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(54) **Films for the transfer print**

(57) A polyvinyl alcohol film or composite film formed by a polyvinyl alcohol film coupled with a crosslinked silicone film, usable for the transfer print by colour sublimation on tridimensional articles by the vacuum technique.

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Description

[0001] The present invention relates to new films for the use in the transfer print through colour sublimation.

[0002] More specifically it relates to films which are used in the transfer print preferably on tridimensional articles, in particular having curved surfaces, such as for example pendant lamps or bell-shaped lamps, pots, bottles, plates, etc., or having irregular surfaces, such as for example ornamental articles.

[0003] It is known in the prior art that the transfer print on tridimensional articles having curved surfaces is carried out by techniques which allow, by applying vacuum, the complete adhesion of the film with the drawing to be transferred to the tridimensional support which is to be printed. For this kind of transfer print a rubber membrane, under the form of a case, can be used, in which the film to be printed, placed on the support which is to be printed, is introduced. Vacuum is made in the membrane and then it is transferred in an oven at a suitable temperature, so as to obtain the print by colour sublimation. This print technology of tridimensional articles has the drawback that the adhesion between the support and the film can vary depending on the article shape, wherefore the obtained article may show print defects. Besides the membrane must be periodically replaced with a frequency depending on the use conditions, for example on the temperatures at which the transfer print occurs, on the mechanical wear of the rubber by which the membrane is formed, etc. Another technology available on the market used in the transfer print by colour sublimation is the so called bag technology, wherein the vacuum is directly created inside the film. The film forming substance must have suitable mechanical properties to this purpose. The article to be printed is wrapped in the printed film which is sealed on one edge, for example by an adhesive or ultrasounds. The print quality on the tridimensional article depends also on the film flexibility. Furthermore, by using a film with unsuitable adhesion features during the vacuum creation step, folds in the film can form, or small air bubbles can be held between the film and the article. In these cases the print defects on the printed article are such that the obtained article has to be discarded.

[0004] In EP 921,014 in the name of the Applicant, the transfer print by colour sublimation is made by a composite film formed of a polymer film, which is metallized on one side with a thin aluminum layer, on which the colour drawing to be transferred is printed. The film allows to obtain the colour transfer with a high image definition and high chromatic yield. However the Applicant has found that by using this film to print tridimensional articles having curved surfaces, by the so called bag vacuum technology above mentioned, the film sometimes does not result perfectly adaptable to the particular shape of the article, wherefore the obtained print is defective.

[0005] The same drawbacks occur by using as a support of the drawing to be transferred also other substances of the prior art, such as for example paper.

[0006] From the above, it is clear that in order that the transfer print on tridimensional articles having curved surfaces can be made with the utmost definition and can be free from defects, it is necessary that the film has a perfect adhesion to the article, and therefore it must be formed by a substance which remains flexible at the temperature at which the transfer print occurs.

[0007] In this field of the prior art the need was therefore felt to have available a film, having on the surface which comes into contact with the article the printed drawing to be transferred, which put into contact by vacuum, in particular by the bag technology, with any tridimensional article having curved surfaces, warranted the colour transfer with high image definition and chromatic yield, without showing the drawbacks of the films used in the prior art for these applications.

[0008] This technical problem has been solved with the film of the present invention.

[0009] An object of the present invention is the use of a film of polyvinyl alcohol (PVA) having a thickness in the range 100-300 μm , and having on one surface a printed drawing to print articles, as described hereinafter, preferably tridimensional articles.

[0010] It has been found by the Applicant that when the film has a thickness lower than 100 μm the chromatic yield of the transfer process decreases and that with a thickness higher than 300 μm no further advantage is obtained as regards the chromatic yield or the image definition.

[0011] With chromatic yield it is meant the colour amount transferred on the article with respect to the colour amount which remains on the film after the transfer print. In practice the chromatic yield can be visually observed from the amount and quality of the colour transferred on the printed article with respect to the original one.

[0012] The film of polyvinyl alcohol allows to obtain a transfer print free from defects such as foldings, image definition, on tridimensional articles, independently from their shape, also with curved surfaces.

