulation and said third liquid ink formulation; printing said second liquid ink formulation and said third liquid ink formulation by means of said printer along with said liquid ink formulation to form said image in multiple colors on said medium without materially activating said heat activated dye, said heat activated dye of a second color or said heat activated dye of a third color.

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Hale et al.

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[45] Date of Patent: Mar. 31, 1998

[54] **PERMANENT HEAT ACTIVATED TRANSFER PRINTING PROCESS AND COMPOSITION**

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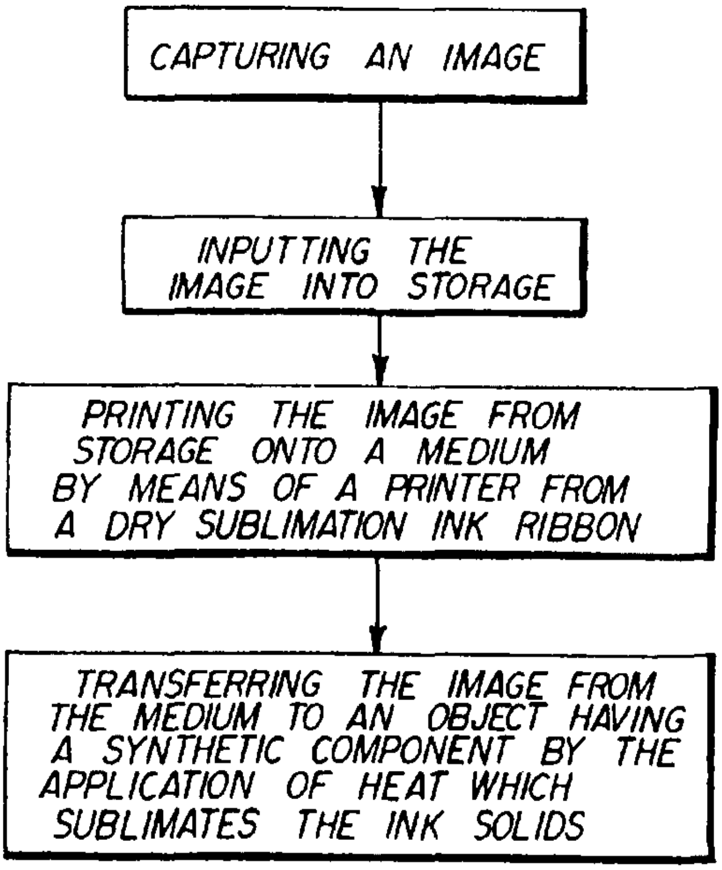
[57] **ABSTRACT**

An image is printed on a medium by means of a computer driven printer using an ink composition comprising heat activated dye solids, without activating the dye solids during the process of printing onto the medium. The image is transferred from the medium to the object on which the image is to permanently appear by applying sufficient heat and pressure to the medium to activate the dye and transfer the image to the object. The liquid form of the ink composition uses a liquid carrier and an emulsifying enforcing agent which has an affinity for the dye. The emulsifying enforcing agent shields the heat activated dye both prior to, and during, the printing process.

6 Claims, 2 Drawing Sheets



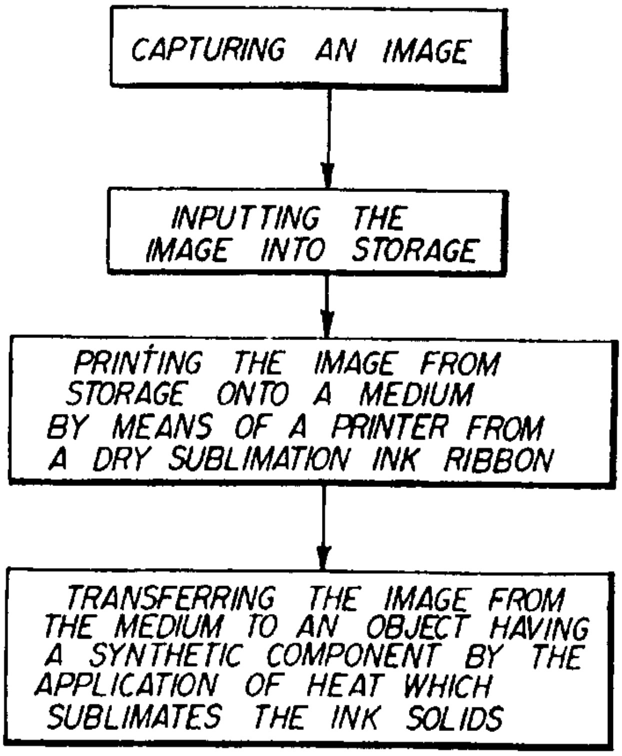

CAPTURING AN IMAGE
INPUTTING THE IMAGE INTO STORAGE
PRINTING THE IMAGE FROM STORAGE ONTO A MEDIUM BY MEANS OF A PRINTER FROM A DRY SUBLIMATION INK RIBBON
TRANSFERRING THE IMAGE FROM THE MEDIUM TO AN OBJECT HAVING A SYNTHETIC COMPONENT BY THE APPLICATION OF HEAT WHICH SUBLIMATES THE INK SOLIDS

FIG 1

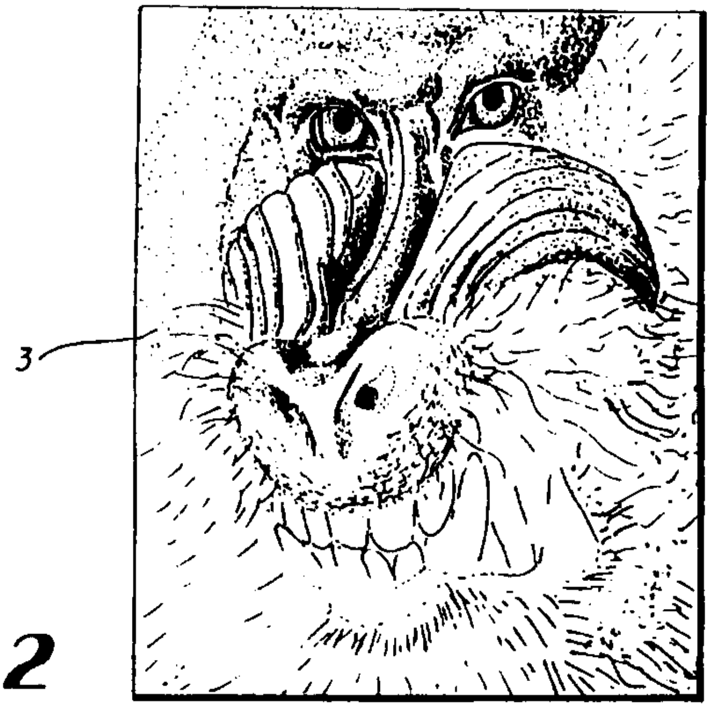

3

FIG 2

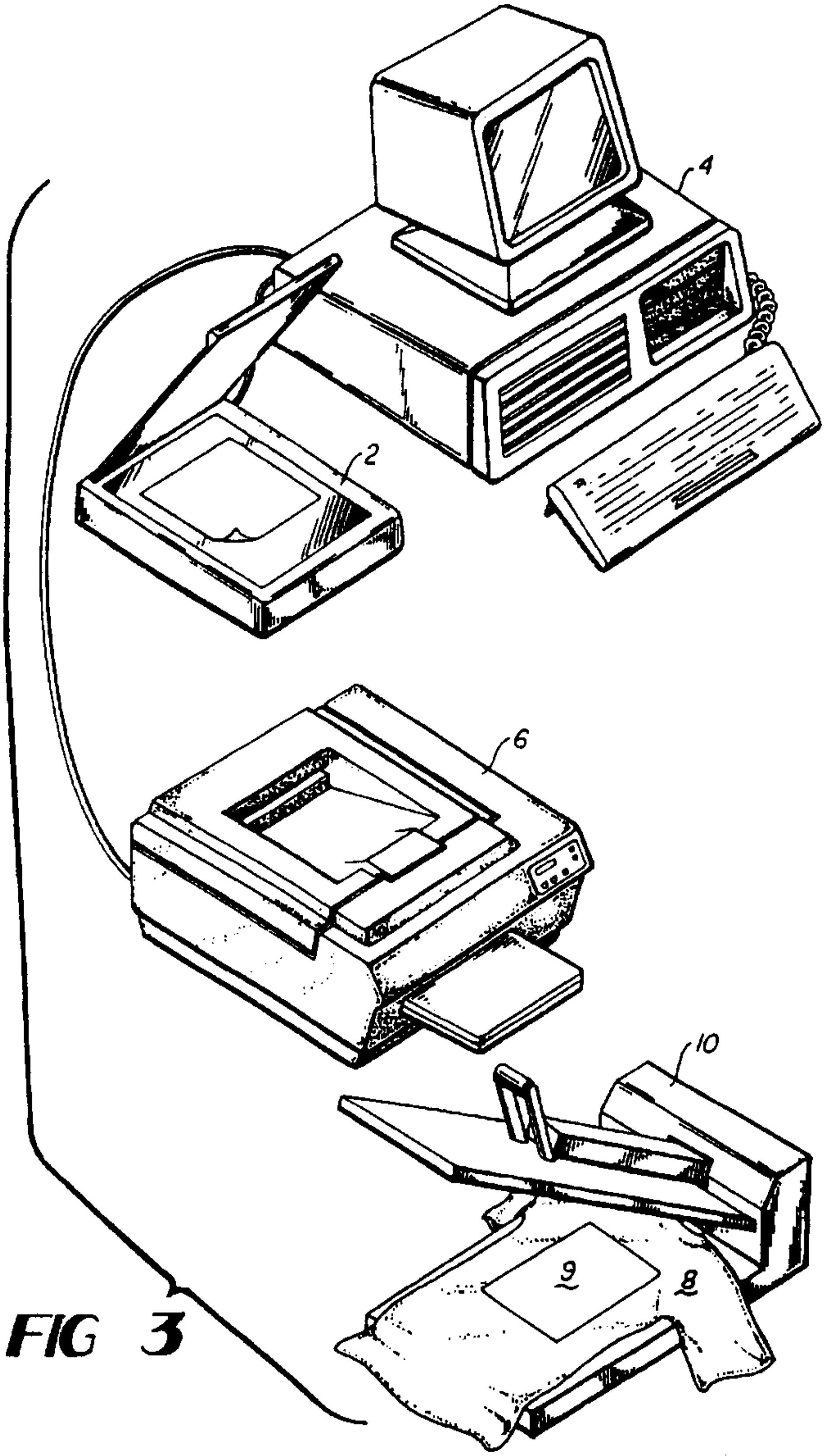


FIG 3

PERMANENT HEAT ACTIVATED TRANSFER PRINTING PROCESS AND COMPOSITION

This application is a continuation-in-part of application Ser. No. 08/299,736 filed Sep. 1, 1994.

