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3,049,077

MULTIPLE COLORED PRINTING INKS AND PIGMENTS

Eugene P. Damm, Jr., Endwell, N.Y., assignor to International Business Machines Corporation, New York, N.Y., a corporation of New York
No Drawing. Filed Oct. 5, 1959, Ser. No. 844,175
11 Claims. (Cl. 101—211)

This invention relates to the art of printing inks or pigments. The invention relates particularly to printing inks or pigments capable of producing multiple colored printing and a method of printing using them.

The novel printing inks or pigments of the invention are particularly useful when employed in magnetic and electrostatic printing processes although, as will be apparent to those skilled in the art, they are useful in other printing techniques.

Magnetic printing is a well-known process and involves the formation of a latent magnetic image on a magnetizable surface followed by the development of the latent image by the deposition of finely-divided magnetic particles on the magnetizable surface after which the developed image is loosely transferred to a print medium, web or other substrate, such as paper and the like, and then "fixed" to the print medium. Electrostatic printing is another well-known process and, generally speaking, it involves first the formation of a latent electrostatic image on an electrostatically charged surface, followed by the development of the latent image by loose deposition of finely-divided electrostatically charged dry ink particles of opposite charge of that of the electrostatically charged surface, to a print medium such as paper. The loosely deposited ink must then be "fixed" to the print medium. In the case of both magnetic and electrostatic printing, it is necessary to fix the image of dry ink on the surface of the print medium or substrate or otherwise cause it to adhere. Heretofore, it has been one common practice to employ magnetic inks containing a resinous substance which permit the transfer image to adhere to the paper surface when thermally fused to the paper. However, this process required that the magnetic particles become fused to the paper. More recently, there has been described in the copending application of Richard K. Mason, Serial No. 784,220, filed December 31, 1958, now abandoned, a process whereby the dry transfer image is fixed to the paper by subjecting the loosely deposited particles of magnetic ink to the solvent action of an atomized spray of a solvent capable of dissolving the single dye which is mixed with the magnetic ink particles of the magnetic ink. The dye and the solvent are absorbed by the surface of the paper and the solvent rapidly evaporated. The magnetic particles are then thoroughly removed from the paper by brushing or other means.

While the process of said copending Mason application provides a significant advance in the art of magnetic printing, it contemplates producing printing in only one color which is determined by the color of the magnetic ink employed in the printing process.

It is therefore an object of the present invention to provide an improved novel printing ink or pigment which provides a means of producing printing in different colors from the same original printing ink.

It is another object of the invention to provide a printing method which provides printing of different colors from the same printing ink or pigment.

It is a further object of the invention to provide a method of fixing magnetic or electrostatic printing inks to a substrate or web to provide printing in more than one color from the same printing ink or pigment.

The foregoing objects are obtained in accordance with the practice of the present invention by means of the

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dry solid free-flowing printing ink or pigment of the invention which comprises a plurality of dye materials at least one of which, but not all, is preferentially soluble in a solvent. Desirably, at least one other of the dye materials is preferentially soluble in a second solvent. A permanent dye image or printing is produced on the surface of a substrate, web or other print medium by selectively removing predominantly at least one, but not all, of the dyes comprising the dry printing ink or pigment. In a preferred form at least one of the dyes is at least partially and preferentially soluble in a liquid solvent, such as water, oil, alcohol, hydrocarbon or other solvent material and its fixation to the substrate, web or other printing medium is effected by application of the solvent in liquid form, or as a condensate of the vapor, or atomized spray, causing some of the dye to become dissolved in the solvent and thereby absorbed by the substrate. The solvent is volatilized and the unabsorbed solid material is subsequently removed from the substrate surface. Since different dyes, having different colors, are employed in the printing ink or pigment of the invention and only some of these dyes are preferentially soluble in different solvents employed in fixing the dye to the substrate, high speed printing may be obtained in different colors, from the same printing ink or pigment, by using different fixing solvents.

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of preferred embodiments of the invention.