[0013] The PVA film is obtainable by known processes, such as for example by extrusion, and are available on the market. Another process is for example the following. A PVA solution in granules, as available on the market, is prepared, for example at 30-40% w/v in water, optionally in admixture with a hydroxylated organic solvent, preferably in an amount not higher than 5% by volume, for example aliphatic alcohols $\text{C}_1\text{-C}_3$, letting under mechanical stirring for 3-4 hours; the obtained paste is spread by a doctor blade, by using a spreading plant, on a surface of a plastic substance sheet having good mechanical properties, such as a polyester for example polyethylene terephthalate; subsequently, in line, by a suitable equipment, the obtained film is dried in an oven, preferably at about 100°C for

about 1-2 minutes. The PVA film is then separated from the plastic substance sheet used as support.

[0014] Preferably the surface of the plastic substance sheet which is spread with polyvinyl alcohol is previously treated with known methods so as to result antiadherent, in order to facilitate the removal of the polyvinyl alcohol film, after the passage in the oven.

[0015] The film of the present invention is used for the transfer print process of tridimensional articles, in particular having curved surfaces, by colour sublimation, by the vacuum technique, preferably by the bag technology, said process comprising the following steps:

- a) print of the coloured drawing to be transferred on a surface of the polyvinyl alcohol film, at a temperature in the range 80°-120°C, by mechanical compression, for example in a calender, by putting the polyvinyl alcohol film into contact with a sheet having impressed the coloured drawing with inks having thermoadhesive properties, said sheet being either of plastic substance such as to maintain good mechanical properties at the process temperatures, such as for example polypropylene or a polyester, polyethylene or polybutylene terephthalate type, or of paper,
- b) wrapping of the printed film of polyvinyl alcohol around the tridimensional article to be printed and vacuum creation between the film and the article,
- c) heating in an oven at 160°-190°C for a time comprised between 3 seconds and 5 minutes, preferably between 30 seconds and 2 minutes,
- d) recovery of the printed article and optional separation of the polyvinyl alcohol film.

[0016] After step b) a preheating at temperatures lower than those indicated in step c) can be effected in order to favour the film adhesion to the article.

[0017] Steps b) and c) of the above described transfer print process can be contemporaneously carried out.

[0018] The sheet used in a) can be printed by using the usual techniques, for example by rotogravure print.

[0019] It has been found by the Applicant that the PVA film cannot be used over 190°C, as it would instead be preferable for lowering the print process times and for obtaining the optimal colour chromatic yield.

[0020] More precisely it has been found by the Applicant that at temperatures higher than 190°C, for example 200°C, the PVA loses its properties and becomes rigid and brittle. In practice the PVA film loses its mechanical properties wherefore the film breaks during the transfer print.

[0021] Besides the Applicant has found that at temperatures of 160°-190°C at which the transfer print occurs according to the above mentioned process, the PVA film causes a deformation of the transferred image, which is vertically elongated. Therefore the drawing

to be transferred results changed with respect to the original one.

[0022] There is therefore the need to improve the transfer print quality by eliminating or substantially decreasing the image deformation obtained by printing with the polyvinyl alcohol film.

[0023] Furthermore, there is the need to operate at higher temperatures, higher than 190°C, to improve the chromatic yield of the obtained print and decrease the print time.

[0024] The Applicant has found a composite film which allows to solve this technical problem.

[0025] Another object of the present invention is a composite film, formed by a polyvinyl alcohol film and a crosslinked silicone film, wherein crosslinkable silicone is spread and directly crosslinked on the surface of the polyvinyl alcohol sheet, said composite having on the free surface of the polyvinyl alcohol film a printed drawing.

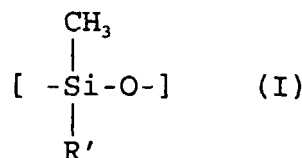
[0026] Said drawing is used to print a tridimensional article as described hereinafter.

[0027] The composite film has a thickness in the range 20-200 µm, preferably 40-150 µm, still more preferably 40-90 µm.

[0028] The silicone film thickness in the composite ranges from 15% to 80% of the total composite thickness.