FIELD OF THE INVENTION

This invention relates to printing generally, and is more specifically directed to a method of printing heat activated ink by means of an ink jet printer onto paper or other printable substrate as a medium, and subsequently heat activating the ink, thereby transferring the design formed by the ink from the medium to a substrate on which the design is to permanently appear.

BACKGROUND OF THE INVENTION

Words and designs are frequently printed onto clothing and other textile materials, and other objects. Common means of applying such designs to objects include the use of silk screens, and mechanically bonded thermal transfers.

The use of computer technology allows substantially instantaneous printing of images. For example, video cameras or scanning may be used to capture an image to a computer. The image may then be printed by any suitable printing means, including mechanical thermal printers, ink jet printers and laser printers. These printers will print in multiple colors.

Color ink jet printers are in common use. Color ink jet printers use combinations of cyan, yellow and magenta inks or dyes to produce multi-color images.

The primary types of ink jet printers currently in use fall into three categories: phase change, free flow, and bubble jet. The inks or dyes used in phase change ink jet printing are contained in a solid compound which changes state by the application of heat to liquify the solid, whereupon the ink composition is printed. Free flow and bubble jet printers use liquid inks, although the actual printing process of free flow ink jet printers differs from bubble jet printers.

Heat activated transfer ink solids change to a gas at about 400° F., and have a high affinity for polyester at the activation temperature and a limited affinity for most other materials. Once the gassification bonding takes place, the ink is permanently printed and highly resistant to change or fading caused by laundry products.

Hale, U.S. Pat. No. 5,246,518, 5,248,363 and 5,302,223 disclose the use of thermal printers to produce an image on a medium or transfer sheet wherein the image is comprised of sublimation or other heat activated inks. The method described in Hale does not activate the ink during the printing of the medium or transfer sheet.

The process of printing heat sensitive ink solids such as sublimation inks by means of a phase change ink jet printer is similar to the process described in Hale, U.S. Pat. No. 5,246,518, 5,248,363 and 5,302,223. The use of heat by all ink jet printers presents the problem recognized in the Hale patents of printing heat activated inks in a non activated form by means of such printers, since the ink is exposed to high temperatures by the printer. Bubble jet printers, for example, heat the ink during the printing process to around the boiling point of the ink solvent, which is typically water. Free flow ink jet printers use heat to form pressure which transports the ink during the printing process.

The use of liquid inks, as required by free flow and bubble jet printers, presents a new set of problems when trying to print ink solids. The orifices or nozzles of free flow and

bubble jet printers are not designed for the dispensing of solids contained within a liquid material. The orifices of these printers are typically 5–10 microns in diameter, and clogging of the orifice will occur when ink solids of large particle size or in high volume are transferred through the orifice.

Further, when the ink solids are placed into the liquid, the ink solids tend to separate from the liquid over time and fall to the bottom of the ink container. The ink composition is typically sealed in a container at a manufacturing facility, for subsequent mounting of the container within the ink jet printer, meaning that a substantial storage time for the ink composition exists prior to use. Separation of the liquid and solids within the ink formulation presents problems with regard to the mechanical operation of the printer and the print quality achieved from use of the ink formulation. Materials which inhibit separation must also inhibit agglomeration of the solid dye particles, while allowing, and not preventing due to insulation or otherwise, activation of the ink or dye during the final printing at elevated temperatures.

SUMMARY OF THE PRESENT INVENTION

The present invention is a method of printing heat activated ink solids in a non activated form onto a medium in a desired image by means of an ink jet printer, for subsequent transfer of the image from the medium by heat activation of the ink solids. The invention includes ink or dye compositions comprising heat activated ink or dye solids for use with the method. The ink compositions presented include solid compositions at ambient temperature for use with phase change ink jet printers, and emulsions or colloids for use with free flow and bubble jet printers.

The ink solids are transferred in the desired design by means of a printer onto a substrate, which acts as a medium. The substrate may be paper, or it may be other material which will facilitate and withstand the transfer temperature, and which facilitates bonding of the ink layer to the substrate.

The ink jet printer incorporates a thermal process, but the ink solids of the invention do not activate at the operational temperatures of the printer. Heat activation of the ink solids does not take place at the time of printing of the image by the printer, but rather, takes place at the time of the transfer of the image from the medium to the substrate on which the image is permanently applied. The non activated ink solids produce a printed image on the medium which is recognizable, but the colors are dull and are not acceptable for most applications.

Sufficient temperature is then applied to the image to transfer the image from the medium to the substrate on which the image is to permanently appear. The heat activates, or sublimates, the ink solids during this transfer from the medium to the substrate. The image is then permanently bonded to the substrate. The permanent image is sharp, with vivid colors forming the image.

When the ink formulation prepared according to the invention is a liquid, finely divided dye solids are present in a liquid carrier, in a collodial or emulsion form. An emulsifying enforcing agent, which has characteristics of a surfactant, surrounds and shields the dye particles to prevent undesired activation at low heat and to prevent agglomeration of the dye particles. However, the emulsifying enforcing agent allows activation of the dye at higher temperatures.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a block diagram showing the printing process.

FIG. 2 illustrates an example of a design printed by a printer using the printing process.

FIG. 3 is a diagrammatic illustration showing exemplary elements of computer and printing systems which could be used to achieve the printing process.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In the preferred embodiment, a video camera or scanning device 2 is used to capture an image 3. The image is then input into a computer 4. The computer directs a printer 6 to print the image. Any means of forming the an image which may be printed from a computer may be used, including images generated by software. Available computer design graphic software may be used, or still photography may be used. The design may be photographic, graphic artistic, or simply letters or words. The use of cyan, yellow and magenta ink compositions allow the printer to print in full color or multi-color designs.

In the present invention, heat activated ink solids are used, and are transferred to a medium by the printer without activating the ink solids. The heat activated ink solids are transferred onto the medium by the printer.

Virtually any material may be used as a medium which can be printed upon by a printer, and which will withstand the heat activated transfer temperature of approximately 400° F., as described herein. This medium may be any paper commonly used with color ink jet printers, however, standard bond paper may be used, or even a sheet of metal, if the metal can be handled by the printer.

Once the image is printed onto the medium, the image may be permanently transferred onto the substrate presently, or at a later time. Most commonly, the design will be transferred onto a textile substrate, such as a shirt 8, although the image may be transferred onto other materials which act as a substrate, such as metal, ceramic, wood, or plastic. The design 3, which is printed onto the medium 9 without activating the ink, is placed against the object 8. A temperature which is sufficient to activate the ink solids is then applied. This temperature will typically be around 400° F. This temperature is applied for a time sufficient to heat activate and transfer the ink solids. A heat transfer machine 10 may be used to accomplish the transfer of the inks from the medium to the substrate. Activation, or sublimation, does not take place at the time of printing the image onto the medium, even though heat may be used to accomplish the printing of the image onto the medium, but occurs during the transfer from the medium to the substrate.

Phase change ink jet printers use an ink composition which is solid at ambient temperature. The ink composition may be in a solid stick form. This "ink stick" comprises heat activated inks, and a phase change material, or transfer vehicle, which will liquify upon the application of heat to the ink composition. A polymer binder and additives may be added to the ink composition. The additives may be used to control melting, flow, drying, corrosion and other variables. The composition is changed from solid to liquid by melting the ink stick in a controlled fashion, to apply the ink solids to the medium, and achieve printing. The melted ink composition is contained in a liquid form in a reservoir at the necessary elevated temperature to maintain the ink composition in liquid form. The liquified ink composition is then taken from the reservoir and printed on demand. The ink composition may be present in the printer in three or more colors, such as cyan, yellow and magenta, and applied by the printer in combination to achieve multiple color or full color printing.

The transfer vehicle may be a wax or wax like material, such as a certain polymers having a low molecular weight

and low melting point. Since wax and wax like materials in liquid form tend to have an affinity for paper, the transfer vehicle will readily bond with the paper medium, holding the ink solids to the medium, until the ink solids are released by the application of heat which is sufficient to activate and transfer the ink solids.

The formulation for an ink composition used with a phase change ink jet printer is as follows:

Material	Weight %
Heat Activated Dye/Ink Solid	5–30
Transfer Vehicle	20–70
Emulsifying Enforcing Agent	1–20
Binder	0–30
Plasticizer	0–15
Foam Control Agent	0–10
Viscosity Control Agent	0–10
Surface Tension Control Agent	0–10
Diffusion Control Agent	0–10
Flow Control Agent	0–15
Corrosion Control Agent	0–10
Antioxidant	0–5
TOTAL	100%

The heat sensitive or heat activated dye or ink solid may be a sublimation ink which is finely divided. It is preferred that the solid particle have a diameter which is no larger than 0.1 micron. The transfer material is a wax or wax like material which liquifies at a temperature of 70 to 120 degrees C. to allow printing of the ink onto the medium.

