United States Patent [19]

Mizuno et al.

[11] **3,922,445**

[45] **Nov. 25, 1975**

[54] **HEAT TRANSFER PRINTING SHEET**

[75] Inventors: **Shogo Mizuno**, Toride; **Sumio Ishii**, Inaki, both of Japan

[73] Assignee: **Dai Nippon Printing Company Limited**, Tokyo, Japan

[22] Filed: **May 18, 1973**

[21] Appl. No.: **361,583**

[30] **Foreign Application Priority Data**

May 19, 1972 Japan 47-49136
Mar. 20, 1973 Japan 48-31440

[52] **U.S. Cl.** **428/467**; 8/2.5; 101/470; 428/497; 428/498; 428/500; 428/514; 428/537; 428/538

[51] **Int. Cl.**[2] **B41M 5/26**; B41M 1/12; B41M 01/26; D06P 01/42

[58] **Field of Search** 8/2.5; 117/36.8, 36.9, 117/38, 45, 15, 12; 101/467, 470, 471, 473

[56] **References Cited**

UNITED STATES PATENTS

2,401,755	6/1946	Griffin et al.	117/15 X
2,663,654	12/1953	Miller et al.	117/36.8
2,770,534	11/1956	Marx, Jr.	8/2.5 X
3,108,896	10/1963	Owen	117/36.8
3,505,956	4/1970	Pizzi	101/473 X
3,647,503	3/1972	Mizutani et al.	117/38 X
3,649,332	3/1972	Dybvig	8/2.5 X

FOREIGN PATENTS OR APPLICATIONS

882,208	11/1961	United Kingdom	117/15

OTHER PUBLICATIONS

American Dyestuff Reporter, Vol. 54, No. 1, Jan. 4, 1965. Howes Publishing Co., Inc., New York, N.Y., pp. 26–38.

Primary Examiner—Charles E. Van Horn
Assistant Examiner—Thomas Bokan
Attorney, Agent, or Firm—Stewart and Kolasch, Ltd.

[57] **ABSTRACT**

A heat transfer printing sheet wherein a pattern comprising a basic dye having a poor heat transferable property, an oxidizing agent having the property of increasing the heat transferable property of the basic dye and a binder is formed on a base support sheet and a process for heat transfer printing wherein the above heat transfer printing sheet is brought into contact with a material to be transfer printed with the surface of the heat transfer printing sheet which contains said pattern, and the whole is heated under a pressure to effect the transfer of the basic dye but not of the oxidizing agent and the binder and then the heat transfer printing sheet is peeled off from the latter to transfer print the optional pattern onto said material. The pattern can comprise two layers in which one comprises the basic dye and the binder and other comprises the oxidizing agent and the binder. The base support sheet can be formed of a resin film through which the basic dye cannot be passed when the heat transfer printing is not carried out. The pattern can be coated with a resin film through which the basic dye cannot be passed when the heat transfer printing is not carried out, but can be passed when the heat transfer printing is carried out.

18 Claims, No Drawings

HEAT TRANSFER PRINTING SHEET

The present invention relates to a heat transfer printing sheet and heat transfer printing method using the same, and more particularly relates to a heat transfer printing sheet and heat transfer printing method using the same wherein beautiful transfer printed articles have a clear color tone and good color fastness can be produced by temporarily increasing the heat transferability of a coloring agent without damage of tinting strength of the latter.

Various processes for coloring various materials have been hitherto developed and proposed, and among them there are such sublimiting transfer printing methods as described in U.S. Pat. No. 3,363,557 and British Pat. No. 951,987.

Normally these processes are such as to form any patterns on any support by using ink composition containing as a main ingredient a coloring agent such as a disperse and oil-soluble dye which are rich in a sublimating property and then to bring a material to be transfer printed into contact with the pattern-formed surface of the sheet and to heat them together, and thereby the material to be transfer printed is colored by transfer printing the above-mentioned patterns on the former due to the sublimation of the coloring agent by heat. Therefore, these processes have very superior advantages that the coloring can be effected in a dry-heat state because printing, steaming or washing steps can be omitted.

Since, the sublimating transfer printing method has the under-mentioned disadvantages, however, the development has been greatly obstructed in spite of the presence of the above-mentioned superior advantages.

In the sublimating transfer printing method, namely, dispense dyes having the sublimating property have been generally used as the coloring agent and as a result of the kind of material to be transfer printed is considerably limited.

The fiber which can be colored with the disperse dye is principally all synthetic fibers including polyester fibers and triacetate fibers, but the fiber which can be substantially used is only the polyester fiber in the consideration of various fastnesses such as heat resistance and washing resistance and further the heat resistance of the fiber itself at the dyeing step. Therefore, the disperse dyes substantially cannot be applied for other synthetic fibers, and particularly the disperse dye can not be absolutely applied for the dying of natural fibers such as silk, wool and cotton due to the absence of dyeability thereof by disperse dye.

Accordingly, if the range of kind of the material to be transfer printed is enlarged for the application in the sublimating transfer printing method, coloring agents other than the disperse dyes must be necessarily used, but these coloring agents substantially do not have a heat-sublimating property. Even if a heat-transfer printing is effected by using these coloring agents it is difficult to obtain a very beautiful transfer printed product having a sufficient commodity value. Furthermore, said sublimating transfer printing method has an indispensable disadvantage that the fastness of the sublimation printing is considerably poor.

Namely, since sublimation transfer printing method is the process wherein the coloring is effected by diffusing and penetrating a disperse dye having a high sublimatability into fibers, the dye is again activated to reversely sublimate when the colored base material is again subjected to heating and as a result there are disadvantages that the colored pattern is degraded and the coloring agent contaminates other material.

The object of the present invention is to provide a heat transfer printing sheet which can produce a beautiful transfer printed article having very clear color tone and various fastness properties.

Another object of the present invention is to provide a heat transfer printing sheet which can produce a transfer printed article having a superior fastness for sublimation.

A further object of the present invention is to provide a heat transfer printing sheet which can enlarge the range for the application of the material to be transfer printed.

As a result of our investigation in order to attain the above-mentioned objects we have found that when a basic dye having a poor transferable property based upon the phenomena such as heat-melting, -evaporation or -sublimation is acted with an oxidizing agent, the heat-transferability of the basic dye can be temporarily increased by the occurance of change of phenomena such as heat-melting, -evaporation or -sublimation due to heating, and thereby the range for the application of the material to be transfer printed can be enlarged, after the above-mentioned coloring agent in transferred onto the material to be transfer printed the basic dye is returned to the original basic dye having superior fastness properties and as a result a beautiful transfer printed article having very clear tone and various fastness properties can be obtained.

According to one feature of the present invention, therefore, there is provided a heat transfer printing sheet characterized in that a pattern comprising a basic dye having a poor heat transferability property, an oxidizing agent having a property of increasing the heat transferable property thereof and a binder is formed on a base support sheet.

According to another feature of the present invention, furthermore, there is provided a process for heat transferability printing characterized in that a heat transfer printing sheet which has formed thereon a pattern comprising a basic dye having a poor heat transferable property, an oxidizing agent having a property of increasing the heat transferable property thereof and a binder on a base support sheet is brought into contact with a material to be transfer printed, said contact being made with the pattern-formed surface of the heat transfer printing sheet, and the whole is heated under a pressure to effect the transfer of the basic dye but not of the oxidizing agent and the binder and thereafter the heat transfer printing sheet is peeled off from the latter to transfer print the optional pattern on the material to be transfer printed.

The present invention will now be explained in detail in the following.

As examples of the base support sheet which may be used according to the present invention, it is preferable to use one which is not effected under various conditions for forming optional patterns and also heat transfer printing and therefore there are mentioned for example various kinds of papers and coverted papers, cellophane, film and sheets of various resins having a thermal resistance, various metal foils and plates and laminated films made of them.