The dry, solid, free-flowing printing ink or pigment of the invention desirably comprises a mixture of at least two dye materials, having different solubility properties and preferably having distinctly different colors, such as black in one case and red in another. For many uses it is desirable that the printing ink or pigment of the invention contain a carrier or other inert substantially solvent-insoluble finely-divided solid material. Such a carrier is particularly suitable in the case of a printing ink that is intended for use in magnetic or electrostatic printing processes. In the case of a printing ink intended for magnetic printing it is desirable to employ as a carrier a finely-divided magnetic metal or metal oxide. Magnetic Iron B-215, which is a magnetic relatively soft iron of about 35-75 microns particle size range is one such suitable carrier. Another is carbonyl iron powder manufactured by General Aniline & Film Corp. Of course, other finely-divided magnetizable materials such as those of iron, nickel and cobalt, may be employed. While control of the particle size of the magnetic material is not essential, a particle size range of about 1 to 150 microns is usually preferable. The printing ink, containing the mixed plurality of dyes and the magnetic particles, is produced by mixing or grinding the materials together to cause the dyes to adhere to the magnetic particles, either as a coating or loosely as a powder. It is necessary only to insure intimate contact between the dye and magnetic particles and it is not necessary to mix the components to a degree which would alter the particle size of the magnetic particles. Desirably, the resulting magnetic ink is screened to select the particle size range desired for the particular printing process in which it is to be employed and to remove dye particles not attached to the magnetic particles. Varying proportions of dye components to magnetic particles may be employed with satisfactory results. For most purposes 1/2 to 10% by weight of total dye components has been found to provide excellent results.

In the case of printing inks in accordance with the present invention intended for use in electrostatic processes, it is preferable, but not essential, to employ a finely-divided solid inert carrier. A carrier such as glass beads, pref-

erably having a particle size range of from about 1 to 10 microns, or other material which is electrostatically active may be employed. Glass beads are excellent for the purpose since they are readily attracted by electrostatic charges and thus enhance the deposition of the electrostatic printing ink of the invention onto a surface having an electrostatically induced latent image on its surface. Other electrostatically active finely-divided solid materials will be apparent to those skilled in the art. Varying concentrations of dye components may be suitably employed but concentrations from about ¼ to 10% by weight have been found to be particularly suitable. While it is preferred to employ an electrostatically active carrier in producing electrostatic printing inks in accordance with the present invention, mixtures of a plurality of dyes in accordance with the invention normally have sufficient electrostatic activity to be attracted to an electrostatically induced surface. Thus a carrier such as glass beads need be used only to enhance the electrostatic properties of the printing ink.

For printing processes which are not magnetic or electrostatic in nature, the printing ink or pigment in accordance with the present invention may comprise merely a mixture of a plurality of dyes, at least one of which is preferentially soluble in a particular solvent. Printing inks without a carrier may be prepared by merely mechanically mixing together the dye substances.

The method of multiple colored printing in accordance with the present invention comprises permanently fixing or transferring a loosely deposited image of dry printing ink positioned on the surface of a substrate, web or print medium, whereby a portion of at least one of the dyes of the dry printing ink is dissolved in a vaporious, liquid or atomized spray of a solvent. The solvent dissolves a portion of at least some of the dyes from the dry finely-divided printing ink and when the solvent is absorbed by the substrate and the solvent volatilized, such as by normal room temperature evaporation, the image becomes fixed to the surface of the substrate. The color of the resulting printing is determined by the color of the portion of at least one of the plurality of dyes contained in the printing ink which is dissolved by the fixing solvent. By using a different solvent, which preferentially dissolves a proportion of another of the dyes of the printing ink, printing of a different color may be fixed to the surface of the substrate. Thus the printing ink and the process of the present invention enable one to produce printing of different colors from the same dry printing ink, merely by using different fixing solvents. Examples of different combinations of dyes and solvents are fully illustrated by examples hereinbelow. This feature of the invention is believed to have important significance in high speed printing processes in which multiple copies are desired some of which have printing of a different color or where it is desired to have certain portions of the printing on a single substrate in one color and other portions in a different color. The differences in color are obtained by merely selecting different fixing solvents capable of dissolving different portions of the dye components of the printing ink of the invention.