The emulsifying enforcing agent acts as a dispersing agent through which the ink solids are distributed. The emulsifying enforcing agent may be one or more polymers or surfactants, which should be anionic. The binder may be a polymer which strengthens the ink stick when the ink stick is in solid form. The plasticizer increases the solubility of the ink for formulation of the ink stick. The foam control agent and viscosity control agent aid in formulating the ink stick.

The surface tension control agent may be a surfactant. This agent aids in printing of the ink formulation. The diffusion control agent helps control the diffusion of the ink as it is applied to the medium. The flow control agent helps control the melting temperature and rate of the ink during the printing process.

FORMULATION EXAMPLE #1:
Cyan phase-change ink-Jet Ink Formula:

Material	Weight %
SUBLAPRINT ® Blue 70014[1]	10.0
POLYWAX ® PE500[2]	10.0
EXXON FN ® 3505[3]	58.0
DISPER BYK ® 182[4]	0.5
VINNAPAS ® B1.5[5]	1.5
PICCOLASTIC ® A25[6]	10.0
POLYGARD ®[7]	5.0
Dibutyl Phthalate	5.0
Total:	100.0

[1]Keystone Aniline Corporation
[2]Petrolite Corp.
[3]Exxon Chemical Co.
[4]BYK-Chemie, USA
[5]Wacker Chemicals (USA)
[6]Hercules Inc.
[7]Uniroyal Chemical Co.

Sublaprint® is a heat sensitive or sublimation, dye.
Polywax® is a synthetic polyethylene wax.
Exxon FN® is a hydrocarbon wax.

Disperbyk® is a co polymer with pigment affined groups.
Vinnapas® is a vinylacetate homo-co-and-ter-polymeres.
Pi ccolastic® is a polysterene resin.

Polywax PE500 is a transfer vehicle. This transfer vehicle is a wax-like polymer material. Exxon FN 3505 is a hydrocarbon wax used as part of the transfer vehicle. Other waxes or combinations could be used as the transfer vehicle depending on the printer, its operation temperature, the ink to be printed and the medium to be printed.

DisperByk 182 is an emulsifying enforcing agent. An anionic emulsifying enforcing agent should be used. DispersByk is a polymer type surfactant. Vinnapas B1.5 and Piccolastic are used as binders. Polygard is an antioxidant which is used for corrosion control. Dibutyl phthalate is a plasticizer.

Free flow ink jet printers and bubble jet ink jet printers use inks which are in a liquid form. Free flow ink jet printers dispense ink through an orifice in an ink container. The printer commands and controls the flow of ink through the orifice to print in the desired manner.

Bubble jet printers also use inks which are in a liquid form, and which are held in a container. Bubble jet printers use a different orifice or nozzle system than free flow printers. A channel and heating system is used to form a bubble. The formation of the bubble is controlled by the printer by the application of heat to the ink to print as desired.

The heat activated inks or dyes are solid particles. Free flow and bubble jet printers are designed to be used with liquid inks, but not with inks having solid particulate within the liquid. The presence of solid material clogs the orifice or nozzle of the printer. Further, liquid ink compositions into which a solid particulate is placed or dissolved are not homogenous over time. The solid ink particles in the mixture settle from the liquid toward the bottom of the ink container. This settling increases the clogging of the orifice. Further, print quality is affected if the ink is not consistent.

The liquid ink composition of the present invention is an emulsion comprised of finely divided heat activated ink solids which are placed in an emulsion by means of an emulsifying enforcing agent which is present in a solvent. Humectants, corrosion inhibitors, surfactants, and anti-foaming agents may also be included in the composition.

The formulation of an emulsion comprising heat activated ink solids which is used with ink jet printers requiring liquid inks is as follows:

Material	Weight %
Heat Activated Dye/Ink Solid	5–30
Emulsifying Enforcing Agent	1–20
Binder	0–30
Humectants	0–40
Foam Control Agent	0–10
Fungicide	0–2
Viscosity Control Agent	0–10
Surface Tension Control Agent	0–10
Diffusion Control Agent	0–10
Flow Control Agent	0–15
Evaporation Control Agent	0–20
Corrosion Control Agent	0–10
Cosolvent	0–30
Solvent	30–90
TOTAL	100%

The heat activated dye or ink solid is finely divided and placed into an emulsion by means of the emulsifying agent and the solvent, which may be water. The remaining agents

may be added to facilitate formulation, storage and/or printing of the liquid ink composition.

FORMULATION EXAMPLE #2-
Yellow Ink-Jet Formula:

Material	Weight %
BIFIXAN ® Yellow 3FE[8]	2.0
Dipropylene Glycol	4.5
DMSO	1.5
COBRATEC ®	0.45
NaOH (10N)	3.0
Distilled H_2O	88.55
Total:	100

[8]BASF Corporation
[9]FMC Specialties Group

Bifixan® is a stabilizer resin.
Cobratec® is a heat sensitive, or sublimation, dye.
Lignosol® is a lignosulfonate.
Intratherm® is a heat sensitive, or sublimation, dye.
Deefo® is a organosiloxane polymer.

Formulation Example 2 comprises a heat activated yellow ink solid or dye. Dipropylene glycol and DMSO are co-solvents. Sodium Hydroxide is an inorganic emulsifying enforcing agent, which also acts as a fungicide. Distilled water acts as a solvent. Cobratec® acts as a corrosion inhibitor.

In this formulation, a particular ink solid is finely divided to yield a small particle size. The particular ink solid of Example 2 will tend to substantially dissolve within sodium hydroxide, which is used as the emulsifying enforcing agent. The combination of the sodium hydroxide and the solvent, which is the formulation example is distilled water, yield an emulsion which may be used in bubble jet and free flow ink jet printer.

Genericaly, a "humectant" is a moisturizing agent. In the relevant are, the term "humectant" is used to describe agents which are included in ink formulations to regulate the rate at which the ink dries and to control the viscosity of the ink. In addition to these properties, the present invention may comprise one or more humectants which will prevent clogging of the orifice or nozzle. With certain inks, the humectants will regulate the sublimation rate of the inks or dyes as they are transferred from the medium to the objects on which the printed design is to permanently appear. The humectant in formulation example 2 is dipropylene glycol, which acts as a co-solvent and humectant.

FORMULATION EXAMPLE #3;
Cyan Ink-Jet Formula:

Material	Weight %
SUBLAPRINT ® Blue 70013[10]	1.0
LIGNOSOL ® FTA[11]	3.5
ME ® 39235[12]	10.0
Diethylene Glycol	9.5
DMSO	1.0
Distilled H_2O	75.0
Total:	100.00

[10]Keystone Aniline Corporation
[11]Lignotech (U.S.) Inc.
[12]Michelman, Inc.

SUBLAPRINT® Blue 70013 is a heat activated ink or dye solid. Lignosol® FTA and ME® 39235 are emulsifying enforcing agents. LIGNOSOL® FTA also acts as a fungicide. ME® 39235 is a polymer, and more specifically, it is a polyethylene binder. Diethylene Glycol and DMSO act as humectants. The solven is distilled water.

SUBLAPRINT® Blue 70013 is more difficult to sublimate than BIFAXAN® Yellow 3GH, and is less soluble in the emulsifying enforcing agent. Diethylene glycol is used as a humectant to facilitate sublimation of the SUBLAPRINT® Blue ink solid.

The heat activated ink solid is finely divided to a small particle size. The finely divided ink solid is combined with one or more emulsifying enforcing agents, which are in turn combined with the solvent.

Formulation Example #4:
Magenta Ink-Jet Ink Formula:

Material	Weight %
INTRATHERM ® Brill Red P-31NT[13]	.5
LIGNOSOL ® FTA[14]	3.0
ME ® 39235[15]	11.0
NA-SUL ®[16]	1.0
DEEFO ® 806-102[17]	0.2
Sorbitol	0.5
Dipropylene Glycol	3.5
Distilled H_2O	79.3
Total:	100

[13]Crompton & Knowles Corporation
[14]Lignotech (U.S.) Inc.
[15]Michelman, Inc.
[16]King Industries
[17]Ultra Additives

Formulation Example #4 comprises a heat activated ink solid or dye which is finely divided and combined in an emulsifying enforcing agent. The emulsifying enforcing agent or medium is, as with Example #3, Lignosol® FTA and ME® 39235. Distilled water is used as a solvent. Dipropylene Glycol is used as a humectant.

Formulation Example #4 further comprises an anti-foaming or foaming control agent, DEEFO® 806-102 to retard foaming of the liquid ink composition. Formulation Example #4 further comprises a surfactant, which may be SORBITOL®, and a corrosion inhibitor, which, in this example, is NA-SUL®.

Formulation Examples 2, 3 and 4 are emulsions. In Example 2, the particular dye has a tendency to dissolve in the emulsifying enforcing agent. Formulation Examples 3 and 4 may also be described as colloids, having finely divided ink particles of not larger than 0.1 microns in diameter present within the disperse medium.

The invention provides an emulsion or colloid which will work within free flow ink jet printers, piezio electric printers, and bubble jet printers, without experiencing problems relating to orifice clogging which results from the use of an ink solid. Further, the use of an emulsion or colloid prevents the separation of the ink solids from the liquid components, rendering an ink composition which is stable over time. Typically, the liquid ink formulations are present within the printers in containers. Three or more colors of liquid ink are present. The containers may be factory sealed, and as such, the ink formulation may be held within the container for a long period of time.