The basic dye which is used according to the present invention includes the so-called basic dyes and cationic

dyes.

Examples of the basic dyes which are used according to the present invention are basic dyes and cationic dyes which have been substantially used in a prior sublimating transfer printing method and which have a comparatively poor heat transferability property in the heat transfer printing of these dyes onto other base material due to a phenomena such as heat-melting, -evaporation or -sublimation.

The above mentioned dyes are for example methine (cyanine) type basic dyes or cationic dyes such as mono-methine type, di-methine type or tri-methine type dyes, for example 3,3'-diethyloxacyanine iodide, Asotrazon Pink FG (Bayer, C.I.48015), 2,2'-carboxyanine (C.I.808), Astra Pholoxine FF (C.I. 48070), Astrazon Yellow 7GLL (C.I. Basic Yellow 21), Aizen Cathilon Yellow 3GLH (Hodogaya Chemical K.K. C.I. 48055) and Aizen Cathilon Red 6BH) C.I. 48020); diphenylmethane type basic dyes or cationic dyes such as Auramine (C.I. 655); tryphenylmethane type basic dyes or cationic dyes such as Malachite Green (C.I. 42000), Brilliant Green (C.I. 42040), Magenta (C.I. 42410), Methyl Violet (C.I 42535), Crystal Violet (C.I. 42444), Methyl Green (C.I. 684) and Victoria Blue B (C.I. 44045); xanthene type basic dyes or cationic dyes such as pyronine G (C.I. 739), Rhodamine B (C.I. 45170) and Rhodamine 6G (C.I. 45160); acridine type basic dyes or cationic dyes such as Acridine Yellow G (C.I. 785), Rheomine AL (C.I. 46075), Bensoflavine (C.I. 791), and phosphine (C.I. 46045); quinoneimine type basic dyes or cationic dyes such as Neitral Red (C.I. 50040), Astrazon Blue BGE/X 125% (C.I. 51005) and Methylene Blue (C.I. 52015; and other basic or cationic dyes such as anthraquinone type dyes having a quaterary amine.

The oxidizing agent which may be used in the heat transfer printing sheet is one having a property of increasing the heat transferability property through the reaction of the basic dye therewith.

As examples of the oxidizing agent, there are mentioned for example permanganic acid or its salts such as potassium and sodium permanganates; chromic acid or its related compounds such a potassium chromate, potassium bichromate, sodium and ammonium chromates, sodium and ammonium bichromate, magnesium and calcium chromate, potassium chlorochromate and chromye chloride; peroxides such as hydrogen peroxide and sodium, barium and calcium peroxides and nitrates such as potassium, sodium and ammonium nitrates.

According to the present invention, the amount of the above oxidizing agent employed is preferably 0.1 to 20 molar equivalent of oxidizing agent per molar equivalent of the basic and more preferably is 1 to 10 molar equivalent per molar equivalent of the basic dye.

The heat transfer printing sheet can be produced by various methods.

For example, an ink or paint composition comprising as a main component a binder, basic dye and oxidizing agent is applied onto any base support sheet as an optional mono- or multi-color pattern of for example a letter, mark and figure by a normal printing, drawing or painting method, and thereby a heat transfer printing sheet on which the optional pattern is formed on the base support sheet of the basic dye and oxidizing agent are present on the optional pattern part can be produced.

As an alternative procedure, an ink or paint composition comprising as a main component a binder and basic dye is firstly applied onto any base support sheet as an optional mono- or multi-color pattern by a normal printing, drawing or painting method and then a composition comprising as a main component the oxidizing agent is secondly applied on the above optional pattern, and a heat transfer printing sheet on which the optional pattern is formed on the base support sheet and the basic dye and oxidizing agent are present on the optional pattern part can be produced.

As another alternative procedure, inversely, a composition comprising as a main component the oxidizing agent is firstly applied onto any base support sheet as an optional pattern by the same method as the above and then an ink or paint composition comprising as a main component the binder and the basic dye is secondly applied onto the optional pattern, and thereby an optional mono- or multi-color pattern is formed on the base support sheet and the heat transfer printing sheet on which the basic dye and oxidizing agent are present on the optional pattern part can be produced.

As a further alternative procedure, an ink and paint composition comprising as a main component a binder and a basic dye which is previously treated with a composition comprising as a main component the oxidizing agent is applied onto any base support by a normal printing, drawing or painting method to form a mono- or multi-color pattern thereon, and thereby a heat transfer printing sheet on which an optional pattern is formed and the above basic dye and oxidizing agent are present on the optional pattern part.

According to the present invention it is preferable to produce a heat transfer printing sheet by selecting the most beneficial method from the abovementioned methods for the production thereof depending upon the desired purpose.

The above mentioned processes for the production of a heat transfer printing sheet according to the present invention can be used together.

The optional pattern which may be formed on a base support sheet according to the present invention may be a wholly covered layer containing the basic dye and oxidizing agent.

As examples of the binder which may be used for the process of production of the above heat transfer printing sheet, there are mentioned well known binders such as for example, methyl cellulose, ethyl cellulose, carboxymethyl cellulose, cellulose acetate, cellulose butyrate and sodium alginate and its derivatives; polyvinyl alcohol; polyvinyl acetate; polycarbonate resin; polyester resin; polyamide resin; phenol resin; aminoplast resin; homopolymers or copolymers of various vinyl monomers such as unsaturated carboxylic acids such as acrylic acid, methacrylic acid, itaconic acid, fumaric acid and maleic acid or ester-, nitrile- or amide derivatives of these unsaturated carboxylic acids, vinyl chloride, vinylidene chloride, vinyl acetate, styrene, vinylpyrrolidone, vinyl methyl ether, butadiene, ethylene and propylene; starch; gun arabic; tragacanth gum and gelatin.

The above-mentioned binder which soften or melt at the heating temperature under the heat transfer printing conditions are not preferable for the purpose of the present invention. When the binders which soften or melt are used, the binders themselves are also heat transfer printed on the base material to be heat transfer

printed and consequently heat transfer printed articles having a poor handling quality are obtained.

According to the above mentioned methods for the production of a heat transfer printing sheet, if necessary in addition to the binder, basic dye and oxidizing agent, a coloring assistant having an effect that it penetrates into the base material to be heat transfer printed at the time of heat transfer printing to swell the intermicelles and thereby to increase the penetration of the basic dye, or various addition agents which can regulate the state of the composition comprising the basic dye, binder or oxidizing agent can be used.

The coloring assistant includes for example, urea, naphthalene, ammonium tartrate, glycine A, the oxalate of an aliphalic amine such as cyclohexylamine, ammonium acetate, benzylamine and various surface active agents having an anionic, nonionic or amphoteric property.

The addition agents include for example a plasticizer, stabilizer, wax, grease, drier, auxiliary drier, hardener, emulsifier, viscosity increasing agent, filler and dispersing agent.

In the process for the production of a heat transfer printing sheet as described above, the composition comprising the basic dye, oxidizing agent and position comprising the basic dye, oxidizing agent and binder is in any state, for example solution-, emulsion-, suspension- or sol-state.

When the heat transfer printing sheets according to the present invention which are produced by the above-mentioned process are piled up in order to store them, there are disadvantages that the basic dye having a poor heat transferable property and the oxidizing agent having a property of increasing the heat transferable property of the basic dye which constitute a pattern in one heat transfer printing sheet are transferred into the base support sheet of another heat transfer printing sheet to contaminate it, and consquently the quantity of the basic dye of the former heat transfer printing sheet is decreased. When it is used, therefore, the concentration of the basic dye to be heat transfer printed is gradually faded, or even if the transfer printing is effected the color tone obtained is not clear, or in very bad cases it cannot be used.

