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(54) Title: PROCESS FOR PRINTING SUBSTRATES

(57) Abstract: The process for printing a substrate, comprises in succession: a stage of pre-treatment of the substrate; a stage of printing the substrate, wherein a pigmented ink is used; and a post-printing drying stage; wherein the pre-treatment stage comprises impregnation of the substrate in the presence of at least one polyvinylpyrrolidone, at least one acrylic resin having a low glass transition temperature, and at least one multivalent ion.



PROCESS FOR PRINTING SUBSTRATES

This invention relates to a process for printing substrates according to the precharacterising part of the principal claim.

More specifically the invention relates to a composition and a process for ink-jet printing, which can also be adapted to printing of the conventional type (silk screen, rotary) on various substrates, for example textile and non-textile substrates, making use of both organic and inorganic pigmented inks.

The invention also relates to the use of at least one polyvinylpyrrolidone in the process of printing on substrates, and a printed substrate obtained by the process.

At the present time the printing of substrates with pigments comprises processes and quality standards in terms of definition, brightness, intensity and reproducibility on different substrates, which can be improved in terms of economy of process, and in qualitative terms as described above, as well as in terms of reproducibility on different substrates.

In particular it is known that pigmented inks are not wholly appropriate for all types of substrate. For example there is a clear deterioration in the quality of printing on substrates such as viscose, elastomer and mixed elastomer substrates, polyamides, polyethylenes, PVC, nylon fibres and knitted fabrics.

One object of this invention is therefore that of providing a process for printing substrates with pigmented inks through which a high definition printing can be made with better and more reproducible qualitative standards.

A further object of the invention is to provide a process which makes it possible to use pigmented inks with substrates of all kinds.

Yet another object of the invention is to provide a composition for pre-treating a substrate before the printing process with pigmented inks.

A further object of the invention is to provide a process and a composition which are "green", that is they are not harmful to the environment and health.

These and other objects will be accomplished by providing a process and a composition for printing substrates made in accordance with the technical teaching in the appended claims.

The basic idea of the invention is to coat the substrates with film-forming substances to produce a cross-linked structure in the film obtained which acts as a

matrix for the pigments. It is important that the film should have the ability to be highly absorbent for water, should not be capable of being redissolved, should be stable to temperature and have good compatibility with most organic and inorganic substances.

The process for the printing of a substrate comprises in succession a stage of pre-treatment of the substrate, a stage of printing the substrate in which a pigmented ink is used, and a stage of post-printing drying.

In accordance with the invention the pre-treatment stage comprises impregnation of the substrate in the presence of at least one polyvinylpyrrolidone, at least one acrylic resin with a low glass transition temperature, and at least one multivalent ion.

This makes it possible to obtain high definition when printing, a brightness or liveliness and an intensity of colour which is appreciably better than that obtained by means of known processes. In addition to this it also makes it possible to obtain good to very good robustness of the printing without having to resort to subsequent stages of impregnating and fixing the printed substrate. This makes it possible to shorten the process, with considerable reductions in the consumption of energy and water.

The abovementioned process also has the advantage that it is "green", in that it provides for the use of chemical compounds which are not harmful to the environment or health.

Polyvinylpyrrolidone (PVP) is a substance which makes it possible to obtain a film which has the desired characteristics mentioned previously.

It must also be mentioned that the PVP film maintains its ability to absorb water after a possible drying stage, which is greatly to the advantage of the subsequent deposition of pigment during the printing stage, as the pigment is in an aqueous phase.

The best results are obtained with PVP having a molecular weight of between 900000 and 1500000. It has in fact been observed that the film-forming capacity of PVP increases with its molecular weight. The film obtained is poorly soluble in water, has good film-forming activity and furthermore has the advantage that it is toxicologically inert.

Also, working at a temperature above 100°C, a PVP film which has a

uniform structure and a good capacity to swell again absorbing large quantities of water is obtained in acceptable times. The film obtained is transparent, clear, strong and forms wholly around the fibre, that is over the entire outer surface of the fibre. PVP has the further advantage of having a high degree of compatibility, both in solution and in the form of film, with most inorganic salt solutions and with many natural and synthetic resins, as well as other chemical substances.

The role of the acrylic resin is to polymerise in the PVP film so as to create a porous structure within it. This porous structure makes it possible to prevent the migration of water-based pigments within the PVP film, but enables the latter to maintain its high capacity for the absorption and desorption of water.