The bubble jet printer forms the bubble which is used to print the ink at approximately the boiling point of the ink solvent. In most formulations, water will be used as the solvent, so that the ink is exposed to temperatures of 100 degrees C. or higher as the ink is printed. Comparable temperatures may be used in free flow ink jet printers to create pressure for the purpose of transporting the ink for printing. As with the phase change ink jet printer, the ink is exposed to temperatures which will activate or sublimate some heat activated inks or dyes. The inks or dyes used in the ink compositions herein will not activate or sublimate at the operational temperatures of the printer.

The liquid ink formulation comprises a liquid carrier. The liquid carrier, or solvent, may be water. An emulsifying enforcing agent, which is soluable in the liquid carrier, forms an emulsion or a colloid in the liquid carrier. The emulsifying enforcing agent has an affinity for the heat activated dye, and attaches to, or may surround, all or part of individual particles of the dye particles.

The heat activated dye as used is a finely divided solid which is substantially insoluable in the liquid carrier. The dye particles, when placed in a liquid, will tend to agglomerate, vastly reducing, and practically eliminating, the efficacy of the ink formulation. The emulsifying enforcing agent is used to form an emulsion or a colloid, and in the present invention, also surrounds and shields, and thereby separates, the individual dye particles from the liquid carrier and from each other, preventing agglomeration of the dye particles, and thereby preventing the ink formulation from clogging the orifices of the printer, such as the ink jets. The emulsifying enforcing agent shields and insulates the dye particles, preventing activation or sublimation of the dye due to exposure to heat present in the printer and the printer processes. The emulsifying enforcing agent shields the dye particles, and improves the shelf life of the ink formulation. The adverse effects of heat, chemical reactions, light, time, and other factors present in packaging or the environment are reduced by the emulsifying enforcing agent. However, while the emulsifying enforcing agent shields the dye particles, the insulation properties of the emulsifying enforcing agent are such that heat activation of the heat activated dye is achieved during final transfer of the image from the medium, which is performed at, or above, the temperature at which the dye activates, and the required optical density of the dye after final transfer by heat activation is attained.

An example of an emulsifying enforcing agent which will achieve the objects of the invention, when used with water as a liquid carrier, is a metallic sulfonate salt known as lignin sulfonate. Lignin sulfonates are sold under various brand names, including Lignosol and Raykrome.

What is claimed is:

1. A method of printing a design by means of a computer driven printer using heat activated dye solids, comprising the steps of:

a. preparing an ink formulation comprising a heat activated dye, a liquid carrier, and an emulsifying enforcing agent which is soluble in said liquid carrier and has an affinity for said heat activated dye, wherein said emulsifying enforcing agent surrounds and shields individual particles of said heat activated dye and separates said individual particles from said liquid carrier, and wherein said heat activated dye is a finely divided solid which is substantially insoluble in said liquid carrier;

b. supplying a computer driven printer with said ink formulation;

c. printing said ink formulation in a desired image by means of said computer driven printer onto a medium at a temperature which is below the temperature at which said heat activated dye activates; and

d. transferring said image from said medium to an object on which the image is to appear by thermal means at a temperature which is sufficient to activate the heat activated dye, so as to cause the heat activated dye to transfer onto said object.

2. A method of printing a design by means of a computer driven printer using heat activated dye solids as described in claim 1, wherein the emulsifying enforcing agent is a sulphonated lignin.

3. A method of printing a design by means of a computer driven printer using heat activated dye solids as described in claim 2, wherein the emulsifying enforcing agent is Lignosol.

4. A method of printing a design by means of a computer driven printer using heat activated dye solids, comprising the steps of:

a. preparing an ink formulation comprising a heat activated dye, a liquid carrier, and an emulsifying enforcing agent which is soluble in said liquid carrier and has an affinity for said heat activated dye, wherein said emulsifying enforcing agent surrounds and shields individual particles of said heat activated dye and separates said individual particles from said liquid carrier, and wherein said heat activated dye is a finely divided solid which is substantially insoluble in said liquid carrier;

b. supplying a computer driven printer with said ink formulation;

c. printing said ink formulation in a desired image by means of said computer driven printer onto a medium at a temperature which is below the temperature at which said heat activated dye activates; and

d. subsequently activating said heat activated dye by the application of heat to said heat activated dye at a temperature which is sufficient to activate the heat activated dye.

5. A method of printing a design by means of a computer driven printer using heat activated dye solids as described in claim 4, wherein the emulsifying enforcing agent is a sulphonated lignin.

6. A method of printing a design by means of a computer driven printer using heat activated dye solids as described in claim 5, wherein the emulsifying enforcing agent is Lignosol.

* * * * *

US005830263A

United States Patent [19]

[11] Patent Number: 5,830,263

Hale et al.

[45] Date of Patent: Nov. 3, 1998

[54] **LOW ENERGY HEAT ACTIVATED TRANSFER PRINTING PROCESS**

[75] Inventors: **Nathan Hale; Ming Xu**, both of Mt. Pleasant, S.C.

[73] Assignee: **Sawgrass Systems, Inc.**, Mt. Pleasant, S.C.

[21] Appl. No.: **807,964**

[22] Filed: **Feb. 28, 1997**

Related U.S. Application Data

[60] Division of Ser. No. 710,171, Sep. 12, 1996, Pat. No. 5,640,180, which is a continuation-in-part of Ser. No. 695,121, Aug. 5, 1996, Pat. No. 5,642,141, Ser. No. 565,999, Dec. 1, 1995, Pat. No. 5,601,023, Ser. No. 207,756, Mar. 8, 1994, Pat. No. 5,487,614, and a continuation-in-part of Ser. No. 506,894, Jul. 25, 1995, which is a continuation-in-part of Ser. No. 299,736, Sep. 1, 1994, Pat. No. 5,488,907.

[51] **Int. Cl.**[6] **C09D 11/02**

[52] **U.S. Cl.** **106/31.27**; 106/31.35

[58] **Field of Search** 106/31.35, 31.27

[56] **References Cited**

U.S. PATENT DOCUMENTS

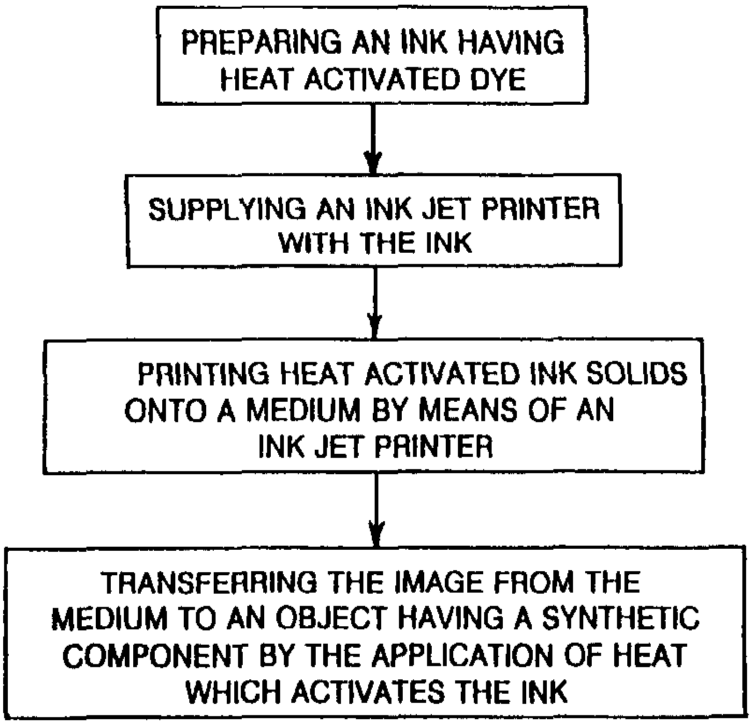
4,265,630	5/1981	Bauerle	8/456
4,422,854	12/1983	Hahnle	8/471
5,028,262	7/1991	Barlow, Jr. et al.	106/22

Primary Examiner—Deborah Jones
Attorney, Agent, or Firm—B. Craig Killough

[57] **ABSTRACT**

A method of printing a liquid ink which is produced from a heat activated dye which is selected from a limited group of dyes which are capable of transfer at low energy. A printer which uses liquid ink, such as an ink jet printer, prints an image onto an intermediate substrate medium. The dyes contained in the ink are not substantially activated during the process of printing on to the medium. The image formed by the printed ink is transferred from the medium to a final substrate by the application of heat and pressure for a short period of time to activate the ink. The dye and dispersing/emulsifying agent(s) are selected from a limited group to produce an ink which permits thermal transfer at low energy, with the resulting image, as deposited on the final substrate, having an optical density of 1.0 or greater.