Therefore, it cannot be said that the aforesaid heat transfer printing sheet is always completely satisfactory from the point of storage life.

According to the present invention, in such case, it is preferable to use a heat transfer printing sheet wherein a pattern comprising a basic dye having a poor heat transferable property, an oxidizing agent having a property of increasing the heat transferable property of the basic dye and a binder is formed on a base support sheet and then a film of resin through which the basic dye cannot be passed when the heat transfer printing is not carried out, but can be passed when the heat transfer printing is carried out is applied on the pattern.

When the heat transfer printing sheet as described above is used, the aforesaid disadvantages can be overcome by the application of the resin film and the storage life of the sheet can be very much prolonged.

As the examples of resin which can be used as a film having the property as described above, there are preferably mentioned for example sodium polyacrylate, polyvinyl alcohol, dextrin, methyl cellulose, carboxymethyl cellulose, polyvinyl-pyrolidone, vinylmethylether-acrylic acid copolymer, water-soluble thermosetting acrylic resin, rosin modified maleic resin ester gum, rosin modified phenol resin, xylene resin, polyacrylic ester, butyral resin, epoxy resin and polystyrene. These resin films may be formed by a normal coating method such as gravure-coating method, roll-coating method, barcoating method, silk-screen coating method, air-knife coating method, spray coating method and the like. The quantity of resin to be painted is preferably 0.2 – 4.0 g/m^2 depending upon the kind of resin.

Among these resins, it is preferable to use water-soluble resins such as polyvinyl alcohol, sodium polyacrylate and polyvinyl pyrrolidone and oil-soluble resins such as xylene resin, rosin modified phenol resin, polyvinyl butyral, epoxy resin, polystyrene and petroleum resin, because these resins not only to not contaminate the base support sheet but also do not damage the heat transfer printing property of the basic dye and thus the heat transfer printing having an accurate pattern can be obtained.

The production of the above heat transfer printing sheet is carried out by forming any mono- or multi-color pattern such as for example a letter, mark and figure on the base support sheet by a normal printing, drawing or painting method using an ink or paint composition containing as a main component the basic dye, oxidizing agent and binder, and thereby there are obtained a sheet in which the basic dye and oxidizing agent are present in any part of the pattern.

As an alternative process of the present invention, any mono- or multi-color pattern is formed on any base support sheet by a normal printing, drawing or painting method using an ink or paint composition containing as a main component the basic dye and binder and then by applying a composition containing as a component the oxidizing agent onto the above pattern, there is obtained a sheet in which the basic dye and oxidizing agent are presented in any part of the pattern. Conversely, any mono- or multi-color pattern is formed on any base support sheet by the same method as described above using a composition containing as a main component the oxidizing agent and then by applying an ink or paint composition containing as a main component the basic dye and the binder, there is obtained a sheet in which the basic dye and the oxidizing agent are presented in any part of the pattern.

As a further alternative process of the present invention, the basic dye is previously treated with a composition containing the oxidizing agent as a main component and then any mono- or multi-color pattern is formed on the base support sheet by a normal printing, drawing and painting method using an ink or paint component containing as a main component the above treated basic dye and the binder, and thereby there is obtained a sheet in which the basic dye and the oxidizing agent are presented in any part of the pattern.

Furthermore, a resin composition containing as a main component a resin through which the basic dye can not be passed when the heat transfer printing is not carried out, but can be passed when the heat transfer printing, can be carried out is coated onto the pattern-formed surface of the above-mentioned sheet in whcih the basic dye and the oxidizing agent are presented in any part of the pattern, for example by coating methods such as roll coat, gravure coat, bar coat, air knife coat and screen coat. As other methods therefore, the heat transfer printing sheet of the present invention can be obtained by laminating a film or sheet, of resin through which the basic dye can not be passed when the heat transfer printing is not carried out, but can be passed

when the heat transfer printing is carried out, on the pattern-formed surface of the above-mentioned sheet in which the basic dye and the oxidizing agent are presented in any part of the pattern.

According to the heat transfer printing sheet of the present invention, on the other hand, the basic dye passes through optionally the base support sheet depending upon the kind of the material thereof. In this case, the base support sheet can be previously formed with a film of resin through which the basic dye and the oxidizing agent are not passed through under non-heateing conditions.

Namely, the heat transfer printing sheet of the present invention may be the sheet in which the base support is applied with a resin film through which the basic dye having a poor heat transferable property and also the oxidizing agent having a property of increasing the heat transferable property of the basic dye are not passed and then a pattern comprising the basic dye and the oxidizing agent can be formed onto the resin film, and further a resin film throught which the basic dye can not be passed during the non-heat transfer printing but can be passed during the heat transfer printing can be covered on the pattern.

As an examples of the resin which does not pass the basic dye and the oxidizing agent through the base support and may be used in the heat transfer printing sheet of the present invention, there are mentioned polyvinyl alcohol, sodium polyacrylate, polyacrylamide, dextrin, methyl cellulose carboxymethyl cellulose, polyvinyl-pyrrolidone, vinylmethyletheracrylic acid copolymer, water soluble thermosetting acrylic resin, British gum, casein, Crystal gum, gum arabic, tragacanth gum, ester gum, rosin modified phenol resin, hard resins such as xylene resin, acrylic esters, butyrak resin, epoxy resin, aceto-butyric cellulose and thermal setting acrylic resin. Among these, it is especially preferable to use water soluble resins such as sodium polyacrylate, polyvinyl alcohol, dextrine and polyvinyl pyrrolidone and oil soluble resins such as rosin modified phenol resin, xylene resin, polyvinyl butyral, epoxy resin, polystyrene and petroleum resin. Although the coating amount of the resin is different depending upon the kind of resin, it is preferably 0.2 to 4 g/m^2 and the coating can be effected by various coating machines such as a gravure coating machine, silk screen or airknife.

The production of the above heat transfer printing sheet may be carried out for example by coating the composition containing as a main component the resin on the base support sheet with the same coating as described above, or by laminating the film or sheet of the resin which is manufactured by a normal method on the base support sheet to form an undercoat layer on the latter and then by applying the before-mentioned heat transfer printing sheet in the manner described above on the undercoat formed on the base support sheet.

In the case of using as the base support sheet, for example, aluminum foil, a film or sheet of resin, rubber sheet, glassine paper having very high density and parchment paper, it is not necessary to apply on the base support sheet a film through which the basic and the oxidizing agent can not be passed when the heat transfer printing is not effected.

In the present invention, it is preferable to produce the heat transfer printing sheet by selecting a very economical method from the above-mentioned methods depending upon the desired object.

In the present invention, furthermore, two or more coats or laminates of the resin through which the basic dye and the oxidizing agent can not be passed when the heat transfer printing is not effected and also through which the basic dye and the oxidizing agent can not be passed when the heat transfer printing is not effected but can be passed when the heat transfer printing is effected may be used.

In connection with the coating of the resin, it is necessary that the pattern provided on the base support sheet not be effected, for example it is necessary that the letter, mark and figure provided on the base support sheet is not damaged.

The process for heat transfer printing according to the present invention is specifically explained in the following:

Firstly, the surface of the pattern or resin film of the heat transfer printing sheet is laminated so as to contact with the surface of the material to be transfer printed and the whole is heated under pressure between two heated pressing plates or is heated and pressed by passing though two heated rollers to effect the transfer of the basic dye but not of the oxidizing agent and the binder and then heat transfer printing sheet is peeled off from the material which was heat transfer printed.

By this process, it is possible to manufacture the heat transfer printed product in which only the basic dye in any pattern of heat transfer printing sheet is transferred onto the material to be transfer printed and which has very clear color tone and various fastness properties.