[0029] The silicone resin in the composite is crosslinked. In order to obtain these crosslinked silicone resins, a crosslinkable silicon resin is used as specified below.

[0030] With silicone it is meant preferably a polymer formed by siloxane units of formula:



is meant, wherein R' is a monovalent hydrocarbon radical selected from one or more of the following: a hydrocarbon group from 1 to 10 carbon atoms or a halogenated hydrocarbon group from 1 to 10 carbon atoms; preferably an alkyl or alkoxy group having a number of carbon atoms from 1 to 4, or a phenyl group, said monovalent hydrocarbon radical preferably selected from the group comprising methyl, phenyl and chlorophenyl.

[0031] Crosslinkable organopolysiloxane compositions (silicone) are classified in the prior art in the following groups: organopolysiloxane compositions crosslinkable by condensation reaction, which are crosslinked by humidity; organopolysiloxane compositions crosslinkable by addition reaction, which are crosslinked at room temperature or by heating, and

organopolysiloxane compositions crosslinkable by radical reaction, which are crosslinked by heating.

[0032] An organopolysiloxane composition crosslinkable by condensation reaction easily crosslinks when it is in contact with atmospheric humidity giving a crosslinked silicone substance. In particular, by using a titanium type catalyst for the condensation reaction of an alkoxy-organopolysiloxane composition a crosslinked silicone substance is formed.

[0033] For organopolysiloxane compositions crosslinkable by addition reactions, crosslinking can be quickly carried out at room temperature or by heating.

[0034] A type of an organopolysiloxane composition crosslinkable by condensation reaction formed by an organopolysiloxane having at least two alkoxy groups linked to the silicon and at least two shorter alkenyl groups linked to the silicon in each molecule, and by an organopolysiloxane having at least two hydrogen atoms linked to the silicon in each molecule, and by a hydrosilylation catalyst, is known from USP 4,477,641 and JP-A64-2626.

[0035] Crosslinkable polysiloxane compositions are well known in the prior art and are available on the market. Preferably organopolysiloxane compositions crosslinkable by heating are used. See for example EP 664,322 and the prior art mentioned therein.

[0036] The crosslinkable polysiloxane resin is used under the form of a paste so that it is spreadable, for example by a doctor blade. For the spreadability the polysiloxane resin has a viscosity suitable for this application.

[0037] With the composite film of the invention it is possible to operate at temperatures in the range 200°-230°C, since it maintains the mechanical properties.

[0038] The Applicant has found that the composite film, differently from the polyvinyl alcohol, maintains the elastic properties and completely adheres to the article to be printed also at the above mentioned temperatures, at which the PVA film, as said, cannot be used since it loses the mechanical properties and therefore it breaks.

[0039] The composite according to the present invention facilitates the adhesion to the article to be printed already at temperatures lower than 100°C, so that it is possible to verify if the composite film is correctly placed on the article. This represents an advantage with respect to the polyvinyl alcohol since it has been found by the Applicant that with the polyvinyl alcohol one has generally to heat at temperatures higher than 100°C.

[0040] With the composite according to the invention it is possible to use in the transfer print films of polyvinyl alcohol having a thickness even lower than 100 µm which as such, as seen, could not be used since the chromatic yield obtainable with the process would be insufficient.

[0041] Besides with the composites of the invention the transfer print process can be carried out also at high temperatures, 200°-230°C as said, reducing the times

for obtaining a very good chromatic yield. The Applicant has found that by using only the PVA film it is not possible to operate at these temperatures since the film decomposes. Therefore, when the PVA film is used it is necessary to operate at lower temperatures and also an increasing of the transfer times does not allow to obtain chromatic yields comparable to those obtainable with the composite of the invention. Anyway an increasing of times implies a reduction of the process productivity.

[0042] As said, the higher temperatures which can be used in the transfer print process with the composite allow a better chromatic yield. Furthermore it has been found by the Applicant that the drawing reproduced on the final article results less deformed and that it has besides a better resistance to the sunlight action and to the mechanical abrasion.