12 Claims, 2 Drawing Sheets



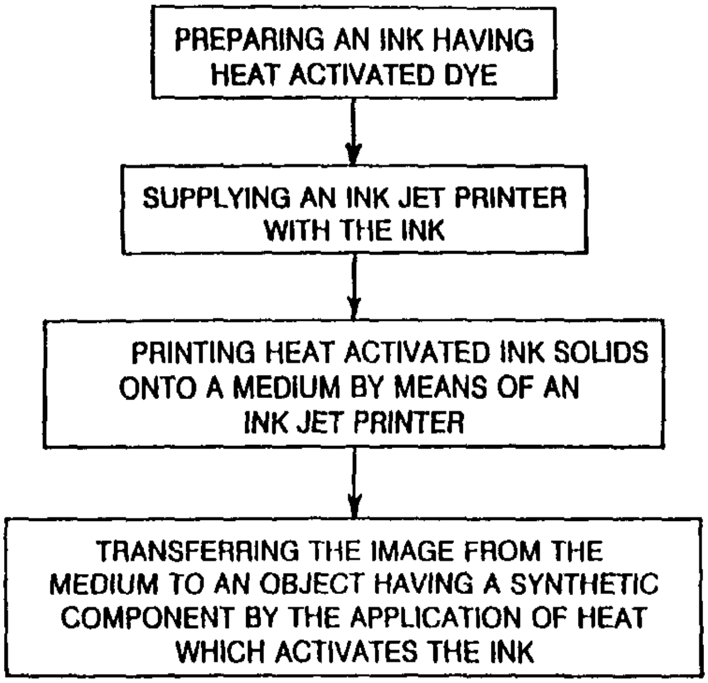

PREPARING AN INK HAVING HEAT ACTIVATED DYE
SUPPLYING AN INK JET PRINTER WITH THE INK
PRINTING HEAT ACTIVATED INK SOLIDS ONTO A MEDIUM BY MEANS OF AN INK JET PRINTER
TRANSFERRING THE IMAGE FROM THE MEDIUM TO AN OBJECT HAVING A SYNTHETIC COMPONENT BY THE APPLICATION OF HEAT WHICH ACTIVATES THE INK

FIG 1

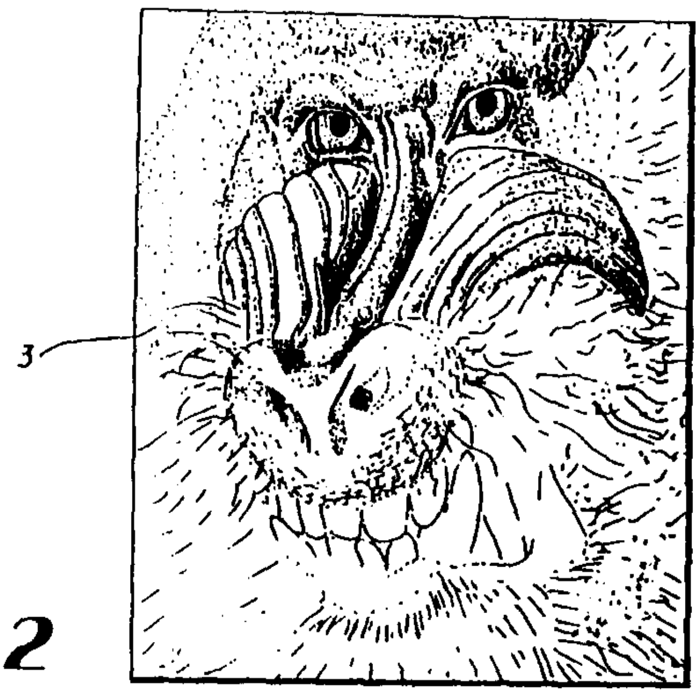

3

FIG 2

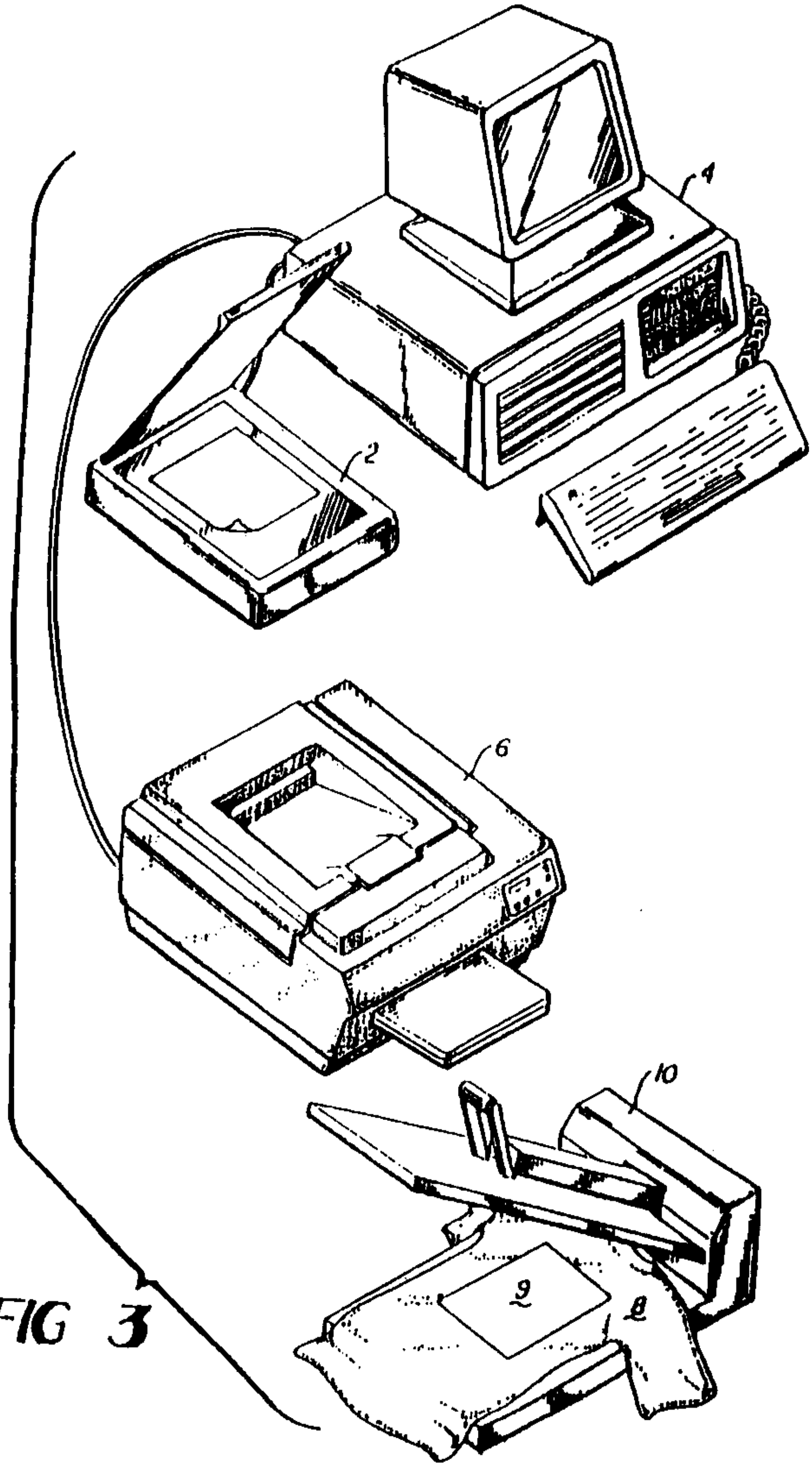


FIG 3

LOW ENERGY HEAT ACTIVATED TRANSFER PRINTING PROCESS

This application is a divisional of U.S. Ser. No. 08/710,171, filed Sep. 12, 1996, now U.S. Pat. No. 5,640,180, which is a continuation-in-part of U.S. Ser. No. 08/695,121, filed Aug. 5, 1996, now U.S. Pat. No. 5,642,141, which is a continuation-in-part of U.S. Ser. No. 08/565,999, filed Dec. 1, 1995, now U.S. Pat. No. 5,601,023, which is a continuation-in-part of U.S. Ser. No. 08/207,756, filed Mar. 8, 1994, now U.S. Pat. No. 5,487,614, and a continuation-in-part of U.S. Ser. No. 08/506,894, filed Jul. 25, 1995, which is a continuation-in-part of U.S. Ser. No. 08/299,736, filed Sep. 1, 1994, now U.S. Pat. No. 5,488,907.

FIELD OF THE INVENTION

This invention relates to printing heat sensitive, dye diffusion or sublimation inks generally, and is more specifically related to a method of printing liquid inks comprising these dyes onto an intermediate transfer sheet by means of an ink let printer or other printer which uses liquid inks, and subsequently transferring the printed image from the intermediate sheet by the application of heat and pressure.

BACKGROUND OF THE INVENTION

Words and designs are frequently printed onto clothing and other textile materials, and other objects. The use of computer technology allows substantially instantaneous printing of images. For example, video cameras or scanning may be used to capture an image to a computer. The image may then be printed by any suitable printing means, including mechanical thermal printers, ink let printers and laser printers. These printers will print multiple color images.

Color ink jet printers are in common use. Color ink jet printers use combinations of cyan, yellow and magenta inks or dyes to produce multiple color images. Most ink jet printers in common use employ inks which are in liquid form.

Heat activated, dye diffusion and sublimation ink solids change to a gas at about 400° F., and have a high affinity for polyester and other synthetic materials at the activation temperature, and a limited affinity for most other materials. Once the bonding from gassification and condensation takes place, the ink is permanently printed, and is resistant to change or fading caused by laundry products, heat or light.

Hale, U.S. Pat. Nos. 5,246,518, 5,248,363, 5,302,223, and 5,485,614 and Hale et al., U.S. Pat. No. 5,488,907, disclose the use of printers to produce an image on a medium or transfer sheet wherein the image is comprised of sublimation, dye diffusion or other heat activated inks. The ink is not activated during the printing of the medium or transfer sheet.

Problems are associated with liquid inks prepared from insoluble dye solids. The orifices or nozzles of most ink jet printers are not designed for the dispensing of dye solids contained within a liquid material. The orifices of these printers are typically 5–30 microns in diameter, and clogging of the orifice will occur when ink solids of large particle size or in high volume are transferred through the orifice.