In the above heat transfer printing process, it be not necessary that the heating temperature is higher than the melting point or sublimating point of the basic dye itself which is used for the production of the heat transfer printing sheet, and although the heating temperature is varied depending upon the kind of the basic dye it is preferable to optionally use a temperature in the range of about 80° to 250°C.

The condition of the pressure is preferably about 50 g/cm^2 to 20 kg/cm^2.

The duration of heating and pressing treatment is preferably about 30 to 90 seconds.

In the present invention, furthermore, it is possible to carry out the heat transfer printing process by using the heat transfer printing sheet formed with the color layer containing the basic dye, oxidizing agent and binder which covers the whole surface thereof, and a masking member having an optional open pattern is laminated on the color layer of the heat transfer printing sheet, and then a material to be transfer printed is laminated on the masking member and the whole is heated under pressure.

As examples of the masking member, there are mentioned stencil papers for mimeographing such as stencil paper for hand writing, typewriting and ball pen writing, and heat sensitive stencil paper which have formed thereon an optional open pattern such as a letter, mark or figure; a screen printing plate (stencil for screen printing) having an optional pattern for use in screen printing; and films and sheets of various synthetic resins, various papers and various metal foils and thin metal sheets which are formed with an optional open pattern such as a letter, mark, figure or design by a punching or corroding treatment.

In addition to the above masking member, it is possible to use photosensitive dry films such as Liston film (Du pont) and Raminer film (Dynachem) which are

formed with an optional open pattern by normal exposing, developing and fixing.

The material to be transfer printed which may be used in the process for the heat transfer printing process according to the present invention includes vegetable fibers such as cotton and hemp fibers; animal fibers such as wool and silk fibers; glass fiber; rayon fiber, acetate and staple fibers; various fibers such as polyamide, polyester, polyacrylonitrile, polypropylene, polyvinyl chloride, and polyvinyl alcohol fibers; films and sheets of various synthetic resins; various paper; foils and plates of various metals; glass plate; potteries; leather, collagen and synthetic leather; rubber sheet and mould; wood; plywood; slate plate; hard board; gypsum board; and complex materials made of organic compounds and inorganic compounds.

The process for heat transfer printing process can be simply carried out by the use of a heating iron at the time of heating under pressure and consequently this step is easy.

According to the present invention, after an optional pattern is heat transferred on the material to be transfer printed, on the base material is subjected to a steam heating or acid-steam heating treatment to obtain a clearer coloring. It is worth noting in this case that the treatment time, namely the time which is necessary for the complete coloring of the basic dye is very much shorter than that of the prior printing method using a coloring ink containing vehicle.

As is clear from the above explanation, according to the present invention, the heat transfer printing is carried out using a heat transfer printing sheet in which an optional pattern comprising a basic dye having a poor heat transferable property based upon heat-melting, -evaporation or -sublimation phenomena and an oxidizing agent having the property of increasing the heat transferable property through the action of a basic dye with the oxidizing agent and a binder is formed on a base support sheet.

By such fact, therefore, there are very valuable advantages that the basic dye which was scarcely used in the prior sublimation transfer printing process due to the fact that the phenomena such as heat-melting, -evaporation or -sublimation is comparatively poor can be applied for the sublimation transfer printing process. As a result, the application range of the material to be transfer printed can be very much enlarged by the fact that the basic dye can be used in the present invention. Since only disperse dyes could be used in the prior sublimation transfer printing process, the fiber as the material to be transfer printed was limited to polyester type fiber. In the process of the present invention, on the other hand, by suitably selecting the basic dye any fiber which is suitable for coloring with said basic dye can be easily colored. By using the basic dye, for example a synthetic fiber such as polyacrylonitrile fiber and animal fibers such as silk and wool can be colored.

In the process of the present invention, the heat transferable property can be considerably increased by reacting the basic dye which was scarcely used in the prior sublimation transfer printing process due to the fact that the phenomena such as heat-melting, -evaporation or -sublimation is poor by the use of the oxidizing agent, and also when the oxidizing agent-treated basic dye is once heat transfer printed on the material to be transfer printed, it is returned to the original basic dye. Therefore, the fixed color has various considerable superior fastness such as weather resistance, abrasion resistance, heat resistance, solvent resistance, water resistance and chemical resistance. By applying furthermore a stream heating treatment, a heat transfer printed article having more clear color tones can be obtained.

By using the heat transfer printing sheet of the present invention, the storage life and easy handling are improved and the contamination is decreased. Therefore there is the advantage that the value of the commodity can be highly increased.

In order that the present invention may be well understood, the following examples are given by way of illustration only. Unless otherwise stated, quantities are expressed as parts by weight.

EXAMPLE 1

100 parts of polyvinylbutyral resin (Sekisui Chemical Co., Ltd.: Trade name: Eslex BL-1) were dissolved in 900 parts of a mixed solvent of xylene and ethanol (7:3). 900 parts of the obtained solution was mixed with a solution of 50 g of sodium bichromate in 50 g of water (pH 3.2) and then the whole was sufficiently agitated. 900 parts of the mixture and 100 parts of Aizen Cathilon Blue 5G (C.I. 51005; Color tone: Blue) were thoroughly kneaded together in a ball mill to obtain a blue ink composition.

Using Aizen Cathilon Red 6BH (C.I. 48020; color ton: Red) and Aizen Cathilon Yellow 3GLH (C.I. 48055; Color tone: Yellow), similarly, a red ink composition and a yellow ink composition were respectively obtained.

Using the above obtained blue ink composition, red ink composition and yellow ink composition, a heat transfer print sheet for a multi-color printing was obtained by printing a desired pattern with a gravure printing procedure onto a paper for a gravure printing. The heat transfer printing sheet was laminated with a plain weave cloth made of polyacrylonitrile fibers having a thickness of 0.4 mm and the whole was heated with a heated plate of 190°C for 60 seconds and then a deep and clear multi-color heat transfer printed cloth was obtained by stripping off the heat transfer printing sheet. The obtained printed cloth was laminated with a white cloth made of acrylonitrile fibers and then the whole was heated at 180°C for 15 seconds. As a result, the sublimtion fastness shows Grade 4 – 5 and the white cloth was not contaminated. The light fastness of the blue, yellow and red colors showed respectively Grades 5, 6 and 3 so that they were good. The wash fastness, abrasion fastness and dry-cleaning fastness were respectively Grade 5. Therefore various fastness properties showed a good result.

The above procedure was repeated except that the following dyes were used in the place of the above dyes. Similar results were obtained.

a. Aizen Basic Cyanine 6GH (C.I. 42025; Color tone: Turquoise)
b. Aizen Methylene Blue FZ (C.I. 52015; Color tone: Blue)
c. Aizen Cathilon Brilliant Yellow 5GLH (C.I. Basic Yellow 13; Color tone: Yellow)
d. Astrazon Red 6B (C.I. 48020; Color tone: Red)
e. Aizen Cathilon Orange RH (C.I. 48040; Color tone: Orange)
f. Aizen Malachite Green (C.I. 42000; Color tone: Green)
g. Aizen Cathilon Brilliant Pink BF (C.I. Basic red 36; Color tone: Pink)

h. Astrazon Pink FG (C.I. 48015; Color tone: Pink)
i. Astrazon Blue BG F/X 120% (C.I. 51005; Color tone: Turquoise)
j. Mixture of Aizen Cathilon Blue 5G (C.I. 51005) and Aizen Cathilon Yellow 3GCH (C.I. 48055) in the weight ratio of 1:1 [Color tone: Green]
k. Mixture of Aizen Cathilon Blue 5G (C.I. 51005) and Aizen Cathilon Red 6BH (C.I. 48020) in the weight ratio of 4:6 [Color tone: Violet]
l. Mixture of Aizen Cathilon Red 6BH (C.I. 48020) and Aizen Cathilon Yellow 3GCH (C.I. 48055) in the weight ratio of 2:8 [Color tone: Orange]

When the above basic dyes are used without the oxidizing agent the heat transfer printing property is inferior to the case of using the oxidizing agent.