An acrylic resin with a low glass transition temperature is used in the process because it yields a polymer structure having optimum flexibility, elasticity and porosity.

Preferably the glass transition temperature of the acrylic resin is a temperature substantially equal to -19°C .

Always according to the invention the pre-treatment stage is also performed in the presence of at least one multivalent ion. In fact it is known that multivalent ions, in particular di- and trivalent ions, can modify the surface properties of the substrate with a view to subsequent printing. These salts give rise to effective destabilisation of the pigment dispersion, causing it to aggregate and thus preventing migration. This has an important impact on the quality of printing, and in particular results in an extreme detail for the printed patterns, as well as high brilliance and intensity of colour in the printed image.

Preferably the multivalent ion is the calcium ion Ca^{2+} , to which the acrylic resin tends to bind. Calcium chloride CaCl_2 or calcium nitrate $\text{Ca}(\text{NO}_3)_2$ are advantageously used to add the Ca^{2+} ions.

The process according to the invention also makes it possible to print the pre-treated substrate without having to dry it, resulting in a process which is faster and cheaper in terms of energy and time.

It is however possible to provide that the pre-treatment stage also comprises a stage of pre-printing drying at a temperature of between 90°C and 170°C , preferably between 120 and 130°C , over a time of less than 5 minutes. More preferably the pre-treatment stage is carried out at a temperature of 120°C

for a time of 1 minute, with the view to drying but not drying out.

On the other hand, as far as the post-printing drying stage is concerned this is preferably performed at a temperature above 140°C. At temperatures of this order the drying stage also gives rise to polymerisation.

In the case where for commercial reasons it is necessary to have particular improvement in the robustness of the printing it is possible to provide a second stage of impregnation in the presence of at least one cross-linking agent after the post-printing drying stage, and a subsequent heat treatment stage.

It is also possible to provide that this second impregnation stage be also carried out in the presence of a polymer or pre-polymer with carboxyl groups, in addition to the cross-linking agent.

The use of cross-linking compound in the post-treatment stage is explained by the fact that even after printing the PVP film maintains its ability to absorb and desorb water.

Cross-linking agents in common use, such as for example of both blocked and non-blocked polyurethanes and isocyanates can be used in this stage.

However a cross-linking agent which comprises at least one carbodiimide is preferable. This compound, which replaces the cross-linking agents normally in use, makes it possible to maintain the "green" aspect of the process according to the invention.

According to another preferred aspect of the invention the pre-treatment impregnation stage is also carried out in the presence of at least one carbodiimide or an oxazoline. The addition of at least one of these chemical compounds during the pre-treatment stage makes it possible to carry out printing of the substrate without the need to dry it.

Oxazoline is more advantageous than carbodiimide, in that it makes it possible for the polymerisation temperature of the acrylic resin to be lowered further (to around 110°C with oxazoline, whereas with carbodiimide the polymerisation takes place at approximately 150°C).

It should be noted that the carbodiimide and oxazoline cross-link exclusively with carboxyl groups –COOH, which in our case derive from the acrylic resin. But it is possible to provide that these carboxyl groups derive from other pre-polymers or polymers.

The subsequent heat treatment stage may be carried out at relatively low temperatures over short times in comparison with known processes. It is preferably carried out at a temperature of between 150°C and 200°C for a time of between 30 seconds and 5 minutes, and more preferably at a temperature of 160°C for a time of between 1 and 2 minutes.

The process described above thus makes it possible to obtain substrates printed with pigmented inks with excellent results in terms of the detail and brightness of the printing.

This is due to the presence of the PVP film and the cross-linked acrylic resin, which offer an additional substrate for the placing of pigments together with the cellulose fibre. The presence of PVP film also makes it possible to increase definition when printing fabrics, and even go beyond saturation, that is the maximum definition permitted by the substrate being printed. In fact tests performed have made it possible to print at 1200 dpi on fabrics which generally only permit a maximum definition of 600 dpi.

Another advantage of the process according to the invention is that it makes it possible to use pigmented inks on substrates which are not appropriate for them. Given that the substrate is completely coated with the PVP film, sufficient printing takes place on the PVP film without the need to require the presence of a substrate which is compatible with the ink used.

This invention also relates to the use of polyvinylpyrrolidone having a molecular weight between 900000 and 1500000 in a process of printing with pigmented inks on a cellulose substrate. In fact in known processes for printing with pigments the use of polyvinylpyrrolidone has been limited to PVP of molecular weight 300000 or 600000 as a coadjuvant for the dyes. In this invention instead PVP is used to create a film all around the cellulose fibres which have to be printed.