Further, when the ink solids are placed into a liquid carrier, the ink solids tend to separate from the liquid over time and fall to the bottom of the ink container. The ink is typically packaged in a container at a manufacturing facility for subsequent mounting of the container within the ink Jet printer, meaning that a substantial storage time for the ink composition exists prior to use. Separation of the liquid and solids comprising the ink formulation presents problems with regard to the mechanical operation of the printer and the print quality achieved from use of the ink formulation. Agents which are included within the ink formulation to inhibit separation must also inhibit agglomeration of the solid dye particles, but the agents must not inhibit activation of the dye during the final transfer at elevated temperatures, by insulating the dye or reacting with the dye, or otherwise.

Accordingly, the production of stable liquid inks from dyes which are not water soluble is difficult to achieve without destroying or reducing the properties of the dye which are required for practicing the process of the invention. In the prior art, liquid inks have been produced from dyes that initially have properties suitable for practicing the process. However, the production of liquid inks from these dyes changes or masks the required properties, and therefore, the resulting inks cannot be satisfactorily used to practice the process. For example, additives which will inhibit the dye particles from settling out of the liquid carrier, or which will inhibit agglomeration, tend to insulate the dye particles, meaning that the energy required for sublimation, diffusion or activation of the dye is elevated to unacceptable levels for practicing the process. Other additives which are used in the prior art to produce a liquid ink from the solid dyes are reactive with the dye, and modify or eliminate required properties of the dyes. Other "side effects" of using these additives include undesired color modification or contamination, bonding with the intermediate substrate, or optical density on the final substrate which is inadequate.

While certain solvents will dissolve the dyes, the requirements of the process makes the use of these solvents impractical. Dye materials solubilized to the molecular level have a tendency to bond with fibers, both synthetic and natural. Accordingly, the dyes cannot be effectively transferred from a substrate used as an intermediate transfer sheet by the application of heat and pressure as required by the process of the present invention.

SUMMARY OF THE PRESENT INVENTION

This invention is a method of printing a liquid ink which is produced from sublimation, dye diffusion, or heat sensitive dyes. A printer which uses liquid ink, such as an ink jet printer, prints the image onto a medium, or intermediate substrate, which may be paper. The sublimation, dye diffusion, or heat sensitive dyes (hereinafter collectively referred to as "heat activated dyes") contained in the ink are not substantially sublimated or activated during the process of printing on to the medium. The image formed by the printed ink is transferred from the medium to a final substrate by the application of heat and pressure which sublimates or activates the ink. This thermal transfer step is achieved at low energy when compared to other sublimation or activation processes known and used in the art. One of the goals of the process requires that the thermal transfer occur by applying heat and pressure for no more than three and one-half minutes, and preferably less time. In the prior art, heat at the activation temperature is applied for up to thirty minutes. Accordingly, as used herein, a low energy transfer is a thermal transfer of the image from the intermediate sheet to the final substrate by applying a temperature which is not higher than 450° F., for no more than three and one-half minutes, with the resulting image, as deposited on the final substrate, having an optical density of 1.0 or greater, as measured by an X-Rite 418 densitometer in the density operation mode with background corrections.

The dyes, or perhaps pigments, which are suitable for practicing the invention are dyes which are capable of low energy transfer from the medium onto the final substrate to produce an image on the final substrate which is waterfast and colorfast. After transfer, the dyes are no longer substantially heat sensitive. Dyes which have these characteristics are found in various classifications of dyes, including disperse dyes, solvent dyes, basic dyes, acid dyes and vat dyes. However, none of the dyes which are currently available and which are suitable for producing a liquid ink for practicing the invention are soluble in water.

Accordingly, only a relatively small range of dyes in combination with a relatively small range of dispersing/emulsifying agents will produce a stable liquid ink which will allow the printing method to be practiced. Characteristics of acceptable dyes and dispersing/emulsifying agents which will produce a liquid ink with which to practice the printing method are disclosed herein.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a block diagram showing the printing process.

FIG. 2 illustrates an example of a design printed by a printer using the printing process.

FIG. 3 is a diagrammatic illustration showing exemplary elements of computer and printing systems which could be used to achieve the printing process.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

An image is input into a computer **4**. The computer directs a printer **6** to print the image. Any means of forming an image which may be printed from a computer may be used, including images generated by software. Available computer design graphic software may be used, or still photography may be used. The design may be read and communicated by a scanner **2**, which is connected to computer **4**. The design may be photographic, graphic artistic, or simply letters or words. The use of cyan, yellow and magenta ink compositions allow the printer to print in full color or multi-color designs.

After the image is printed onto the medium, the image may be permanently transferred by thermal means. Most commonly, the design will be transferred onto a textile substrate, such as a shirt **8**, although the image may be transferred onto other materials which act as a substrate, such as metal, ceramic, wood, or plastic. The design **3**, which is printed onto the medium **9** without activating the ink, is placed against the final substrate which may be a shirt **8**. A temperature which is sufficient to activate the dye is applied. This temperature will typically be around 400° F. This temperature is applied for a time sufficient to heat activate and transfer the ink solids in accordance with the requirements of the invention. A heat transfer machine **10** may be used to accomplish the transfer of the inks from the medium to the substrate. Activation, or sublimation, of the dye does not take place at the time of printing the image onto the medium, but occurs during the transfer from the medium to the substrate. The group of heat activated dyes from which dyes may be selected for use in the invention are dyes which substantially sublimate or activate at low energy to form an image which has an optical density value of no less than 1.0, and which is waterfast and colorfast. Each of the dyes which comprise this group will achieve an optical density of 1.25 or greater after activation, when optical density is measured by an X-Rite 418 densitometer in the density operation mode with background correction.

The invention requires the dyes to be transferred at low energy (as defined above) after the dyes are formulated into a liquid ink as described herein and printed onto the medium (the "acceptable dyes"). While a larger group of dyes can be sublimated at low energy, dyes which are not acceptable cannot be formulated into a liquid ink which retains the required properties. While most of the acceptable dyes are disperse dyes, certain other dyes which will perform according to the goals of the invention are included in the group of acceptable dyes.

In general, the acceptable dyes are not reactive, and do not have strong polar function groups, such as sulfonate or carboxyl groups. Reacting the dyes with chemical agents added to the formulation in order to form a liquid ink, as is sometimes done in the prior art, tends to inhibit the activation of the dyes at low energy, which is contrary to the present invention. The acceptable dyes have a molecular weight which is less than 600, and is preferably within a range of 200–400. Most of the acceptable dyes are disperse dyes but certain solvent dyes, vat dyes, basic or cationic dyes (such as carbinol base dyes or anthraquinone type dyes having a quarternary amine), acid dyes, direct dyes, mordant dyes and oxidizing colors also fall within the group of acceptable dyes.

The ink formulation prepared according to the invention is a liquid. Dye solids of small particle size are dispersed in a liquid carrier, and one or more agents are used to maintain what may be called, according to various definitions, a collodial, dispersion or emulsion system. The term "emulsion" is used herein to describe the system, even though the system could, in some forms, be called a colloid or a dispersion.

The heat activated solid dye particles are of small size. It is preferred that the individual solid dye particles have no dimension which is greater than 0.5 microns.

The solid dye particles are dispersed into the liquid carrier. The dispersion is normally achieved by the introduction of a dispersing agent, although mechanical or other physical means could be used. An emulsifying agent is introduced to prevent coagulation or coalescense of the individual dye particles and to stabilize the system.

As set forth in the examples, a single agent may be used as a dispersing and emulsifying agent. Multiple agents may be used in accordance with the goals of the invention. The agent or agents stabilize the system, so that the system remains sufficiently homogenous over time to allow successful printing and transfer of the dye according to the method of the invention. Further, the agent shields the individual particles from the adverse effects of the storage, transportation and printer environments, such as heat, cold and light. While the agent shields the dye particles while they are in the liquid system, it does not inhibit low energy transfer of the dyes in the form of the printed image.

The agents used to disperse and/or emulsify the dye particles include various dispersant materials, surfactants (including cationic, anionic, amphoteric, and nonionic surfactants) and polymeric surfactants. Polymeric materials with dispersing ability, but which are not surfactants, can also be used. Either synthetic or natural materials can be used. The dispersing/emulsifying agents each have a molecular weight which is less than 100,000, and preferably less than 10,000. Thermal stability of the agents is essential to prevent decomposition and/or chemical reaction between the agents and the other components in the systems.

As with the dye, to accomplish the printing method of the invention, the agent(s) do not have active function groups which will react or crosslink with the medium, or which will react or crosslink with the dye or pigment in the system, since such reactions or linkages inhibit the required properties of the dye at the time of activation. The agent(s) must form the emulsion from the finely divided dye particle and the liquid carrier, but must not materially insulate or otherwise materially inhibit the activation of the dye at the time of final transfer.

Agents having the required properties when used with some or all of the acceptable dyes include Lignosulfonate products such as Marasperse 52CP (Lignotech), Lignosol FTA (Lignotech), Lignosol SFX-65 (Lignotech), Marasperse CBA-1 (Lignotech), Temsperse S002 (Temfibre, Inc.) Stepsperse DF series (Stephan Co.), and Weschem NA-4 (Wesco Technologies, LTD), Kraft lignin products such as Diwatex XP (Lignotech), and Reax 85 (Westvaco), and oxylignin products such as Marasperse CBOS-6 and Vanisperse CB.