EXAMPLE 2

90 parts of ethyl cellulose (Hercules: Trade name "Ethyl cellulose N7CP), 90 parts of Aizen Cathilon Red 6BH (C.I. 48020) and 90 parts of potasium bichromate were added into 770 parts of a mixed solvent of xylene and ethanol (8:2) and the whole was sufficiently kneaded in a ball mill to obtain a red ink composition. Using the obtained red ink composition, a heat transfer printing sheet was obtained by printing a desired pattern with a gravure printing procedure onto a paper from a gravure printing. This heat transfer printing sheet has similar properties as described in Example 1.

When this example was repeated except that potassium permaganate was used in the place of potassium bichromate, similar result was obtained.

EXAMPLE 3

950 parts of 15% aqueous solution of polyvinyl alcohol (Nippon Synthetic Chemical Industry Co., Ltd.; Trade name: Gohsenol GSS1173) were sufficiently kneaded together with 50 parts of ammonium bichromate. 900 parts of the obtained aqueous solution of ammonium bichromate and 100 parts of Aizen Cathilon Blue 5G (C.I. 51005) were sufficiently kneaded in a ball mill to obtain a blue ink composition.

Using the obtained blue ink composition, a heat transfer printing sheet was obtained by printing a desired pattern with a silk screen procedure onto a paper for a gravure printing. The heat transfer printing was carried out by using the above heat transfer printing sheet as described in Example 1. A sufficient heat transfer printing property was obtained.

EXAMPLE 4

100 parts of ethyl cellulose N7CP and 100 parts of Astrazon Blue BG E/X were mixed together with 800 parts of a solvent mixture of xylene-butanol (8:2) in a ball mill and then the whole was sufficiently kneaded to obtain a blue ink composition.

Using the obtained blue ink composition, a desired pattern was printed onto a paper for a gravure printing by a gravure printing procedure. 6 parts of potassium bichromate were dissolved in 94 parts of 4% aqueous solution of methyl cellulose (Shinetsu Chemical Co., Ltd.; Trade name: Metolose 65SH50). The obtained solution was over-coated on the dye layer of the printed paper by the use of Mayerbar No. 4 and then the overcoat was sufficiently dried to obtain a heat transfer printing sheet. The heat transfer printing sheet was laminated with a plain weave cloth made of polyacrylonitrile fibers having a thickness of 0.4 mm and the whole was pressed with press plates heated at 190°C for 60 seconds, and thereby a deep blue heat transfer printed cloth was obtained.

EXAMPLE 5

100 parts of sodium bichromate were dissolved in 900 parts of 15% aqueous solution of polyvinyl alcohol (Nippon synthetic Chemical Industry Co., Ltd.; Trade name: "Gohsenol GSS1173"). 55 kg/m² of U-lap (Kasuga paper making Co., Ltd.) were coated with the above solution by a gravure printing machine. The coating quantity was 3 g/m². The above surface of the coating was printed with a desired pattern of a blue ink composition used in Example 4 to obtain a heat transfer printing sheet. By using this heat transfer printing sheet, a heat transfer printing was carried out in a similar manner as described in Example 4. Similar heat transfer printing effect was obtained.

EXAMPLE 6

100 parts of ethyl cellulose N7CP, 100 parts of Aizen Cathilon Red 6BH, 20 parts of sodium bichromate and 20 parts of water were charged into a ball mill together with 760 parts of the mixture of xylene-butanol (8:2) and then the whole was sufficiently kneaded to obtain a red ink composition. By using the above red ink composition, a desired pattern was printed on a paper for a gravure printing by a gravure printing procedure. Then 6 parts of urea (Jynsei Chemical Co., Ltd.) were added with 94 parts of 15% aqueous solution of polyvinyl alcohol GL-05 to uniformly dissolve the former into the latter. The aqueous polyvinyl alcohol in which urea is dissolved was over-coated on the dye layer of the printed pattern by using Mayerbar No. 4 to obtain a heat transfer printing sheet.

The heat transfer printing sheet was laminated with a cloth made of polyacrylonitrile fibers and the laminated material was heated at 190°C with an iron for 45 seconds. The obtained heat transfer printed cloth shows very good dyability and was colored with a clear deep red. The urea showed that the permeability of the dye into the cloth and the color developing property are considerably increased.

EXAMPLE 7

Using the following kinds of oxidizing agents as the oxidizing agent which should be acted with a basic dye or cationic dye, an ink composition was prepared in a ball mill. The ink composition was printed on the base support sheet to obtain a heat transfer printing sheet. The heat transfer printing property of the obtained sheet was very good and could be increased.

1. Chromic anhydride

10 parts of chromic anhydride were dissolved in 90 parts of 4% aqueous solution of methyl cellulose (Shinetsu Chemical Co., Ltd.; Trade name: Metolose 65 SH50), 10 parts of Aizen cathilon Red 6BH was added to 90 parts of the above solution and then sufficiently kneaded in a ball mill to obtain a red ink composition. A heat transfer printing sheet was produced by the use of the red ink composition.

2. Potassium nitrate

The following ink composition was sufficiently kneaded in a ball mill to obtain a green ink composition. Using the green ink composition a heat transfer printing sheet was produced.

Ethyl cellulose	100 parts

-continued

Potassium nitrate	100 parts
Malachite green	100 parts
Xylene	56 parts
Butanol	14 parts

Similar result was obtained by using sodium nitrate in the place of potassium nitrate.

3. Hydrogen peroxide solution

A yellow ink composition was prepared from 100 parts of ethyl cellulose N7CP, 100 parts of Aizen Cathilon Yellow 3GLH and 800 parts of a solvent mixture of xylene and butanol (8:2). A paper for gravure printing was printed with the yellow ink composition. Then the coating solution prepared by dissolving 4 parts of hydrogen peroxide solution into 96 parts of 40% aqueous solution of Metolose was coated on the above printed surface by Mayerbar No. 4 to obtain a heat transfer printing sheet.

4. Potassium chromate

800 parts of 12% solution of ethyl cellulose in xylene-ethanol mixture (7:3), 100 parts of Malachite green and 100 parts of a saturated aqueous solution of potassium chromate (25°C) were sufficiently kneaded in a ball mill to obtain a green ink composition. A heat transfer printing sheet was obtained by the carrying out of definite printing.

Similar result was obtained when ammonium chromate was used in the place of potassium chromate.

5. Sodium permanganate

100 parts of sodium permanganate was dissolved in 90 parts of 4% aqueous solution of Metolose. 100 parts of Aizen Cathilon Blue 5G were added to the above solution containing the oxidizing agent and then the whole was sufficiently kneaded to obtain a blue ink composition. A heat transfer printing sheet was obtained by printing the blue ink composition on a paper for a gravure printing.

6. Anhydrous barium peroxide

100 parts of anhydrous barium peroxide were added to 900 parts of 4% aqueous solution of Metolose and then sufficiently kneaded. 100 parts of Aizen Cathilon Red 6BH were added to 900 parts of the above barium peroxide dispersion and then sufficiently kneaded in a ball mill to obtain a red ink composition. A heat transfer printing sheet was obtained by printing the red ink composition on a paper for a gravure printing.

7. Magnesium chromate

100 parts of magnesium chromate were dissolved in 900 parts of 4% aqueous solution of Metolose and then 100 parts of Malachite green were added to 900 parts of this solution and then sufficiently kneaded in a ball mill to obtain a green ink composition. A heat transfer printing sheet was obtained by printing the green ink composition on a paper for a gravure printing.