A substrate printed using the process described above is also included within the scope of protection of this application.

The substrate can in fact be told apart from fabrics printed using known techniques through the improved brilliance and greater detail of the printed patterns, as well as the softness achieved.

This invention also relates to a composition which can be used in the

process described above.

This composition comprises water, at least one polyvinylpyrrolidone, at least one acrylic resin with a low glass transition temperature, and at least one multivalent ion.

Preferably the polyvinylpyrrolidone has a molecular weight of between 900000 and 1500000.

The acrylic resin preferably has a glass transition temperature which is substantially equal to -19°C .

According to a preferred aspect of the invention the multivalent ion is Ca^{2+} . In this case it is preferable that the composition should comprise calcium chloride CaCl_2 or calcium nitrate $\text{Ca}(\text{NO}_3)_2$ as a source of Ca^{2+} .

It is also advantageous for the composition to comprise at least one cross-linking compound, which may be one in common use, such as for example polyurethanes with isocyanates both blocked and non-blocked.

Preferably this cross-linking compound comprises at least one carbodiimide or one oxazoline.

In the case in which a carbodiimide or oxazoline is present, it is also desirable to provide a base, or more generally an alkali donor, to maintain the pH at a predetermined value; in particular with regard to toxicological and ecological aspects it is preferable to use 2-amino-2-methyl-1-propanol, known as alkamine.

Alkamine has the advantage that it is not an alkali which persists on the fibres that can come into contact with the skin, for example where they are used to produce fabrics for clothing, given that in the polymerisation stage described above the volatility of the alkamine through the effect of temperature gives rise to its decomposition to volatile ammonia and methyl-propanol, which is also volatile, allowing the substrate to return to a pH compatible with contact with the skin. This specification is provided due to the fact that the composition is suitable for being used in a process which does not provide for a final washing stage.

A second advantage of alkamine is that it inhibits the high reactivity of oxazoline or carbodiimide at pH below 9 - 9.5, maintaining that pH during the stage of preparation and storage of the composition during impregnation, to the advantage of the stability of the composition. The volatility of alkamine with temperature also makes it possible to restore the reactivity needed for cross-

linking in the polymerisation stage.

Preferably reactive polymers which are functionalised with oxazoline are used, in particular acrylic polymers known as Epocross WS 500 or Epocross WS 700.

In accordance with one variant of the composition which can be used during the second impregnation stage (after printing) this comprises an isocyanate and a branched polyethylenimine. The latter compound has the special feature that it possesses both primary amine functional groups and secondary amine functional groups as well as tertiary amine functional groups.

Preferably the polyethylenimine has a molecular mass of 750000 and has a ratio of 1/1/0.7 between the primary, secondary and tertiary amines.

A commercially available polyethylenimine is known by the name of Lupasol.

Examples of embodiments of the composition according to the invention, and the corresponding process, are presented below.

Example 1

The composition comprised water, powdered PVP of molecular weight 900000 (also known as K90) at a concentration of 13 g/L of solution, PN8 resin at 50 g/L and calcium chloride from 20 to 50 g/L.

Example 2

5 to 10 g/L of alkamine and between 20 and 80 g/L of carbodiimide were added to the composition in Example 1.

After the pre-treatment stage, carried out by impregnation, printing was performed using an ink-jet and was immediately followed by the heat treatment stage.

During heat treatment there was a gradual lowering of pH due to decomposition of the alkamine, which allowed the stage of cross-linking of the acrylic resin through carbodiimide to start.

Example 3

6 to 8 g/L of alkamine and 5 to 6 g/L of Epocross WS 500 were added to the composition in Example 1.

In the above concentrations the alkamine made it possible to maintain the pH at a value of 8.5 - 9, which made it possible to inhibit the Epocross WS500

during the pre-treatment stage, as explained in Example 2.

The process of printing was carried out in exactly the same way as in Example 2.

Example 4

The composition was prepared in water with 25 g/L of powdered K90 PVP, 20 to 80 g/L of PN8 resin, 20 to 80 g/L of carbodiimide, 20 g/L of polydimethylsiloxane and 5 to 10 g/L of alkamine, for a pH of 9 - 9.5.

This composition was used in a process performed in two separate stages.