In selecting the dye components for use in a printing ink in accordance with the present invention, it is preferable to employ dyes having distinctly different colors with each dye being preferentially soluble in different solvents. It is frequently convenient to employ one dye which is soluble in a substantially polar solvent, such as water, alcohols, including methanol and ethanol, acetone, etc., and another dye of a distinctly different color which is preferentially soluble in a non-polar solvent such as a hydrocarbon, including benzene, toluene and hexane, halogenated hydrocarbons including chloroform, ethylene dichloride, carbon tetrachloride and fluorinated hydrocarbons, including the "Freons." "Freon" is a trademark of the E. I. du Pont de Nemours & Co., Inc. By selecting fixing solvents having substantially different polarity and

dyes which are preferentially soluble in one of the solvents, it is possible to obtain printing of more distinctly different colors. However, it is not necessary that the solvents employed in the fixing method have widely divergent polarities, and, in fact, solvents which are classified as either polar or non-polar may be employed so long as the dye components of the printing ink are each preferentially soluble in only one of the solvents. As will be noted in a number of the examples, colored printing may be obtained using two different closely related fluorinated hydrocarbons such as two of the Freons.

As will be apparent from the present description, the printing ink and method of the present invention are applicable to many printing processes. While the invention is described more specifically in connection with magnetic and electrostatic printing processes, the invention is useful in printing and dyeing processes employing a substantially dry, finely-divided ink or pigment. Other suitable processes include printing of fabrics, textiles, felts, leather, and the like, or any substance capable of absorbing a dye.

Magnetic and electrostatic printing methods are well-known to those skilled in the high speed printing art. Both of these types of printing processes rely upon the loose deposition of a dry printing ink in the form of images or characters on the surface of a substrate. These techniques, per se, do not constitute a part of the present invention. It is necessary to fix or transfer the images or characters of the loosely-deposited dry printing ink to the substrate to provide a permanent image and it is to this step in the printing process to which the method of the present invention is directed. There are numerous processes for loosely depositing the dry, unfixed characters or images of printing ink to the substrate. Among such magnetic processes are those described in Patent No. 2,820,956 issued to W. J. Rueger January 21, 1958; Patent No. 2,857,290 issued to W. D. Bolton October 21, 1958, and the copending patent application of Richard K. Mason, Serial No. 784,220, filed December 31, 1958. Among such electrostatic printing processes are those described in Patent No. 2,894,799 issued to H. J. McCreary July 14, 1959, and Patent No. 2,776,907 issued to C. F. Carlson January 8, 1957. Any of the foregoing patents and copending application may be employed to deposit unfixed images of the dry, free flowing printing ink of the present invention on a substrate and it is intended to incorporate the disclosures of these foregoing patents and application in the present description in their entirety.

The terms "ink" and "pigment" are frequently employed interchangeably in describing dry printing compositions, although the former is considered by many to refer to a liquid composition. In the present description and claims which follow, the term "ink" will be employed, but its use is intended to contemplate either term and the use of the printing composition described herein.

In order more clearly to disclose the nature of the present invention, the following examples illustrating the invention are disclosed. It should be understood, however, that this is done solely by way of example and is intended neither to delineate the scope of the invention nor limit the ambit of the appended claims. In the examples which follow, and throughout the specification, the quantities of materials are expressed in terms of parts by weight, unless otherwise specified.

Example 1

One percent by weight of mixture of 70 parts of Sudan Black BR (an oil soluble azo dye of Colour Index No. Solvent Black 12) and 30 parts of Sudan Yellow GRN (Color Index No. Solvent Yellow 29-[21230]) is mechanically mixed in a high speed stirrer with finely divided Magnetic Iron B-215 (a magnetic relatively soft iron of about 35-75 microns particle size range obtained from Plastic Metals Co.) to produce a free flowing, dry,

multiple dye pigment or magnetic printing ink with the mixed dyes adhering to the magnetic iron.