8. Mixture of anhydrous barium peroxide and sodium bichromate

50 parts of anhydrous barium peroxide and 50 parts of sodium bichromate were added to 900 parts of 4% aqueous solution of Metolose and then the whole was sufficiently kneaded. The 100 parts of Aizen Cathilon Red 6BH were added to 900 parts of the above barium peroxide dispersion and then sufficiently kneaded in a ball mill to obtain a red ink composition. A heat transfer printing sheet was obtained by printing the red ink composition on a paper for a gravure printing.

9. Mixture of sodium permanganate and magnesium chromate

50 parts of sodium permanganate and 50 parts of magnesium chromate were dissolved in 900 parts of 4% aqueous solution of Metolose. 100 parts of Aizen Cathilon Blue 5G were added to 900 parts of this aqueous solution of the oxidizing agent and then sufficiently kneaded in a ball mill to obtain a blue ink composition. A heat transfer printing sheet was obtained by printing the blue ink composition on a paper for a gravure printing.

EXAMPLE 8

80 parts of Crystal Violet (C.I. 42555) were dissolved in 1720 parts of water and then 200 parts of 20% aqueous solution of sodium dichromate were gradually added to the above dye solution and finally after the completion of the addition the solution was left to stand. The formed precipitate was filtered off from the solution and washed and dried. Then 70 parts of Crystal Violet treated with the above oxidizing agent and 120 parts of ethyl cellulose N7CP were mixed with 810 parts of mixed solvent of xylene and butanol (8:2) and the whole was sufficiently kneaded in a ball mill to obtain a violet ink composition. Using the violet ink composition, the desired pattern was printed on a paper for a gravure printing by a gravure printing procedure to give a heat transfer printing sheet. The heat transfer printing sheet was laminated with a plain weave cloth made of polyacrylonitrile fibers and the whole was heated with heated plates at 190°C for 60 seconds. As a result, a deep violet-color heat transfer printed cloth was obtained.

EXAMPLE 9

SP base paper 64 g/m² (Honshu Paper Making Co., Ltd.) was printed with the desired pattern in a gravure printing machine using the yellow, red and blue inks having the following respective composition to obtain a multi-color printed material.

(1)	Yellow ink	
	Aizen Cathilon Yellow 3GLH	100 parts
	Polyvinyl butyral (Eslex BL-1)	100 parts
	$Na_2Cr_2O_7$	45 parts
	Water	45 parts
	Xylene-Ethanol (7:3)	710 parts
	Total	1000 parts
(2)	Red ink	
	Aizen Cathilon Red 6BH	100 parts
	Polyvinyl butyral (Eslex BL-1)	100 parts
	$Na_2Cr_2O_7$	45 parts
	Water	45 parts
	Xylene-Ethanol (7:3)	710 parts
	Total	1000 parts
(3)	Blue ink	
	Aizen Cathilon Blue 5G	100 parts
	Polyvinyl butyral (Eslex BL-1)	100 parts
	$Na_2Cr_2O_7$	45 parts
	Water	45 parts
	Xylene-Ethanol (7:3)	710 parts
	Total	1000 parts

The printing speed was 30 m/min.

Then the multi-color printed material was coated by using 15% aqueous solution of polyvinyl alcohol (Nippon Synthetic Chemical Industry Co., Ltd.: Trade name: Gohsenol GSS 1173) in a gravure rotary printing machine to obtain a heat transfer printing sheet. The coating speed was 20 m/min. The drying was also com-

pletely carried out. The coating quantities was about 1.2 g/m².

The contamination of the heat transfer printing sheet having an overcoat resulting from time lapse was compared with that of the heat transfer printing sheet having no overcoat. The sheet of the present invention shows a storage life of about 3 months and about 3 to 4 times the storage life in comparison with the sheet having no overcoat. Similar result was obtained in the heat transfer printing sheets which were applied with an overcoat having respectively the coating quantities of about 2 g/m² and consisting of two layers of sodium polyacrylate, polyvinyl pyrrolidone or polyvinyl alcohol and butyral resin or polystyrene in the place of polyvinyl alcohol only which is a watersoluble resin. The heat transfer printing method using the heat transfer printing sheet which is prepared as above was carried out as follows:

The above heat transfer printing sheet was laminated with a plain weave cloth made of polyacrylonitrile fibers having a thickness of 0.4 mm and then the whole was heated by a heated plate at 190°C for 75 seconds and SP base paper of the above heat transfer printing sheet was stripped and thereby clear yellow-, red- and blue-color heat transfer printed cloths were obtained. The obtained printed cloths show a good fastness, namely washing fastness grade 5, abrasion fastness grade 5, drycleaning fastness grade 5 in Japanese Industrial Standard and sublimation fastness shows grades 4 to 5 at 180°C, for 15 seconds.

EXAMPLE 10

Example 9 was repeated except that in the place of the water-soluble resin which was used for the overcoat butyral resin (Sekisui Chemical Co., Ltd.; Trade name: Eslex BL-1) was used and was dissolved in a mixed solvent of toluene-alcohol to prepare 15% solution and the coating quantities were about 2.0 g/m².

The obtained heat transfer printing sheet shows a good result similar to Example 9 in the point of the storage life and heat transferring property due to the time lapse.

When oil-soluble resins such as polystyrene, epoxy resin, petroleum resin and xylene resin were used in the place of butyral resin in the above example, similar result was obtained.

EXAMPLE 12

The under-mentioned painting liquid was undercoated on U-lap (Kasuga Paper Manufacturing Co., Ltd: 55kg/m²) in a rotary gravure printing machine. The drying was sufficiently carried out. The painting quantities were 2 to 3 g/m². Then the paper with the undercoat was printed with the ink composition as used in Example 9 by the same procedure of Example 9 in a gravure printing machine to obtain a multi-color printed material. The under-mentioned coating liquid was coated on the printed surface of the above multicolor printed material to obtain a heat transfer printing sheet with an over-coating layer. The coating method is carried out as in Example 9. The painting quantities of the coating were was about 1 to 2 g/m².

The storage life of the heat transfer printing sheet having undercoat and overcoat was compared with that of the heat transfer printing sheet having no undercoat and overcoat.

The process for the testing of contamination of these transfer printing sheets was as follows:

The ink-printed surface of the transfer printing sheet was laminated with one white paper (white paper 1) and also the non-printed surface of the transfer printing sheet was laminated with one white paper (white paper 2) and then the whole was charged in a blocking tester to storage at 30°C for three months therein, thereby the contamination of the transfer printing sheet was determined by the contamination degree of white papers 1 and 2.

In the transfer printing sheet having no undercoat and overcoat, white papers 1 and 2 were extremely contaminated. In the transfer printing sheet having undercoat and overcoat which are applied thereon by using the under-mentioned resins, on the other hand, a good storage life was attained and the contamination of white papers 1 and 2 could not be hardly found.

The heat stability of the transfer printing sheet having undercoat and overcoat was good as similar as in Example 9 and a clear colored cloth was obtained.

The compositions of coating liquids for the undercoat and overcoat are shown in Table 1.

Table 1

Nos.	Undercoating liquid	Overcoating liquid
1	15% aqueous solution of polyvinyl alcohol	15% aqueous solution of polyvinyl alcohol
2	15% aqueous solution of polyvinyl alcohol	15% solution of butyral resin in toluene-isopropyl alcohol mixture (7:3)
3	15% solution of butyral resin in toluene-isopropyl alcohol mixture (7:3)	15% aqueous solution of polyvinyl alcohol
4	15% solution of butyral resin in toluene-isopropyl alcohol mixture (7:3)	15% solution of butyral resin in toluene-isopropyl alcohol mixture (7:3)

The following resins were used in the place of the resins used for the undercoating liquid as described in Table 1. Respectively similar result as the above was obtained.

In Nos. 1 and 2 in Table 1, sodium polyacrylate, dextrine or polyvinylpyrrolidone was used.

