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(54) Heat transfer printing of natural silk substrates.

(57) Impregnating agents are disclosed which can be coated on paper and then be heat transferred with conventional heat transfer printing equipment on silk fabric which obtains thereby an affinity for the dyestuffs known from heat transfer printing of polyester.

Yellowing of the silk fabrik is reduced by the addition to the coating of an optical brightening agent of the type normally used for polyester.

With these impregnating agents, easily migrating dyestuffs can be used which are transferred to the fabric at relatively low temperatures.

These techniques produce deep and brilliant shades; the prints have excellent fastnesses.

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HEAT TRANSFER PRINTING OF NATURAL SILK SUBSTRATES

The present invention refers to methods for printing of textile materials fully or partially consisting of natural silk fibers, according to the principles of the so-called heat transfer printing, from a transfer sheet at an elevated temperature. These principles are for example described in French patents nos. 1 223 330 and 1 585 119.

It is well known that natural silk has substantially no affinity for dispersion dyestuffs which are commonly used in heat transfer printing, so that it is not possible to produce prints having acceptable fastnesses. However, since textile materials and articles of natural silk or containing mixtures of such fibers, are essential fashion products, heat transfer printing would bring about outstanding advantages such as flexibility in design storage, the possibility of an economic production of a valuable design even in relatively small quantities, the simplicity of the method, the absence of wash water

contamination, the possibility of half-tone dyeing, etc. Furthermore, silk fabrics are often very light, having weights of as low as 20 g/m^2, which could be printed easily by heat transfer but only very difficultly, if at all, dyed by conventional liquor dyeing techniques.

It has already been tried to overcome the lack of affinity mentioned above, in order to get the silk dyeable by heat transfer printing. A first approach was the chemical modification of the silk fiber by grafting reactions or by acylation, but these methods are complex and expensive and do alter the hand and other physical properties of the silk materials. These methods could therefore not succeed.

Another possibility of rendering silk materials temporarily more affine to dispersion dyestuffs was for example disclosed in Japanese patent applications nos. 53-78386 (Toyo Ink Mfg. KK) and 52-66785 (Sumitomo Chemical KK), French patent no. 2 296 537, and U.K. Patents nos. 2 112 422 (which appears to be a selection from FR-A 2 296 537) and 1 529 199. The method comprises treating a textile material of natural silk with an aqueous composition, containing certain swelling agents, and then drying the treated textile material. It is believed that the effect of this pre-treatment consists in swelling the silk fiber and to maintain the swollen state of the fiber even after drying, i.e. in its water free condition. Afterwards, a heat transfer printing step is accomplished, and the remaining swelling agent seems to act as a solvent phase for the dispersion dyes during the transfer step. Acceptable fastnesses are generally obtained after a final washing or rinsing of the silk textile material whereby the swelling agent is eliminated.

It has further been found that the heat transfer printing of silk which has been pre-treated as depicted above, namely which contains a swelling or impregnating agent, for example a polyhydric alcohol, suffers from the disadvantage that the silk strongly yellows in the heating step during the heat transfer printing, at the temperatures normally used in heat transfer printing. Attempts to avoid yellowing by reducing the transfer temperatures to 190° to 200°C have not been successful since the brilliant shades required in silk printing, are no more attained with the dyestuffs used for the heat transfer printing of polyester, and furthermore, yellowing is only reduced but not eliminated.

Dispersion dyestuffs have become known from U.K. patent no. 2 112 422 which can be transferred at relatively low temperatures, e.g. at 170° to 180°C, in about 30 to 40 seconds from the transfer sheet to silk fabrics, e.g. C.I. Solvent Blue 36. However, these dyestuffs are so mobile even at room temperature that they migrate and recrystallize in the swelling agent used for the silk pre-treatment, namely polyhydric alcohols or their derivatives, to such an extent that already after a dwell time of a few hours - such a time lag must normally be accepted before rinsing and cannot be shortened -, there are perceptible level differences in the originally produced print design.

Next to the problems mentioned above, the most important reason why the liquid pretreatment process taught in the above mentioned patents and patent applications has not had much commercial success, is that liquid pretreatment is difficult to integrate into a heat transfer printing process line. Liquid pretreatment has

practically always to be applied at locations different from those where the heat transfer is to be executed, and generates organisational problems resulting in long delivery times thereby destroying an important advantage of heat transfer printing over conventional printing.