The resulting dye pigment is employed in the magnetic printing process described in the copending application of Richard K. Mason, Serial No. 784,220, filed December 31, 1958. In accordance with that process, images of the above dry magnetic printing ink are produced on the surface of a paper record card from latent magnetic images formed from a character generator of the type disclosed in U.S. Patent 2,820,956 of W. J. Rueger, entitled Magnetic Printing Machine, issued January 21, 1958. The magnetic ink images are fixed to the card by spraying them with Freon 112 (1,1,2,2-tetrachloro-1,2-difluoroethane) from a pneumatic atomizing spray nozzle. The Freon 112 preferentially dissolves portions of the Sudan Black BR to provide black colored images or printing on the record card. The Freon 112 evaporates almost instantly from the card. The residual unfixed magnetic ink or pigment is then swept from the surface of the record card by means of a brush.

When Freon 112 is replaced by Freon 113 (trichlorotrifluoroethane) in the foregoing printing process, the color of the printing is olive-drab.

Example 2

One percent by weight of a mixture of 63 parts of Sudan Black BR, 27 parts of Sudan Yellow GRN and 10 parts of Du Pont Oil Red (Color Index No. Solvent Red 24-[26105]) is mechanically mixed in a mortar and pestle with Magnetic Iron B-215 to produce a free-flowing, dry, multiple dye pigment or magnetic printing ink with the mixed dyes adhering to the magnetic iron particles.

When this magnetic ink is employed in the magnetic printing process described in Example 1 and the magnetic ink which transfers to the record card is fixed to the card by spraying the images with Freon 11 (Trichloromonofluoromethane), deep red violet colored printing is obtained. When the Freon 11 is replaced with Freon 113, reddish orange printing is obtained.

Example 3

One percent by weight of a mixture of 50 parts of Sudan Black BR, 37.5 parts of Sudan Yellow GRN and 12.5 parts of Amaplast Red GG is mechanically mixed in a high-speed stirrer with Magnetic Iron B-215 to produce a free-flowing, dry, multiple dye pigment or magnetic printing ink with the mixed dyes adhering to the magnetic iron particles.

When the resulting magnetic printing ink is employed in the magnetic printing process described in Example 1 and the magnetic ink which transfers to the record card is fixed to the card by spraying the images with a mixture of equal parts of Freons 11 and 112, chocolate brown colored printing is obtained. When the mixture of Freons 11 and 112 is replaced with Freon 113, a yellowish-brown colored printing is obtained.

Example 4

One-half percent by weight of a mixture of 70 parts of Sudan Black BR, 30 parts of Sudan Yellow GRN and 20 parts of Amaranth (Colour Index No. Acid Red 27-[16185]) is mechanically mixed in a high-speed stirrer with Magnetic Iron B-215 to produce a free-flowing, dry, multiple dye pigment or magnetic printing ink with the mixed dyes adhering to the magnetic iron particles.

When the resulting magnetic printing ink is employed in the magnetic printing process described in Example 1 and the magnetic ink which transfers to the record card is fixed to the card by spraying the images with a mixture of equal parts of Freons 11 and 112, black colored printing is obtained. When the mixture of Freons 11 and 112 is replaced with steam (water vapor), red-colored printing is obtained.

Example 5

One percent by weight of a mixture of equal parts of Latyl Violet BN (a dispersed dye sold by the Du Pont Co.) and Polar Red G (Colour Index No. Red 85-[22245]) is mechanically mixed in a high-speed stirrer with Magnetic Iron B-215 to produce a free-flowing, dry, multiple dye pigment or magnetic printing ink with the mixed dyes adhering to the magnetic iron particles.

When the resulting magnetic printing ink is employed in the magnetic printing process described in Example 1 and the magnetic ink which transfers to the record card is fixed to the card by spraying the images with an atomized toluene spray, violet colored printing is obtained. When the atomized toluene spray is replaced with an atomized spray of ethanol, orange colored printing is obtained.