In Nos. 3 and 4 in Table 1, rosin modified phenol resin, xylene resin, polystyrene, epoxy resin or petroleum resin was used.

The following resins were used in the place of the resins used for the overcoating liquid as described in Table 1. Respectively, similar result as the above was obtained.

In Nos. 1 and 2 in Table 1, sodium polyacrylate, polyvinyl pyrrolidone, two coats of polyvinyl alcohol and butyral resin or polystyrene was used.

In Nos. 3 and 4 in Table 1, xylene resin, rosin modified phenol resin, polystyrene, epoxy resin or petroleum resin was used.

EXAMPLE 12

When the overcoating liquid was coated in Examples 10 and 11, the dye on the heat transfer printing sheet was dissolved into the solvent of the above liquid depending upon the kinds of dyes and because of this the sheet was often liable to be contaminated. In such case, a first overcoat was preliminarily applied using 15% aqueous solution of polyvinyl alcohol (coating quantity: 0.5 to 1.0 g/m²) and then was sufficiently dried and thereafter a second overcoat was finally applied using 15% solution of polystyrene in a mixed solvent of gaso-

line for rubber, ligroin and toluene (3:3:4). By such two coats the contamination at the coating could be prevented.

The storage life and heat transfer printing property of the heat transfer printing sheet which was obtained in this way were good.

EXAMPLE 13

An undercoat was provided on U-lap (Kasuga Paper Manufacturing Co., Ltd.: 55 kg/m²) using 15% aqueous solution of polyvinyl alcohol. After the undercoat was sufficiently dried an oxidizing agent layer was coated thereon using an oxidizing agent sclution in which 60 parts of $Na_2Cr_2O_7$ were dissolved in 6% aqueous solution of methyl cellulose 65SH50 and then sufficiently dried. A red ink was obtained by adding 120 parts of ethylcellulose N7CP and 100 parts of Aizen Cathilon Red 6BH (C.I. 48020) into 780 parts of a mixed solvent of xylene and butanol (8:2) and by sufficiently kneading the whole in a ball mill. The above oxidizing agent layer was printed with the red ink in a gravure printing machine to form a desired pattern.

Thereafter, an overcoat was formed onto the pattern by using 15% solution of butyral resin in a mixed solvent of toluene and isopropyl alcohol (7:3) in a gravure printing machine to obtain a heat transfer printing sheet. The coating quantity was about 1.2 g/m².

The storage life of the above sheet is good and the transfer printing property is good when the transfer printing was carried out as described in Example 9.

A heat transfer printing sheet having a similar storage life as described above and superior transfer printing property was obtained when sodium acrylate, dextrine, epoxy resin or xylene resin was used in the place of polyvinyl alcohol as the resin of the undercoat and also two coats consisting of polystyrene or polyvinyl alcohol and butyral resin or polystyrene were used in the place of butyral resin as the resin of the overcoat.

EXAMPLE 14

Example 13 was repeated except that the ink pattern layer was firstly printed and then the oxidizing agent layer was secondly coated. Similar results as described in Example 13 were obtained.

EXAMPLE 15

80 parts of Crystal Violet (C.I. 42555) were dissolved in 1720 parts of water and then 200 parts of 20% $Na_2Cr_2O_7$ aqueous solution were gradually added thereto and after the completion of the addition the solution was left to stand. The formed precipitate was filtered off, washed with water and then sufficiently dried. 70 parts of Crystal Violet treated with the above oxidizing agent and 120 parts of ethyl cellulose N7CP were mixed and the whole was sufficiently kneaded in a ball mill to obtain a violet ink composition.

An undercoat was provided on U-lap (Kasuga Paper Manufacturing Co., Ltd.: 55 kg/m²) using 15% aqueous solution of polyvinyl alcohol. After the undercoat was sufficiently dried the above violet ink composition was printed on the above undercoat to obtain a printed matter formed with the desired pattern. The obtained printed matter was provided with an overcoat thereon by using 15% aqueous solution of polyvinyl alcohol to obtain a heat transfer printing sheet. The coating quantity was about 1.2 g/m².

The storage life and heat transfer printing property of the obtained transfer printing sheet was good.

A heat transfer printing sheet having a similar storage life as described above and superior transfer printing property was obtained when sodium acrylate, dextrined, epoxy resin or xylene resin was used in the place of polyvinyl alcohol as the resin of the undercoat and also two coats consisting of polystyrene of polyvinyl alcohol and butyral resin or polystyrene were used in the place of polyvinyl alcohol as the resin of the overcoat.

EXAMPLE 16

50 parts of $Na_2Cr_2O_7$ were dissolved in 950 parts of 4% aqueous solution of methyl cellulose (Shinetsu Chemical Co., Ltd.; Trade name: Metolose 65SH50) and this aqueous solution containing an oxidizing agent was coated on SP base paper 64 g/m² in a gravure printing machine and then the coat was sufficiently dried.

100 parts of ethyl cellulose N7CP and 100 parts of Aizen Cathilon Red 6BH were mixed together with 800 parts of a mixed solvent of xylene and butanol (8:2) and the whole was sufficiently kneaded to obtain a red ink. The desired pattern was printed in a gravure printing machine on the sheet coated with the oxidizing agent using the above red ink.

And then an overcoat was applied on the above printed surface of the sheet in a gravure printing machine using 15% aqueous solution of polyvinyl alcohol and the overcoat was sufficiently dried to obtain a heat transfer printing sheet.

Similar heat transfer printing sheet was also obtained when polyvinyl butyral, polystyrene or two coats consisting of polyvinyl alcohol and butyral resin or polystyrene were used.

EXAMPLE 17

Example 16 was repeated except that the coat of oxidizing agent was applied on the printed pattern and then the overcoat was applied on the coat of oxidizing agent. Similar result was obtained.

EXAMPLE 18

80 parts of Crystal Violet (C.I. 42555) were dissolved in 1720 parts of water and 200 parts of 20% aqueous solution of $Na_2Cr_2O_7$ were gradually added to the dye solution. After the completion of the addition the whole was left to stand. The formed precipitate was filtered off, washed with water and sufficiently dried. Then 70 parts of Crystal Violet treated with the above oxidizing agent and 120 parts of ethyl cellulose N7CP were mixed with 810 parts of a mixed solvent of xylene and butanol (8:2) and the whole was sufficiently kneaded in a ball mill to obtain a violet ink composition.

The desired pattern was printed on an SP base paper 64 g/m_2 in a gravure printing machine using the above violet ink composition. Then an overcoat was applied on the printed pattern in a gravure printing machine using 15% aqueous solution of polyvinyl alcohol to obtain a heat transfer printing sheet.

EXAMPLE 19

Example 9 was repeated except that a laminate of aluminum foils was used in the place of SP base paper 64 g/m² as the base support sheet. Similar heat transfer printing sheet was obtained.

EXAMPLE 20

The heat transfer printing propery of the basic dye treated with the oxidizing agent was tested in compari-

son with that of the basic dye only.

The preparation of the heat transfer printing sheet using the basic dye treated with the oxidizing agent is carried out as in Example 1, 2, 3 or 7 and the heat transfer printing sheet using the basic dye only is prepared by removing the oxidizing agent from the composition of Examples 1, 2, 3 or 7.

These heat transfer printing sheets using the basic dye treated with the oxidizing agent and using the basic dye alone were respectively laminated with polyacrylonitrile fiber and the whole was heated with a heated plate at 190°C for 75 seconds.