Other examples of emulsifying agents and dispersants are alkylaryl polyether alcohol nonionic surfactants, such as Triton X series (Octylphenoxy-polyethoxyethanol); alkylamine ethoxylates nonionic surfactants such as Triton FW series, Triton CF-10, and Tergitol (Union Carbide Chemicals); polysorbate products such as Tween (ICI Chemicals and Polymers); polyalkylene and polyalkylene modified surfactants, such as Silwet surfactants (polydimethylsioxane copolymers) and CoatOSil surfactants from OSI Specialties; alcohol alkoxylates nonionic surfactants, such as Renex, BRIJ, and Ukanil; Sorbitan ester products such as Span and Arlacel; alkoxylated esters/PEG products, such as Tween, Atlas, Myrj and Cirrasol surfactants from ICI Chemicals and Polymers; unsaturated alcohol products such as surfynol series surfactants from Air Products Co., alkyl phosphoric acid ester surfactant products, such as amyl acid phosphate, Chemphos TR-421; alkyl amine oxide such as Chemoxide series from Chemron Corporation; anionic sarcosinate surfactants such as Hamposyl series from Hampshire Chemical corporation; glycerol esters or polyglycol ester nonionic surfactants such Hodag series from Calgene Chemical, Alphenate (Henkel-Nopco), Solegal W (Hoechst AG), Emultex (Auschem SpA); and polyethylene glycol ether surfactants such as Newkalgen from Takemoto Oil and Fat Co.

Multiple agents may be used in combination to improve the emulsification of the system and to stabilize the system, as long as the agents are not reactive and do not cause precipitation or otherwise negatively impact upon the emulsification process or the transfer process.

Organic solvents, cosolvents, and/or humectants can also be used as additional additives. Aliphatic and/or aromatic alcohols (thioalcohols), alkoxylated alcohols (thioalcohols), halogenated alcohols (thioalcohols) and carboxylated alcohols (thioalcohols), including mono-alcohol (thioalcohol), diol (thiodialcohol), triol (thiotrialcohol) and polyol (thiopolyalcohol), aminoxide, diamine, triamine material, may be used to improve dye dispersibility, solubility and/or stability in the final ink composition. Examples of solvent materials are diethylene glycol, DMSO and dipropylene glycol.

Other additives can also be introduced into the ink, such as surfactants, corrosion control agents, foam control agents, antioxidants, radiation stabilizers, thermal stabilizers, flame retarding agents, pH control agents, viscosity control agents, or surface (interfacial) tension control agents can be added during or after the emulsification process. Other materials, including dispersants, emulsifying agents, and stabilizers,

may be included in the formulation by means of methods known in the art.

EXAMPLES

An example of a liquid ink composition usable in an ink jet printer is as follows:

Material	Weight %
heat sensitive dye(s)	0.05–20%
dispersant/emulsifying agent	0.05–30%
solvent(s)/cosolvent(s)	0–45%
additive(s)	0–15%
water	40–98%
Total	100%

The heat sensitive dye may be a red (magenta), blue (cyan), yellow or brown dye. The dispersant/emulsifying agent may be a sulfonated lignin such as Marasperse CBA-1. The additive(s) may be Tergitol 15-s-9, Triton X-165, Triton X-405 or Surfynol 465. The solvents and/or co-solvents may be diethlene glycol and/or thioglycol and/or 2-pyrrolidone and/or 1-methoxy 2-propanol.

Example A

30 grams of finely divided Spirit Blue Base (CAS# 68389-46-8) is mixed with 15 grams of Ultrazine NA (Lignotech, USA) and 500 grams of de-ionized water. An ultrasonic pulverizer is used to disperse the dye into the aqueous phase for approximately 30 minutes. Two (2.0) grams of Solsperse 27000 (Zenica Colors, USA) is added into the mixture, which is pulverized for another 10 minutes to achieve a stable emulsion. The mixture is filtered to remove particles larger than 0.25 microns. The printing ink for use in the ink jet printer is formulated from the emulsion as follows:

Material	Weight %
Emulsion	87.0
Glycol	4.0
1-methoxy-2-propanol	7.0
Ammonyx LO (1)	2.0
Total	100%

(1) Stepan Co

The resulting ink is printed by the HP 560 Deskjet printer onto plain copy paper in a dark cyan color, and is transferred from the paper medium or receiver onto a polyester fabric substrate by thermal transfer at 400° F. temperature with 40 lb. pressure applied for 20 seconds. The image as applied to the polyester fabric substrate has an optical density value of 1.4–1.5 for the cyan color as read by an X-Rite 418 densitometer.

Example B

Twenty (20) grams of Disperse Yellow 9 (CAS# 6373-73-5) is mixed with four (4) grams of Sulfynol 131 (Air Products) and 5.0 grams of glycerol (CAS# 56-81-5) and 480 grams of de-ionized water. The pulverizer is used to disperse the dye into the aqueous phase for approximately 25 minutes. One (1.0) gram of Sulfynol 104 E (Air Products) is added to the mixture and pulverized for another 10 minutes to produce an emulsion. The mixture is filtered to remove particles larger than 0.25 microns. The liquid ink for use in the ink jet printer is formulated as follows:

Material	Weight %
Emulsion	78.5
Diethylene Glycol	8.0
Thiodiethanol	5.0
Sulfynol 465	4.0
1-2-Propandiol	4.0
DEA	0.5
Total	100%

The resulting liquid ink is printed by a Canon Bubble Jet 4100 printer onto plain copy paper. The printed image is thermally transferred from the paper medium to a polyester textile substrate at 400° F., while applying 40 lb. pressure for 20 seconds. An intense yellow color having an optical density of 1.4, as measured by an X-Rite 418 densitometer with background correction, appears on the substrate.

Example C

Twenty-five (25) grams of finely divided Solvent Red 52 (CAS# 81-390), is mixed with twenty-two (22) grams of Transferin® N-38 (Boehme Filatex, Inc.) and one hundred and fifty (150) grams of de-ionized water. An ultrasonic pulverizer is used to finely divide the dye and to disperse and micronize the solid dye particles into the aqueous phase by operating the pulverizer for approximately Forty-five (45) minutes. Five (5) grams of Tergitol™ 15-S-15 (Union Carbide, USA), Ten (10) grams of 1,4-butanediol, and two hundred and twenty (220) grams of de-ionized water are then added into the dispersion and pulverized for an additional ten (10) minutes. The dispersion is then filtered to remove solid particulate having a dimension which is larger than 0.25 microns. A liquid ink is formulated using the homogenized emulsion as follows:

Component	Weight %
Emulsion	85.0
Tergitol ™ 15-S-9[(1)]	3.997
1-pyrrolidinone	2.0
1-ethoxy-2-propanol	6.0
IPA	3.0
Kathon ®PFM[(2)]	0.003
Total	100%

[(1)]Union Carbide, USA
[(2)]Rohm & Haas Company

The liquid ink is then printed by an Epson Stylus Color Pro or Epson Stylus Color IIs piezo electric ink jet printer to form an image on plain copy paper. The image is transferred from the paper to a polyester fabric substrate by the application of pressure and heat at a temperature of 400° F. for 25 seconds. The image as transferred has an optical density of 1.45 for the magenta color, as measured by an X-Rite 418 densitometer with background correction.

What is claimed is:

1. A liquid ink for use in ink jet printers prepared from heat activated dye solids, comprising:

Material	Weight %
heat sensitive dye solid	0.05–20%
dispersant/emulsifying agent	0.05–30%
solvent	0–45%
water	40–98%
Total	100%

wherein the heat sensitive dye solid is not substantially insoluble in the water.

2. A liquid ink for use in ink jet printers prepared from heat activated dye solids, as described in claim 1, further comprising 0.01% to 15% surfactant.

3. A liquid ink for use in ink jet printers prepared from heat activated dye solids, as described in claim 1, wherein said dispersant/emulsifying agent is a sulfonated lignin.

4. A liquid ink for use in ink jet printers prepared from heat activated dye solids, as described in claim 2, wherein said dispersant/emulsifying agent is a sulfonated lignin.

5. A liquid ink for use in ink jet printers prepared from heat activated dye solids, as described in claim 1, wherein said heat activated dye is a dye which, after the liquid ink is printed, transfers by the application of heat at a temperature which is not higher than 450° F. for no more than three and one-half minutes, with the resulting image, as deposited on the final substrate having an optical density of 1.0 or greater, as measured by an X-Rite 418 densitometer in the density operation mode with background corrections.

6. A liquid ink for use in ink jet printers prepared from heat activated dye solids as described in claim 5, further comprising 0.01% to 15% surfactant.

7. A liquid ink for use in ink jet printers prepared from heat activated dye solids as described in claim 5, wherein said dispersant/emulsifying agent is a sulfonated lignin.

8. A liquid ink for use in ink jet printers prepared from heat activated dye solids as described in claim 6, wherein said dispersant/emulsifying agent is a sulfonated lignin.

9. A liquid ink for use in ink jet printers prepared from heat activated dye solids as described in claim 1, further comprising 0.01% to 45% solvent.

10. A liquid ink for use in ink jet printers prepared from heat activated dye solids as described in claim 5, further comprising 0.01% to 45% solvent.

11. A liquid ink for use in ink jet printers prepared from heat activated dye solids as described in claim 6, further comprising 0.01% to 45% solvent.

12. A liquid ink for use in ink jet printers prepared from heat activated dye solids as described in claim 7, further comprising 0.01% to 45% solvent.

* * * * *

AO 120 (3/85)

TO: Commissioner of Patents and Trademarks Washington, D.C. 20231	**REPORT ON THE FILING OR DETERMINATION OF AN ACTION REGARDING A PATENT**

In compliance with the Act of July 19, 1952 (66 Stat. 814; 35 U.S.C. 290) you are hereby advised that a court action has been filed on the following patent(s) in the U.S. District Court:

DOCKET NO.	DATE FILED	U.S. DISTRICT COURT
00CV386L(LAB)	02/24/00	United States District Court, Southern District of California
PLAINTIFF		DEFENDANT
Sawgrass Systems Inc.		Corporate Copy
PATENT NO.	**DATE OF PATENT**	**PATENTEE**
1 5,487,614	01/30/96	Hale
2 5,488,907	02/06/96	Xu, et. al.
3 5,601023	02/11/97	Hale, et.al.
4 5,640,180	06/17/97	Hale, et.al.
5 5,642,141	06/24/97	Hale, et.al.