It must therefore be concluded that heat transfer printing of silk has only then a chance of commercial success if a pretreatment process can be found which can be used by the heat transfer printer with his current and normal equipment, i.e. a heat transfer printing calender or press.

The main object of the present invention is to provide a new and useful method for the transfer printing of pure and mixed silk textile materials which does not suffer from the above discussed disadvantages and drawbacks.

Another object of this invention is to provide such a method which, however, allows to maintain the outstanding advantages of the transfer printing principles.

Still another object of the invention is to provide such a transfer printing process which can be carried out in the apparatuses, devices and machines already available or already installed at a given place such as a factory, thus minimizing capital investment, and which is economically feasible already with short lengths of silk textile materials to be printed.

A further object of the present invention is to develop a heat transfer printing process avoiding the yellowing of the silk substrate during the transfer heating.

These and still other objects are attained by the method of this invention which, in a first and principal embodiment, comprises the dry pre-treatment of the silk textile with an impregnating composition.

Surprisingly, it has been found that impregnating agents can be applied to natural silk with a melt transfer method resulting in a strong affinity of the impregnated silk for subliming dyestuffs. For this application conventional heat transfer equipment, i.e. calenders and presses, can readily be used.

The following impregnating agents have proven to be particularly appropriate in the method of this invention:
isonicotinamide, ε-caprolactam, nicotinamide, propylene urea, ethylene urea, glyoxal mono-urein, urea, 5,5-dimethyl hydantoin, imidazole, 2-methyl imidazole, N-methyl pyrrolidone, N-hydroxy succinic amide, benzamide, toluol sulfonamide and mixtures from these substances.

It will be noted that the above mentioned organic substances are solid at temperatures below 60°C and liquid in a range between 60 and 200°. Furthermore they contain nitrogen and are substantially colorless. They must further be stable at the heat transfer temperatures, and must not attack the silk substrate.

Since most of the substances listed above are well soluble in water, aliphatic or aromatic hydrocarbons which are water insoluble, or other water insoluble solvents, are preferred as solvents for the printing ink. As a binder in the printing ink, film forming substances must be used which are soluble in water and in these other

solvents as well, because impregnating agent and binder must be capable of being eliminated by water rinsing from the silk substrate following the heat transfer printing.

Furthermore, the film forming binder must either have a melting point (or melting range) between 60° and 200°C, or it must be soluble in the molten impregnating agent. Hydroxypropyl cellulose brands are a particularly well suited film forming binder having the above listed necessary properties. Since the melt which forms during the transfer printing step from impregnating agent and binder, should be as less viscous as possible, it is preferred to combine the binder with a plasticizer.

The heat transfer printing of the silk according to this invention may be carried out in two different manners:

(1) An unprinted base paper for gravure printing is coated with a pre-treatment composition comprising a solvent, a binder and an impregnating agent, in such a manner that a layer containing from 5 to 25 g of impregnating agent per m^2 of base paper is formed.

This layer is then heat transferred to the silk substrate by means of a conventional heat transfer calender or a transfer press at a temperature of about 100° to about 200°C. Then, a coloured pattern on a transfer paper is heat transfer printed in the usual way (e.g. 200°C, about 30 sec) onto the thus pre-treated substrate.

Following this heat transfer printing, the impregnating agent and the binder are removed from the printed product by rinsing it with water.

(2) A transfer printing paper which has been produced using at least one of the dyestuffs listed and discussed below is coated with a composition for simultaneous pre-treatment and printing, composed of an aliphatic or aromatic hydrocarbon as a solvent, the special binder and said impregnating agent in such a manner that the layer which is formed will contain, after drying, from about 5 to about 25 g/m^2 of impregnating agent.

After drying, this paper is placed on untreated silk in a conventional heat transfer printing calender or in a transfer press, and the simultaneous heat transfer of the impregnation agent and the dyestuff is effected, under the conditions specified above. "Untreated silk" means silk which has not specially been pre-treated in view of rendering it more receptive for dyestuffs. Other treatments are of course possible and often necessary.

After rinsing with water, a product is obtained showing a brilliant print and the characteristic hand of silk.

In both cases discussed above, to the coating composition should be added from 0.2 to 5 % of an optical brightener which is well soluble in aromatic or aliphatic solvents but substantially insoluble in water, in order to compensate for a possible yellowing of the silk. Such optical brighteners are proposed for the spin melt dyeing and the cake dyeing of polyester fibers and are mostly benzoxazole derivatives. Representative members thereof are the products called "UVITEX OB" (Ciba-Geigy), "KODEL" (Eastman-Kodak) and "SANDUVOR VSU" (Sandoz).