In a first stage pre-treatment was carried out using the composition in Example 1. After pre-treatment, printing was performed, followed by a stage of drying the printed substrate.

After the drying stage a substrate was treated by impregnation with the composition described above, and then the heat treatment stage was carried out.

Example 5

The composition was prepared in water, dissolving 25 g/L of powdered K90 PVP, 25 g/L of Lupasol, 20 g/L of Ricosil MHS silicone and 20 g/L of non-blocked isocyanate known as poly HDI.

As in the previous example the pre-treatment stage was carried out using the composition mentioned in Example 1, and was followed by a printing stage and then a drying stage.

After drying a second impregnation of the substrate was performed using the composition mentioned above, followed by a heat treatment stage.

It should be noted that the composition according to the invention is particularly suitable for carrying out the process which is the subject of the invention, and therefore incorporates all the advantages already mentioned in respect of the quality of printing obtained in terms of colours, detail of the printing, and qualitative aspects such as robustness to light, washing, alkaline and acid sweat, and robustness to dry and wet rubbing

It will also be noted that the composition according to the invention is very much more ecological in comparison with the compositions already known in the sector. In fact, with the exception of the isocyanate, none of the compounds used offer any hazard to the environment and health. Also for this reason the variant of the composition containing isocyanate (as in Example 5) is less preferred than the

others, as it is the only one which includes a non-ecological component. All the others contain only so-called "green" compounds.

CLAIMS

1. Process for the printing of a substrate comprising in succession:
a stage of pre-treatment of said substrate;
a stage of printing the said substrate, in which a pigmented ink is used;
and
a post-printing drying stage;
wherein the pre-treatment stage comprises impregnation of the said substrate in the presence of at least one polyvinylpyrrolidone, at least one acrylic resin with a low glass transition temperature, and at least one multivalent ion.
2. Process according to claim 1, wherein the polyvinylpyrrolidone has a molecular weight of between 900000 and 1500000.
3. Process according to claim 1 or 2, wherein the acrylic resin has a glass transition temperature of -19°C .
4. Process according to one or more of the previous claims, wherein the multivalent ion is the calcium ion Ca^{2+} .
5. Process according to one or more of the previous claims, wherein the pre-treatment stage also comprises a stage of pre-printing drying at a temperature of between 90°C and 170°C .
6. Process according to claim 5, wherein the post-printing drying stage is carried out at a temperature above 140°C .
7. Process according to claim 5 or 6, comprising a second stage of impregnation in the presence of at least one cross-linking agent after the post-printing drying stage, and a subsequent heat treatment stage.
8. Process according to claim 7, wherein the second impregnation stage is also carried out in the presence of a polymer or pre-polymer containing carboxyl groups.
9. Process according to claim 7 or 8, wherein the cross-linking agent comprises at least one carbodiimide.
10. Process according to one or more of claims 1 to 4, wherein the impregnation stage is also carried out in the presence of at least one carbodiimide or one oxazoline.
11. Process according to claim 10, wherein the impregnation stage is also

- performed in the presence of oxazoline.
12. Use of polyvinylpyrrolidone of molecular weight between 900000 and 1500000 in a process for printing a substrate with a pigmented ink.
 13. Substrate printed by means of the process according to one or more of claims 1 to 11.
 14. Composition for the treatment of a substrate, for printing of the said substrate with pigmented ink, the said composition comprising water, at least one polyvinylpyrrolidone, at least one acrylic resin with a low glass transition temperature, and at least one multivalent ion.
 15. Composition according to the previous claim, wherein the polyvinylpyrrolidone has a molecular weight of between 900000 and 1500000.
 16. Composition according to claim 14 or 15, wherein the acrylic resin has a glass transition temperature of -19°C .
 17. Composition according to one or more of claims 14 to 16, wherein the multivalent ion is Ca^{2+} .
 18. Composition according to claim 17, comprising calcium chloride or calcium nitrate as a source of Ca^{2+} ions.
 19. Composition according to one or more of claims 14 to 18, also comprising at least one cross-linking agent.
 20. Composition according to claim 19, wherein the cross-linking compound comprises at least one carbodiimide or one oxazoline.
 21. Composition according to claim 20, also comprising alkaline as an alkali donor.

INTERNATIONAL SEARCH REPORT

International application No

PCT/IT2016/000127

A. CLASSIFICATION OF SUBJECT MATTER

INV. D06P5/00 D06P1/52 B41M5/52 C09D139/06
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D06P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No

PCT/IT2016/000127

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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