In the above-entitled case, the following patent(s) have been included:

DATE INCLUDED	INCLUDED BY ☐ Amendment ☐ Answer ☐ Cross Bill ☐ Other Pleading	
PATENT NO.	**DATE OF PATENT**	**PATENTEE**
1 5,734,396	03/31/98	Hale, et.al.
2 5,830,263	11/03/98	Hale, et.al.
3		
4		
5		

In the above-entitled case, the following decision has been rendered or judgment issued:

DECISION/JUDGMENT		
CLERK	(BY) DEPUTY CLERK	DATE

Copy 1 - Upon initiation of action, mail this copy to Commissioner Copy 3 - Upon termination of action, mail this copy to Commissioner
Copy 2 - Upon filing document adding patent(s), mail this copy to Commissioner Copy 4 - Case file copy

AO 120 (3/85)

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DECISION/JUDGMENT		
CLERK	(BY) DEPUTY CLERK	DATE

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Copy 2 - Upon filing document adding patent(s), mail this copy to Commissioner Copy 4 - Case file copy

'00 CV 0386 L (LAB)

JS44
(Rev. 07/89)

CIVIL COVER SHEET

The JS-44 civil cover sheet and the information contained herein neither replace nor supplement the filing and service of pleadings or other papers as required by law, except as provided by local rules of court. This form, approved by the Judicial Conference of the United States in September 1974, is required for the use of the Clerk of Court for the purpose of initiating the civil docket sheet. (SEE INSTRUCTIONS ON THE SECOND PAGE OF THIS FORM.)

I (a) PLAINTIFFS

SAWGRASS SYSTEMS, INC., a South Carolina corporation

DEFENDANTS

CORPORATE COPY, a Tennessee corporation, TOM PEASE, an individual; PERSONAL DESIGN CONCEPTS, a Washington corporation; and DON BURNETT, an indvidual

(b) COUNTY OF RESIDENCE OF FIRST LISTED PLAINTIFF CHARLESTON
(EXCEPT IN U.S. PLAINTIFF CASES)

COUNTY OF RESIDENCE OF FIRST LISTED DEFENDANT SHELBY
(IN U.S. PLAINTIFF CASES ONLY)

NOTE: IN LAND CONDEMNATION CASES, USE THE LOCATION OF THE TRACT OF LAND INVOLVED

00 FEB 24 PM 2:53

(c) ATTORNEYS (FIRM NAME, ADDRESS, AND TELEPHONE NUMBER)
Gregory P. Goonan, Esq.
BARNHORST SCHREINER & GOONAN
550 West "C" Street, Suite 1350
San Diego, California 92101

ATTORNEYS (IF KNOWN)

II. BASIS OF JURISDICTION (PLACE AN x IN ONE BOX ONLY)

- ☐ 1 U.S. Government Plaintiff
- ☒ 3 Federal Question (U.S. Government Not a Party)
- ☐ 2 U.S. Government Defendant
- ☐ 4 Diversity (Indicate Citizenship of Parties in Item III)

III. CITIZENSHIP OF PRINCIPAL PARTIES (PLACE AN X IN ONE BOX FOR PLAINTIFF AND ONE BOX FOR DEFENDANT) (For Diversity Cases Only)

	PT	DEF		PT	DEF
Citizen of This State	☐ 1	☐ 1	Incorporated or Principal Place of Business in This State	☐ 4	☐ 4
Citizen of Another State	☐ 2	☐ 2	Incorporated and Principal Place of Business in Another State	☐ 5	☐ 5
Citizen or Subject of a Foreign Country	☐ 3	☐ 3	Foreign Nation	☐ 6	☐ 6

IV. CAUSE OF ACTION (CITE THE US CIVIL STATUTE UNDER WHICH YOU ARE FILING AND WRITE A BRIEF STATEMENT OF CAUSE. DO NOT CITE JURISDICTIONAL STATUTES UNLESS DIVERSITY). PATENT INFRINGEMENT, INDUCEMENT OF PATENT INFRINGEMENT, CONTRIBUTORY PATENT INFRINGEMENT, CONSTRUCTIVE TRUST, ACCOUNTING

V. NATURE OF SUIT (PLACE AN X IN ONE BOX ONLY)

CONTRACT
- ☐ 110 Insurance
- ☐ 120 Marine
- ☐ 130 Miller Act
- ☐ 140 Negotiable Instrument
- ☐ 150 Recovery of Overpayment &Enforcement of Judgment
- ☐ 151 Medicare Act
- ☐ 152 Recovery of Defaulted Student Loans (Excl. Veterans)
- ☐ 153Recovery of Overpayment of Veterans Benefits
- ☐ 160 Stockholders Suits
- ☐ 190 Other Contract
- ☐ 195 Contract Product Liability

REAL PROPERTY
- ☐ 210 Land Condemnation
- ☐ 220 Foreclosure
- ☐ 230 Rent Lease & Ejectment
- ☐ 240 Tort to Land
- ☐ 245 Tort Product Liability
- ☐ 290 All Other Real Property

TORTS — PERSONAL INJURY
- ☐ 310 Airplane
- ☐ 315 Airplane Product Liability
- ☐ 320 Assault, Libel & Slander
- ☐ 330 Federal Employers' Liability
- ☐ 340 Marine
- ☐ 345 Marine Product Liability
- ☐ 350 Motor Vehicle
- ☐ 355 Motor Vehicle Product Liability
- ☐ 360 Other Personal Injury

PERSONAL INJURY
- ☐ 362 Personal Injury-Medical Malpractice
- ☐ 365 Personal Injury - Product Liability
- ☐ 368 Asbestos Personal Injury Product Liability

PERSONAL PROPERTY
- ☐ 370 Other Fraud
- ☐ 371 Truth in Lending
- ☐ 380 Other Personal Property Damage
- ☐ 385 Property Damage Product Liability

CIVIL RIGHTS
- ☐ 441 Voting
- ☐ 442 Employment
- ☐ 443 Housing/Accommodations
- ☐ 444 Welfare
- ☐ 440 Other Civil Rights

PRISONER PETITIONS
- ☐ 510 Motions to Vacate Sentence Habeas Corpus
- ☐ 530 General
- ☐ 535 Death Penalty
- ☐ 540 Mandamus & Other
- ☐ 550 Civil Rights
- ☐ 555 Prisoner Conditions

FORFEITURE/PENALTY
- ☐ 610 Agriculture
- ☐ 620 Other Food & Drug
- ☐ 625 Drug Related Seizure of Property 21 USC881
- ☐ 630 Liquor Laws
- ☐ 640 RR & Truck
- ☐ 650 Airline Regs
- ☐ 660 Occupational Safety/Health
- ☐ 690 Other

LABOR
- ☐ 710Fair Labor Standards Act
- ☐ 720 Labor/Mgmt. Relations
- ☐ 730 Labor/Mgmt. Reporting & Disclosure Act
- ☐ 740 Railway Labor Act
- ☐ 790 Other Labor Litigation
- ☐ 791 Empl. Ret. Inc. Security Act

BANKRUPTCY
- ☐ 422 Appeal 28 USC 158
- ☐ 423 Withdrawal 28 USC 157

PROPERTY RIGHTS
- ☐ 820 Copyrights
- ☒ 830 Patent
- ☐ 840 Trademark

SOCIAL SECURITY
- ☐ 861 HIA (1395ff)
- ☐ 862 Black Lung (923)
- ☐ 863 DIWC/DIWW (405(g))
- ☐ 864 SSID Title XVI
- ☐ 865 RSI (405(g))

FEDERAL TAX SUITS
- ☐ 870 Taxes (U.S. Plaintiff or Defendant)
- ☐ 871 IRS - Third Party 26 USC 7609

OTHER STATUTES
- ☐ 400 State Reappointment
- ☐ 410 Antitrust
- ☐ 430 Banks and Banking
- ☐ 450 Commerce/ICC Rates/etc.
- ☐ 460 Deportation
- ☐ 470 Racketeer Influenced and Corrupt Organizations
- ☐ 810 Selective Service
- ☐ 850 Securities/Commodities Exchange
- ☐ 875 Customer Challenge 12 USC
- ☐ 891 Agricultural Acts
- ☐ 892 Economic Stabilization Act
- ☐ 893 Environmental Matters
- ☐ 894 Energy Allocation Act
- ☐ 895 Freedom of Information Act
- ☐ 900 Appeal of Fee Determination Under Equal Access to Justice
- ☐ 950 Constitutionality of State
- ☐ 890 Other Statutory Actions

VI. ORIGIN (PLACE AN X IN ONE BOX ONLY)

- ☒ 1 Original Proceeding
- ☐ 2 Removal from State Court
- ☐ 3 Remanded from Appelate Court
- ☐ 4 Reinstated or Reopened
- ☐ 5 Transferred from another district (specify)
- ☐ 6 Multidistrict Litigation
- ☐ 7 Appeal to District Judge from Magistrate Judgment

VII. REQUESTED IN COMPLAINT: ☐ CHECK IF THIS IS A CLASS ACTION UNDER f.r.c.p. 23 **DEMAND $** As proven at trial

Check YES only if demanded in complaint: **JURY DEMAND:** ☒ YES ☐ NO

VIII. RELATED CASE(S) IF ANY (See Instructions): JUDGE Thomas J. Whelan Docket Number 98CV1609TW

DATE 2/24/2000 SIGNATURE OF ATTORNEY OF RECORD

::ODMA\PCDOCS\WORDPERFECT\22816\1 January 24, 2000 (3:10pm)

ORIGINAL

#57694 $150 -KBR