[0043] The composite film according to the present invention can be obtained by using the process described hereinafter:

a') by spreading, using a spreading equipment, a polyvinyl alcohol paste at a concentration of 30-40% w/v on a support plastic substance sheet as previously defined, and regulating the thickness by a doctor blade in function of the desired polyvinyl alcohol film thickness in the composite,

b') by drying the film placed on the plastic substance sheet in an oven at 100°C for 1-2 minutes,

c') by spreading in line in the same plant, by a doctor blade on the free surface of the polyvinyl alcohol film a paste formed by a crosslinkable silicone polymer and crosslinking said silicone polymer in an oven at the temperature of 160°-180°C for 1-2 minutes,

d') by removing from the so obtained composite the support plastic substance sheet.

[0044] The composite film of the present invention is used for the transfer print process of tridimensional articles, in particular having curved surfaces, by colour sublimation, by the vacuum technique, preferably by the bag technology.

[0045] The transfer print process with the composite according to the present invention formed by a polyvinyl alcohol film and by a crosslinked silicone film, coupled in the above mentioned way, occurs as described for the polyvinyl alcohol film, with the difference that in step c) of the transfer print process by colour sublimation one operates at a temperature in the range 190°-230°C, preferably 200°-230°C. The times are the same indicated in step c). Therefore the transfer print process with the composite of the present invention comprises the same steps a), b) and d) previously described for the transfer print process with the polyvinyl alcohol film, while in step c) one operates at higher temperatures.

[0046] Also in this process steps b) and c) can be contemporaneously carried out.

[0047] A composite film obtained by overlapping a PVA film with a crosslinked silicone film cannot be used in the above mentioned temperature range since the two component films tend to separate.

[0048] By using the films of the present invention it is possible to reproduce by the transfer print the drawings on the surfaces of various articles, preferably tridimensional articles having curved surfaces, such as for example articles for pendant lamps, for example glass bells, article-holder boxes, pots, handles, ceiling light fixtures, ornamental articles, plates, etc..

[0049] The following examples illustrate the invention with non limitative purposes.

EXAMPLE 1

[0050] By compression transfer as indicated in the description, using as a matrix the same red-coloured polyethyleneterephthalate sheet on a surface by rotogravure print, a surface of the following films is coloured in red:

- A. Polyvinyl alcohol film having a 150 μm thickness;
- C. Composite film according to the invention formed by a layer of polyvinyl alcohol and of a layer of crosslinked silicone, having a total thickness of 75 μm and a silicone layer thickness of 25 μm . The silicone has been obtained by mixing the two compositions available on the market by Dow Corning Silastic® 9252/500P Part A and Silastic® 9252/500P Part B. The composite is coloured on the free surface of the polyvinyl alcohol layer.

[0051] The process for preparing films A and C is carried out as indicated in the specification by using the spreading system by a doctor blade.

[0052] The receiving support is an aluminum sheet pretreated by electrostatic painting with polyester powdered thermosetting paint, having a thickness of 75 μm .

[0053] 3 supports are used for each of the above mentioned films.

[0054] As a colour reference standard, samples formed by the same substance and painted with amounts of colour equal to 100%, 90%, 80%, 70%, 60%, 50% and 40% with respect to that applied on the samples printed by transfer.

[0055] The colour transfer process is carried out at the temperature of 205°C for the sample C and at 180°C for the sample A. The print time by sublimation is 30 seconds.

[0056] The colour transferred on the receiving support is compared with that of the standard ones and classified according to the following scale:

- 10 = Intensity of the red colour transferred on the samples of the pretreated aluminum sheet equal to that of the reference standard painted with a red amount equal to that present on the

films (100%) before the transfer print.

- 9 = Intensity of the red colour transferred on the samples of the pretreated aluminum sheet equal to 90% of that present on the films before the transfer print.
- 8 = Intensity of the red colour transferred on the samples of the pretreated aluminum sheet equal to 80% of that present on the films before the transfer print.
- 7 = Intensity of the red colour transferred on the samples of the pretreated aluminum sheet equal to 70% of that present on the films before the transfer print.
- 6 = Intensity of the red colour transferred on the samples of the pretreated aluminum sheet equal to 60% of that present on the films before the transfer print.
- 5 = Intensity of the red colour transferred on the samples of the pretreated aluminum sheet equal to 60% of that present on the films before the transfer print.
- 4 = Intensity of the red colour transferred on the samples of the pretreated aluminum sheet equal to 60% of that present on the films before the transfer print.