It should further be noticed that there is a fundamental difference between the instant method and that known from French Patent no. 2 277 680 in the transfer printing of hydrophilic fiber materials. That French patent, page 9, line 31, imperatively calls for the binder to completely remain on the base paper after the transfer printing step. It is supposed that the sensibilisation of the hydrophilic fibers should obviously, in the French patent process, be accomplished by the sublimation of the impregnating agent whereas, in the instant method, impregnating agent and binder are transferred together via their melt on the silk. For this reason, only binders with special, outstanding properties can be used in the present method whereas the French patent expressly mentions that all binders known from the lacquer and printing ink industry may be used.

The heat transfer printing step may be carried out in practice as usually; details may be taken from the publications of the prior art mentioned and discussed above.

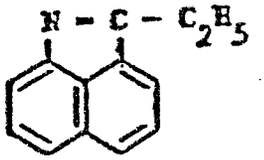
Dyestuffs which may be used are those which can be applied by heat transfer on polyester substrates, generally dispersion dyestuffs, for example C.I. Disperse Red 60, C.I. Disperse Yellow 54, C.I. Disperse Blue 331, C.I. Disperse Blue 72, C.I. Disperse Blue 19, C.I. Disperse Violet 1. The more water insoluble the dyestuffs are, the better are generally the final washing fastnesses.

Particularly good penetration is obtained when dyestuffs are used which are capable of being transferred at a temperature of at least 190° in 40 seconds with substantially 100 % yield from the transfer sheet to the

pre-treated silk. In order to solve the well known problem of the degradation of the print pattern by migration, experiments were made, and it has been found that the melt impregnating agents listed above do not form migrating systems with these rapidly subliming dyestuffs, e.g. C.I. Solvent Blue 36.

The print pattern of the heat transfer prints thus obtained does not degrade until eight weeks when kept at a temperature below 40°C. At this time at the latest, the rinsing or washing should be effected. It will be sufficient to rinse the fabric several times in lukewarm water of 40°C.

The use of a trichromies which contain as a blue dyestuff 1,4-diisopropylamino anthraquinone, as a red dyestuff 1-amino-2-chloro-4-hydroxyanthraquinone (also 1-amino-2-bromo-4-hydroxyanthraquinone can be used), and as a yellow dyestuff the product having the formula



should specially be emphasized.

However, they are the migrating dyestuffs, and in order to keep down the migration, the cited trichromies should only be used together with silk substrates having been pre-treated with one of the above described impregnating agents.

The dyestuffs to be used are typically sparingly water soluble. When the pretreatment of silk fabric has been made with highly water soluble

impregnating agents, rinsing with cold water is sufficient. With benzamide and toluene sulfonamide, warm rinsing is preferred. When surfactants are added in order to improve the wetting of the textile materials, only such agents can be used which do not render the dyestuffs more soluble. After the rinsing step, the textile material is dried.

Another possibility to obtain strong and deep prints and a high penetration is to use transfer papers printed with relatively very high dyestuff amounts. This feature has not been obvious since deep shades normally impair the rubbing fastnesses (see e.g. BASF Publication CTE-072 d, page 10). It has surprisingly been found that this was not the case. On the contrary, it has been found that dyestuffs known for the heat transfer printing on polyester, namely C.I. Disperse Red 60, C.I. Disperse Yellow 54 and C.I. Disperse Blue 331, provide when printed on silk by heat transfer, the standard type depth of 2/1 with the same textile fastnesses as if transfer sheets would be used containing as much dyestuffs as 1 to 2.5 g/m^2, preferably 1.5 g/m^2. When these transfer sheets are prepared by gravure printing using a normal gravure, this value can be obtained with a printing ink containing about 15 % by weight of dyestuffs. It should be noted that the normal heat transfer printing of polyester uses typically dyestuff amounts not exceeding 0.75 g/m^2.

The amounts of dyestuff mentioned above are referred to the the square meter of printed area, i.e. those surface regions are not taken into acount which are free from dyestuffs. It is now especially surprising that the improvement of shade depth is also obtained even on extremely light-weight silk qualities having a weight of less then 50 g/m^2, where already the conventional

dyestuff concentrations of about 0.75 g/m^2 will result in a shade depth which is identical on both sides of the fabric.