Example 6

One percent by weight of a mixture of equal parts of Alizarine Direct Violet EEB (Colour Index No. Acid Blue 56-[62005]) and Cibacet Red 3 BD (Colour Index No. Disperse Red 15-[60710]) is mechanically mixed in a high-speed stirrer with Magnetic Iron B-215 to produce a free-flowing, dry, multiple dye pigment or magnetic printing ink with the mixed dyes adhering to the magnetic iron particles.

When the resulting magnetic printing ink is employed in the magnetic printing process described in Example 1 and the magnetic ink which transfers to the record card is fixed to the card by spraying the images with a spray of steam, blue colored printing is obtained. When the steam spray is replaced with an atomized spray of benzene, red colored printing is obtained.

Example 7

One percent by weight of a mixture of equal parts of Hexovar Blue FC (an acid-basic dye complex with Colour Index No. Solvent Blue 26) and Fast Light Red BA-CF (Colour Index No. Acid Red 37-[17045]) is mechanically mixed in a high-speed stirrer with Magnetic Iron B-215 to produce a free-flowing, dry, multiple dye pigment or magnetic printing ink with the mixed dyes adhering to the magnetic iron particles.

When the resulting magnetic printing ink is employed in the magnetic printing process described in Example 1 and the magnetic ink which transfers to the record card is fixed to the card by spraying the images with an atomized spray of ethanol, violet colored printing is obtained. When the use of ethanol is replaced with steam, red colored printing is obtained.

Example 8

One percent by weight of a mixture of equal parts of Leather Brown 5 RT (Colour Index No. Basic Brown 2 [21030]) and Hexovar Blue FC is mechanically mixed in a high-speed stirrer with Magnetic Iron B-215 to produce a free-flowing, dry, multiple dye pigment or magnetic printing ink with the mixed dyes adhering to the magnetic iron particles.

When the resulting magnetic printing ink is employed in the magnetic printing process described in Example 1 and the magnetic ink which transfers to the record card is fixed to the card by spraying the images with steam, brown colored printing is obtained. When the steam spray is replaced with an atomized spray of acetone, blue colored printing is obtained.

Example 9

One-quarter percent by weight of a mixture of equal parts of Alizarine Direct Violet EEB and Cibacet Red 3 BD is mechanically mixed in a high-speed stirrer with glass beads of between about 1 to 10 microns particle size to produce a free-flowing, dry, multiple dye pigment or electrostatic printing ink with the mixed dyes adhering to the glass beads.

The resulting electrostatic printing ink is employed in the electrostatic printing process described in United States Patent No. 2,894,799, issued to H. J. McCreary on July 14, 1959. In accordance with that process, a positively charged paper record card is moved over a negatively charged target having an image or characters electrostatically charged on the surface, whereby the negatively charged image or characters are induced on to the opposite surface of the record card. This phenomenon is characteristic of most electrostatic printing processes. Onto the negatively charged induced image on the opposite side of the card is blown the dry electrostatic printing ink produced in the foregoing paragraph, which takes on a positive charge as a result of atomization. The positive charged electrostatic printing ink particles adhere to the card only where an electrostatically negative charge of the desired image appears. The electrostatic printing ink is fixed to the record card by spraying the images with a spray of steam, producing a blue colored image on the card. When the steam spray is replaced with an atomized spray of benzene, a red colored image is obtained. The residual unfixed electrostatic printing ink is then swept from the card by means of a brush.

Example 10

An electrostatic printing ink in accordance with the present invention is produced by mixing with a high-speed stirrer equal portions by weight of Hexovar Blue FC and Fast Light Red BA-CF to provide a free-flowing, dry, multiple dye pigment or electrostatic printing ink. It is to be noted that this "pigment" or ink contains no carrier, such as glass beads, etc.

When the resulting electrostatic printing ink is employed in the electrostatic printing process described in Example 9 and the electrostatic printing ink which adheres electrostatically to the record card is fixed to the card by spraying the images with an atomized spray of ethanol, a violet colored printing is obtained. When the spray of ethanol is replaced with steam, red-colored printing is obtained.