[0057] Each coloured support obtained by using the above mentioned films is visually compared with the reference standards. By giving the values as above indicated, the following results are obtained:

Aluminum sheet coloured with the polyvinyl alcohol film having a thickness of 150 μm A) : 7;

Aluminum sheet coloured with the composite film having a thickness of 150 μm C) : 9.

[0058] This experiment shows that with the composite according to the invention the chromatic yield in the transfer process is better than that achieved by using the polyvinyl alcohol film.

EXAMPLE 2 (comparative)

[0059] A round-shaped glass bell to be used for pendant lamps, having an height of about 25 cm, a diameter at the base of about 18 cm and of about 8 cm at the top, is printed with one colour drawing formed by a rose-shaped blue-coloured flower.

[0060] A paper support printed by known methods for example by rotogravure print is used.

[0061] The article is wrapped in the paper. The vacuum is made by a membrane device. The transfer print is carried out at the temperature of 190°C for a time of 3 minutes.

[0062] The article is taken away from the oven, cooled and unwrapped from the paper.

[0063] The printed drawing does not show deforma-

tions. The print shows discontinuities due to folds formed in the paper during the vacuum formation step.

[0064] The article is not commercially accepted.

EXAMPLE 3

[0065] The same bell of Example 2 is printed with the same drawing, by using a polyvinyl alcohol film having a thickness of 150 μm of Example 1 (film A). The polyvinyl alcohol film is printed with the drawing by using the process described in the present application. The film is wrapped around the article directly in an oven, by an equipment which places the film directly on the article by lowering it from the oven top by tools which maintain the film perfectly horizontal until the film comes into contact with the article. In the oven there are some devices in order to automatically create the vacuum between the film and the bell when the film, lowered from the top, completely covers the article.

[0066] The transfer print is carried out at 190°C and lasts three minutes.

[0067] On the printed article the chromatic yield and the drawing definition result acceptable but the drawing visually appears vertically deformed of about 20% with respect to Example 2. The printed flower clearly results lengthened.

EXAMPLE 4

[0068] Example 3 is repeated but by using a composite according to the invention formed by a polyvinyl alcohol layer and by a crosslinked silicone layer, having a total thickness of 120 μm and a silicone layer thickness of 60 μm , obtained as described in Example 1 for the film C).

[0069] The transfer print is carried out at 205°C for 1 minute.

[0070] The print quality is clearly better than that obtained with the polyvinyl alcohol film.

[0071] The printed drawing results vertically deformed with a lengthening of about 10% with respect to the printed drawing obtained in Example 2.

EXAMPLE 5

Evaluation of the resistance characteristics to light and to accelerate ageing.

[0072] Some plates of aluminum sheet, pretreated as described in Example 1, are divided in two groups. The first group is printed, at the temperature of 190°C, with a polyvinyl alcohol film having the thickness of film A) of Example 1 (150 micron). The other plates are printed at the temperature of 210°C with a composite film equal to that described sub C) in Example 1.

[0073] The print motif reproduces the pinewood grain effect.

[0074] On the printed plates the following tests are

carried out:

- Resistance to light (test ISO 2135:1984)
The test is carried out with a temperature of the black panel of 50°C. A part of the surface of the plates which are subjected to the test is covered and acts as reference surface.

After 1000 hours of exposure to the light of xenon lamps the results are evaluated, taking as a reference the blue scale. The test acceptability limit is 7. The plates printed with the polyvinyl alcohol film give in the test a value lower than 7, lower than the test acceptability limit. The plates printed with the composite film give a value of 8, therefore higher than the minimum value required to meet the test. Therefore the light-resistance of the plates printed with the composite film is clearly higher than that of the plates printed with the polyvinyl alcohol film.