The man skilled in the art could not expect that an available dyestuff amount being about twice the normal amount would lead to this surprising results since already the normal amount of dyestuff will leave a dyestuff residue on the transfer sheet after the heat transfer printing.

The exact choice of the method parameters, specially the dyestuff available on the transfer sheet, will depend upon the weight and the construction of the silk fabric and the effects sought for. Generally, the results are outstanding if the dyestuff available will be 50 to 100 % higher than for the conventional heat transfer printing on polyester.

Still more brillant shades and generally good fastnesses are obtained with the following dyestuffs: C.I. Solvent Yellow 160, C.I. Disperse Red 55, C.I. Disperse Blue 56 and C.I. Disperse Blue 60.

It should be expected that these dyestuffs could not be used for the heat transfer printing of silk since they are only slowly subliming and must be transferred on polyester at 210°C as long as 60 seconds (see, i.e., for C.I. Disperse Blue 60: "Transfer printing of Polyester", Technical Headlines BR 1107, Yorkshire Chemicals Limited, Leeds, U.K.). Under these transfer conditions, a strong yellowing of the silk is observed even when swelling agents are absent, and the penetration of the textile material by the dyestuff is not sufficient.

It has surprisingly be found that, when these dyestuffs are mixed with other dyestuffs commercially used for the heat transfer printing of polyester, namely C.I. Disperse Yellow 54, C.I. Disperse Red 60 and C.I. Disperse Blue 331, a dyestuff system is obtained which gives under transfer conditions of 200 to 205°C at 40 seconds prints having an excellent penetration, good brilliance and outstanding fastnesses.

It has been especially surprising that the dyestuff C.I. Solvent Yellow 160, which is giving on natural silk prints of high brilliance but of a very bad light fastness (note 2), provides prints with good brilliance and a good light fastness (note 4.5), when the printing ink for making the transfer sheet contains about 30 to 70 % of this dyestuff, preferably about 50 %, together with 70 to 30 %, preferably about 50 %, of the dyestuff C.I. Disperse Yellow 54.

The transfer sheets which are typically made of paper, can be obtained in the well known conventional manner. This feature of the present method is a described per se in the already mentioned literature.

The method of this invention has the additional advantage that the great variety of pattern and design collections already existing at the transfer printers' can be used without any additional work or modifications.

The following examples are given to illustrate and explain in further details this invention and are not construed to limit it in any way. If not otherwise indicated, all percentages and parts refer to the weight. All numeric amounts and ranges, temperatures included, are to be understood as approximate values.

Where gravure printing is mentioned, other printing methods may as well be used such as offset or screen printing.

Example 1

A coating composition is prepared in a ball mill in which 39 parts of nicotinic acid amide and 6 parts of hydroxypropyl cellulose of the type "Klucel E", of Hercules Inc., dissolved in a mixture of 33 parts of toluene and 22 parts of ethanol, wherein 0.5 part of UVITEX OB has been previously dissolved, are charged. When all ingredients are well distributed, the so obtained coating mass is used to coat a base paper for transfer printing, having a unit weight of 60 g/m^2, in an amount giving after drying a quantity of nicotinic acid amide of 15 g/m^2.

This layer is now transferred in a conventional transfer printing calender on a silk fabric at 140°C and during a contact time of about 20 seconds.

On the so pre-treated textile material, a heat transfer printing paper is transferred at 200°C during a contact time of 30 seconds. After the heat transfer printing, the silk is rinsed with lukewarm water and finally dried. A brilliant print having the typical silk hand is obtained.

Example 2

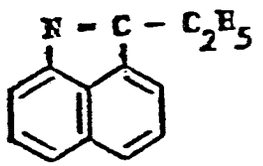
A heat transfer paper obtained by gravure printing, is coated with the coating composition of Example 1 in such amounts that the dried coating layer represents 10 g/m^2 of nicotinic acid amide.

The paper so obtained is transferred, on a conventional transfer calender, at about 205°C and during 25 seconds on a silk fabric not specially pre-treated. The printed material is rinsed with hand-warm water. After drying, a printed silk fabric with brilliant shades and the correct hand is obtained.

Example 3

A silk fabric having a weight of 70 g/m^2, desized and bleached as usual, is pretreated by dry-sensibilisation as shown in Example 1.

The pretreated fabric is covered with a transfer paper having a weight of 60 g/m^2 which has been printed by gravure printing with inks containing as a blue dyestuff 1,4-diisopropylamino anthraquinone, as a red dyestuff 1-amino-2-chloro-4-hydroxyanthraquinone (also 1-amino-2bromo-4-hydroxyanthraquinone may be used), and as a yellow dyestuff a compound of formula



The transfer printing is effected in about 30 seconds at 170°C.

A brilliant print with good fastnesses and excellent penetration of dyestuffs is obtained. There is no yellowing of any remaining white basic bottom shade on uncolored area regions.

Within two months after the transfer printing, the impregnating agent is rinsed from the fabric with water of 40°C and the fabric is dried on a tenter frame.

Example 4

A coating composition is prepared in a ball mill in which are charges 40 parts of benzamide and 5 parts of hydroxypropyl cellulose of the type "Klucel E", of Hercules Inc., dissolved in a mixture of 30 parts of toluene, 20 parts of isopropanol, 10 parts of ethyl diglycol and 17 parts of methyl ethyl ketone, wherein 0.5 part of UVITEX OB has been proviously dissolved. When all ingredients are well dispersed, the so obtained coating mass is used to coat a base paper for heat transfer printing, having a unity weight of 60 g/m^2, in an amount giving after drying an amount of benzamide of 15 g/m^2. This layer is now transferred in a conventional heat transfer printing calender on a silk fabric, quality "chiffon", desized and bleached as usual having a weight of 25 g/m^2.

The silk fabric thus pre-treated is covered with a transfer paper having a weight of 40 g/m^2 which has been printed by gravure printing with a printing ink containing the dyestuffs C.I. Disperse Red 60, C.I. Disperse Yellow 54 and C.I. Disperse Blue 331.

The transfer is made at 30 seconds at 205°C.

After transfer the silk is rinsed with lukewarm water and finally dried.

A brilliant print having a good fastnesses and a good resolution is obtained which could not be realized on an material having such a low weight, with

conventional printing methods. The penetration of the fabric by the dyestuffs is so deep that the upper and the reverse sides show substantially the same intensity.

The man skilled in the art will be aware that there are numerous variations and modification which may be put forward to the process and the other subjects of this invention, which may thus only be limited by the scope of the appending claims.

CLAIMS

1. - In a method of heat transfer printing of textile materials partially or fully consisting of natural silk fibers, from a transfer sheet carrying at least one dyestuff, at a temperature in the range of from 170° to 230°C without the use of a vacuum or a carrier gas, the improvement of treating said textile material prior to or simultaneously with the transfer printing step, with a dry composition, solid at room temperature, containing at least one impregnation agent which is heat stable, solid below 60°C and liquid in the range of from about 60° to about 200°C, colorless and non-attacking silk, selected from low low molecular molecular nitrogen containing organic substances.

2. - The method of claim 1 wherein said treating composition further contains at least one optical brighening agent being soluble in aromatic and/or aliphatic solvents but at most sparingly soluble in water.

3. - The method of claim 1 or 2 wherein said impregnating agent is selected from ε-caprolactam, nicotinamide, isonicotinamide, propylene urea, ethylene urea, glyoxal mono-urein, urea, 5,5-dimethyl hydantoin, imidazole, 2-methyl imidazole, N-methyl pyrrolidone, N-hydroxy succinic amide, benzamide, toluene sulfonamide, and mixtures from these substances.

4. - The method of claim 1 or 2 wherein said composition further contains a water soluble, film-forming binder, and is present as a layer on a transfer sheet.

5. - The method of claim 1 or 2 wherein a transfer sheet is used which carries, in order to produce highly brilliant prints having good fastnesses, from 1 to 2,5 gms of dyestuff per sq.meter of printed surface area, preferably about 1,5 g/m^2.

6. - The method of claim 1 or 2 wherein dyestuffs are used which are capable of being transferred with a yield of practically 100 % from the transfer sheet to the pre-treated textile material during 30 seconds at temperatures not in excess to 190°.

7. - The method of one or more of claims 1 to 6 wherein, in a first step, a dry pretreatment composition is heat transferred, from a transfer paper, to the silk textile substrate to be printed, and the pre-treated silk substrate is heat transfer printed, in a second step, with a coloured pattern previously printed on a transfer paper.

8. - The method of one or more of claims 1 to 6 wherein pre-treatment and printing are effected simultaneously, on contacting an untreated silk substrate under heat transfer conditions with a transfer paper carrying a surface coating comprising an impregnating agent as defined, a binder, and the coloured pattern to be transferred.