The color which was obtained by using the basic dye treated with the oxidizing agent was considerably deeper, clearer and more uniform than that which was obtained by using the basic dye only. These results are shown as follows:

(1) Aizen Cathilon Blue 5G (G.I. 51005)

Oxidizing agent	Preparation of sheet	Concentration of color	State of colored cloth
Sodium permanganate	Example 7(5)	1.30	Good
Anhydrous barium peroxide	" 7(6)	1.32	Good
Sodium bichromate	" 3	1.26	Good
None	—	0.40	Bad, uneven

(2) Aizen Cathilon Red 6BH (C.I. 48020)

Oxidizing agent	Preparation of sheet	Concentration of color	State of colored cloth
Anhydrous barium peroxide	Example 7(6)	1.20	Good
Sodium bichromate	" 2	1.36	Good
None	—	0.50	Bad, uneven

(3) Malachite Green (C.I. 42000)

Oxidizing agent	Preparation of sheet	Concentration of color	State of colored cloth
Sodium permanganate	Example 7(5)	1.20	Good
Anhydrous barium peroxide	" 7(6)	1.14	Good
Sodium bichromate	" 1	1.12	Good
Potassium chromate	" 7(4)	1.26	Good
None	—	0.60	Bad, uneven

The measurement of concentration of color was carried out with a Quantalog Refrection Densitometer Type RD-100 (Macbeth Corporation).

One part of the heat transfer printing sheet using the basic dye (Aizen Cathilon Blue 5G) only was taken, the part was laminated with polyacrylonitrile fibers and the whole was heated with a heated plate at 210°C for 75 seconds. The transfer printed cloth was inferior to the transfer printed cloth which was obtained by using the basic dye treated with the oxidizing agent and by heating at 190°C. Namely the color concnetration of the former was lower than the of the latter and the uneven coloring could not be improved even if the heating temperature was increased. The color of the cloth was changed to yellow and it was not a preferable state.

EXAMPLE 21

Using the heat transfer printing sheet which was produced by the process as described in Example 1, the heat transfer printing was carried out by a heated iron on a cloth made of polyamide fibers (Nylon), silk or wool in the place of a cloth made of polyacrylonitrile fibers. In these cases, a good colored cloth was obtained and the result is shown in Table 2.

Table 2

Dye	Aizen Cathilon Blue 5G	Aizen Cathilon Red 6BH	Aizen Cathilon Blue 5G
Transfer printing condition	170°C 60 seconds	190°C 45 seconds	190°C 60 seconds
Kind of cloth	0.3 mm plain woven nylon	0.3 mm Twill woven cloth	1.0 mm plain woven cloth
Color of printed cloth	Blue	Red	Blue

EXAMPLE 22

The heat transfer printing cloths as described in Examples 1 to 8 were steam-treated to complete the color fixing sufficiently and they become more clear.

The results are shown in Table 3.

Table 3

Kind of cloth	Dye	Steam-heating condition	
Polyacrylonitrile	Aizen Cathilon Blue 5G	105°C	5 minutes
Polyamide	Aizen Cathilon	110°C	3 minutes
Silk	Aizen Cathilon Red 6 BH	110°C	10 minutes
Wool	Aizen Cathilon Blue 5G	110°C	15 minutes

What we claim is:

1. A heat transfer printing sheet comprising a base support sheet having formed thereon a pattern comprising a basic dye having a poor heat transferable property, and oxidizing agent which is capable of sufficiently increasing the heat transferable property of the basic dye when subjected to heating during contact with a material to which the pattern is to be transfer-printed so that only the basic dye can be transferred to said material, and a binder.

2. The heat transfer printing sheet of claim **1**, wherein the pattern comprises an underlayer comprising the basic dye and the binder and an overlayer comprising the oxidizing agent and the binder.

3. The heat transfer printing sheet of claim **1**, wherein the pattern comprises an underlayer comprising the oxidizing agent and the binder and an overlayer comprising the basic dye and the binder.

4. The heat transfer printing sheet of claim **1**, wherein the base support sheet comprises a material selected from the group consisting of paper, converted paper, cellophane, synthetic resin films, metal foils and plates and laminates thereof.

5. The heat transfer printing sheet of claim **1**, wherein the base support sheet is made of a material having a thermal resistance property.

6. The heat transfer printing sheet of claim **1**, wherein the basic dye is selected from the group consisting of methine (cyanine) basic dyes and cationic dyes, diphenylmethane basic dyes and cationic dyes, triphenylmethane basic dyes and cationic dyes, xanthene basic dyes and cationic dyes, acridine basic dyes and cationic dyes, quinoneimine basic dyes and cationic dyes, anthraquinone basic dyes and cationic dyes

containing a quarternary amine.

7. The heat transfer printing sheet of claim **6**, wherein the basic dye is selected from the group consisting of Aizen Cathilon Yellow 3GLH (C.I. 48055), Aizen Cathilon Red 6BH (C.I. 48020), Malachite Green (C.I. 42000), Crystal Violet (C.I. 42555), Aizen Cathilon Blue 5G (C.I. 51005), Aizen Basic Cyanine 6GH (C.I. 42025), Aizen Methylene Blue FZ (C.I. 52015), Aizen Cathilon Brilliant Yellow 5GLH (C.I. Basic yellow 13), Aizen Cathilon Orange RH (C.I. 48040) and Astrazon Pink FG (C.I. 48015).

8. The heat transfer printing sheet of claim **1**, wherein the oxidizing agent is selected from the group consisting of permanganic acid and permanganate salts thereof; chromic acid and chromate, dichromate and chloride salts thereof; hydrogen peroxide; and alkali metal and alkaline earth metal peroxides.

9. The heat transfer printing sheet of claim **8**, wherein said ozidizing agent is selected from the group consisting of permanganic acid, potassium permanganate, sodium permanganate, chromic acid, potassium chromate, potassium dichromate, sodium chromate, ammonium chromate, sodium dichromate, ammonium dichromate, magnesium chromate, calcium chromate, potassium chromate, chromyl chloride, hydrogen peroxide and sodium, barium and calcium peroxides.

10. The heat transfer printing sheet of claim **1**, wherein the binder is selected from the group consisting of methylcellulose, ethylcellulose, carboxymethylcellulose, cellulose acetate, cellulose butyrate, sodium alginate, polyvinyl alcohol, polyvinyl butyral acrylate resins, polyvinyl pyrrolidone, polyvinyl methyl ether, starch, gum arabic, gum tragacanth and gelatin.

11. The heat transfer printing sheet of claim **1**, wherein a resin film through which the basic dye cannot be passed unless it is subjected to a heat transfer printing step but through which it can be passed when the heat transfer printing step is carried out is disposed on said pattern.

12. The heat transfer printing sheet of claim **11**, wherein said resin is water-soluble and is selected from the group consisting of polyvinyl alcohol, sodium polyacrylate and polyvinyl pyrrolidone.

13. The heat transfer printing sheet of claim **11**, wherein said resin is oil-soluble and is selected from the group consisting of xylene resins, rosin-modified phenol resins, polyvinyl butyral epoxy resins, polystyrene and petroleum resins.

14. The heat transfer printing sheet of claim **11**, wherein said resin film is a laminated film consisting of at least two different resin films.

15. The heat transfer printing sheet of claim **1**, wherein the base support sheet is preliminarily coated with a resin film through which the basic dye cannot be passed unless it is subjected to a heat transfer printing step.

16. The heat transfer printing sheet of claim **1**, wherein the base support sheet is preliminarily coated with a resin film through which the basic dye cannot be passed unless it is subjected to a heat transfer printing step and also wherein the pattern is coated with a resin film through which the basic dye cannot be passed unless it is subjected to a heat transfer printing step but through which it can be passed when the heat transfer printing step is carried out.

17. The heat transfer printing sheet of claim **1**, wherein the oxidiaing agent acts to sufficiently increase the heat transferable property of the basic dye at a temperature of from about 80° to 250°C.

18. The heat transfer printing sheet of claim **17**, wherein said heating is conducted under a pressure of from about 50 g/cm^2 to 20 kg/cm^2.

* * * * *