- Accelerate ageing (test ISO 11341:1984)
Samples of plates of the two groups are subjected to treatment cycles with exposure to the combined cyclic action of the light of the xenon lamps and of the humidity, by dipping into water. A part of the surface of the treated plates is covered and is considered as a reference.

After 1000 hours of treatment the colour variation according to the blue scale is determined.

At the end of the test the colour variation of the plates treated with the polyvinyl alcohol film A) is evaluated lower than the 7 value of the blue scale. The colour variation of the plates printed with the composite C) is evaluated 8.

[0075] The results of these two tests show that the print of the plates printed with the composite film C) has a stability during the time and resistance to ageing higher than that of the plates printed with the polyvinyl alcohol film.

EXAMPLE 6

Print on a tridimensional article by using a polyvinyl alcohol film having a thickness lower than 100 micron.

[0076] A glass bell equal to that used in Example 2 is printed with the same one-colour drawing formed by a rose-shaped flower. In this case a polyvinyl alcohol film having a thickness of 80 micron is used. The film is applied to the article by using the procedure and conditions described in Example 3.

[0077] It is noticed that the film breaks during the transfer print process.

[0078] The test shows that the film thickness is not sufficient in this case to guarantee the mechanical properties which are required for its use in the transfer print process.

EXAMPLE 7

Print on a tridimensional article by using a composite C) film formed by a polyvinyl alcohol layer and by crosslinked silicone having a thickness lower than 100 micron.

[0079] Example 6 was repeated using a composite film C) having a thickness of 80 microns wherein the crosslinked silicone layer is 20 μm . The composite film is obtained as described in Example 1.

[0080] The film used in the transfer print process does not break.

Claims

1. Use of a polyvinyl alcohol film having a thickness in the range 100-300 μm having on one surface a printed drawing for the transfer print of articles by colour sublimation, by the vacuum technique.
2. Use of polyvinyl alcohol according to claim 1 wherein the article has a tridimensional shape.
3. Use according to claim 2, wherein the vacuum technique is the bag technology.
4. Use according to claims 2-3, wherein the tridimensional articles have curved surfaces.
5. A transfer print process which uses the polyvinyl alcohol film according to claim 1, comprising the following steps:
 - a) print of the coloured drawing to be transferred on one surface of the polyvinyl alcohol film, at a temperature in the range 80°-120°C, by mechanical compression, by putting the polyvinyl alcohol film into contact with a sheet having impressed the coloured drawing,
 - b) wrapping of the printed film of polyvinyl alcohol around the tridimensional article to be printed and vacuum creation between the film and the article,
 - c) heating in an oven at 160°-190°C for a time comprised between 3 seconds and 5 minutes, preferably between 30 seconds and 2 minutes,
 - d) recovery of the printed article and optional separation of the polyvinyl alcohol film.
6. A process according to claim 5, wherein the sheet with impressed the coloured drawing is of plastic substance or of paper.
7. A process according to claims 5 and 6, wherein steps b) and c) are contemporaneously carried out.
8. A composite film formed by a polyvinyl alcohol film and by a crosslinked silicone film wherein crosslinkable silicone is spread and crosslinked on one surface of the polyvinyl alcohol sheet, said composite having on the free surface of the polyvinyl alcohol film a printed drawing.
9. A composite film according to claim 8 having a thickness in the range 20-200 μm , preferably 40-150 μm , still more preferably 40-90 μm .
10. A composite film according to claims 8 and 9, wherein the silicone film thickness in the composite is in the range 15%-80% of the total composite thickness.
11. Use of the composite according to claims 8-10 for the transfer print of tridimensional articles by colour sublimation by the vacuum technique.
12. Use according to claim 11 wherein the vacuum technique is the bag technology.
13. Use according to claims 11-12, wherein the tridimensional articles have curved surfaces.
14. A transfer print process which uses the composite film according to claims 8-10 comprising steps a), b), d) of the process according to claim 5, and in step c) one operates at temperatures in the range 190°-230°C, preferably 200°-230°C.
15. A process according to claim 14, wherein steps b) and c) are contemporaneously carried out.
16. Printed articles according to claims 1-4 or according to claims 8-10.