Although the foregoing examples are directed principally to the use of the multi-colored printing process and printing ink of the invention in conjunction with magnetic and electrostatic printing, it will be apparent to those skilled in the art that the present invention may be employed to fix images obtained from any image transfer process to a substrate or web. This is so because the present invention is applicable to any dry-printing or transfer process using a dry powder, with or without a carrier, as the ink or pigment. It will also be apparent that, in addition to paper record cards, other substrates and web materials capable of absorbing a dye or having a dye adhere to them, including other paper products and woven fabrics, textiles, felts, leather, and the like, may be used. Other dye combinations may be employed, so long as one of the dyes is preferentially soluble in a solvent. Similarly, other dye fixing solvents may be employed, so long as they exert a preferential solvent action on at least one, but not all, of the dyes in the dry printing ink. Other variations will be apparent to those skilled in the art.

The dyes employed in the foregoing examples have been identified in accordance with the Colour Index numbering system of "Colour Index," Second Edition (1956), published jointly by The Society of Dyers and Colourists and The American Association of Textile Chemists and Colorists.

While the invention has been particularly described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that the foregoing and other changes in form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. A dry free-flowing printing ink capable of producing printing in more than one color, which comprises a

mixture of individual particles each comprising a plurality of dyes, two or more of which are of different colors, with one of the dyes being preferentially soluble in one solvent and another dye being preferentially soluble in another solvent.

2. A dry free-flowing magnetic printing ink capable of producing printing in more than one color, which comprises a mixture of finely-divided magnetic particles each individually comprising a plurality of dyes, two or more of which are of different colors and one of which is preferentially soluble in one solvent and another dye being preferentially soluble in another solvent.

3. A dry free-flowing electrostatic printing ink capable of producing printing in more than one color, which comprises a mixture of finely-divided electrostatically active particles with a plurality of dyes, two or more of which are of different colors and one of which is preferentially soluble in one solvent and another dye being preferentially soluble in another solvent.

4. A method of printing in more than one color from the same printing ink, which comprises producing on at least one substrate images of loosely deposited dry free-flowing printing ink comprising a mixture of a plurality of dyes, two or more of which are of different colors and one of which is preferentially soluble in a solvent, forming permanent images on the substrate by subjecting some of said loosely deposited images of printing ink to the action of a solvent in which one of the dyes is preferentially soluble and subjecting some of said loosely deposited images of printing ink to the action of another solvent in which another of the dyes is preferentially soluble, and removing the unabsorbed ink from the substrate.

5. A method in accordance with claim 4 wherein the printing ink also contains a carrier substantially insoluble in the solvents employed.

6. A method in accordance with claim 4 wherein the ink is a magnetic printing ink containing finely-divided magnetic particles intimately mixed with the plurality of dyes.

7. A method in accordance with claim 4 wherein the ink is an electrostatic printing ink containing finely-divided electrostatically-active particles intimately mixed with the plurality of dyes.

8. A method in accordance with claim 4 wherein the permanent dye image is formed by dissolving a portion of at least one of the dyes in each of the solvents to permit the dyes to be absorbed by the substrate.

9. A method in accordance with claim 4 wherein the solvents are volatilized from the substrate before removing the unabsorbed ink from the substrate.

10. A method in accordance with claim 4 wherein at least one of the dyes is soluble in a substantially polar solvent and another dye is soluble in a substantially non-polar solvent and one of the solvents employed is substantially polar and the other solvent is substantially non-polar.

11. A dry printing ink particle capable of producing printing in more than one color, such particle comprising a plurality of dyes, two or more of which are of different colors, with one of the dyes being preferentially soluble in one solvent and another dye being preferentially soluble in another solvent.

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Hackh: "Chemical Dictionary," 1944 (pages 170 and 75 798 relied on. Copy in Div. 17).

**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

Patent No. 3,049,077

August 14, 1962

Eugene P. Damm, Jr.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 8, line 16, for "with" read -- each individually comprising --.

Signed and sealed this 1st day of January 1963.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents