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(54) MATERIALS AND PROCESS FOR MAKING DECALCOMANIAS

MATERIALIEN UND VERFAHREN ZUR HERSTELLUNG VON ABZIEHBILDERN

MATIÈRES ET PROCÉDÉ DE FABRICATION DE DÉCALCOMANIES

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GB-A- 1 312 635 GB-A- 2 289 866

US-A- 2 104 025

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Description

US 2004/0105966 (Zambelli),

Prior art

US 1420 347,

EP 1 166 983.

[0001] Ceramic decoration, as known, can be carried out using many techniques. In industrial production and for ceramics or glass baked at temperatures ranging between 500 and 1300° decalcomanias are also used.

[0002] The decalcomania decoration consists in a process which, having a lower cost than that of hand painting, has almost completely superseded this technique. The colors used in the decalcomania decorating process are obtained with frits of metals. One decalcomania system is the water-slide decalcomania or water-dip decalcomania, wherein, once the decoration has been transferred onto a workpiece, the latter undergoes a further firing process.

[0003] Currently, industrial decalcomanias are manufactured by means of a photomechanical film, with which a printing stereotype, enabling to print also color decalcomanias, is substantially made.

[0004] The photomechanical film is a means which is now used only in very restricted sectors and its production has become particularly onerous as a consequence of the very poor sales.

[0005] An use example of the photomechanical film is that used for Cromalin film, a trademark of Du Pont, which provides for the following processing steps.

[0006] The image to be reproduced is digitized by a scanner and separated into the four primary colors, for each separated color a transparent photographic film, i.e. a photomechanical film, is to be printed.

[0007] Through the four films of the primary colors, the printing of the initial image is effected, using Du Pont's Cromalin product as follows: a dedicated laminating machine transfers onto paper Du Pont's photosensitive Cromalin film, on which the photographic film of one of the previously separated colors (e.g. Cyan) is laid down, the sheet now consisting of the paper layer, Du Pont's Cromalin film and the transparent photographic film is exposed to UV light so that all the sheet portions not covered with the film will be cured by UV light, while leaving the film-covered portions intact; the covered portions will be slightly tacky and therefore suitable to receive and hold the Cyan pigment, which will be spread with a soft brush or a proper machinery.

[0008] The same operation will be repeated for the other three primary colors (Magenta, Yellow, Black).

[0009] Over the years various techniques for printing decalcomanias have been invented, such as those described in the patents:

US 3.956.558 (Commercial Decal Inc.),

EP 0 669 215 (Kyoto Ceramic Art Kyodokumiai),

EP 2 189 850 (BALTEA D.C. SRL),

[0010] The cited patents provide for the realization of proper devices or the use of special colors to print decalcomanias for ceramics to be baked.

[0011] In patent GB 2 289 866 (D1), it is disclosed a process for manufacturing decalcomanias which includes the following steps: separating the image, by means of a PC, into four files, each one pertaining to one of the four CMYK basic colours; coating and laminating a primer onto a release paper sheet; transferring, by means of an inkjet printer connected to a PC, the primer activator liquid relative to the file of the colour being processed on the laminating release paper; dusting with a ceramic pigment having a colour corresponding to the file of the colour being processed; cleaning the sheet; the described operations are repeated for the remaining three colours.

[0012] However, the process described in patent GB 2 289 866 does not provide that the primer and the primer activator liquid are those described in the present invention. Other prior art patents are GB 1312635 (Keramik WTB) and US 2 104 025 which describe a dry transfer to effect decalcomanias to mark either glass or ceramic articles; the patent in question differs from the cited documents in that the primer comprises acrylic resin, plasticizer of the butyl glycol type, oil and vegetable resin and in that the outer layer comprises a mixture of colophony and aromatic hydrocarbon.

Field of the invention

[0013] The object of the present invention is to provide the components and the manufacturing process by which the decalcomania production is executed using, inter alia, also a common inkjet printer.

Description of the invention

[0014] The object of the present invention is the production of color and non-color decalcomanias for ceramics and glass for baking at temperatures between 500° and 1300°, which are made by the use of sheets of laminating release paper coated with a primer layer transferred with a laminating machine onto a decalcomania transfer paper, and a common inkjet printer which uses a specific liquid activator of the "primer" instead of common ink.

[0015] According to the present invention, the "primer" to be coated on a paper with a high release index consists of:

- Acrylic resin for ceramic use;

- Plasticizer of the butyl glycol type loaded with plumbic, not plumbic or boric fluxes;
- Vegetable resin, such as oil of turpentine or shellac, so as to confer vulnerability to the primer film towards the activator liquid which is ethanol-based;
- Silicone oil whose function is to improve the coating on the release paper;

[0016] It may be possible to add or use separately a mixture composed of colophony and aromatic hydrocarbon with a ratio ranging from 1:1 to 1:3 dissolved at a temperature of 70/80°.

[0017] From carried out experiments, satisfactory results have been reached by using acrylic resin of the Mitsubishi BR 115 or 117 type, or others of the same family, with a percentage of acrylic resin and plasticizer ranging from 30/70% to 70/30% up to a 1:1 ratio, to which have been added a vegetable resin such as turpentine or shellac in a percentage between 5 and 40%, and silicone oil in a percentage ranging from 0,1 to 0,3%.

[0018] The compound in the form of paste thus obtained is accurately milled and prepared to be coated on the sheet of laminating release paper using a flexographic or lithographic or silkscreen or pad or inkjet or spray type printing machine.

[0019] After 12 hours, if necessary, the mixture comprising colophony and aromatic hydrocarbon, which are present in a ratio ranging from 1:1 to 1:3 and dissolved at a temperature of 70/80°, is laid down on the primer sheet.

[0020] After a 12-hour wait, the laminating release paper treated with the primer is ready to use.

[0021] According to the invention, the specific liquid functioning as a primer activator is formulated so as to respect the features of common inkjet printers and accordingly it has the following characteristics indispensable for a proper and long-lasting use:

- Fluidity suitable for the proper flowing within the ink feeding circuits without altering, under no circumstances, their normal operation.
- Nearly infinite drying time.
- Lack of aggressiveness towards printer mechanical components (made of either plastic or metal).

[0022] According to the invention, the formulation of the specific liquid serving as a primer activator is a composition of ethanol or methanol, butyl glycol or propylene glycol, vegetable oil, such as oil of turpentine or another oil with an adequate content of ricinoleic acid.

[0023] From carried out experiments it has been found that optimal results for the production of the specific liquid serving as a primer activator are obtained with a mixture having the following percentages:

Ethanol or methanol 70 %

Propylene glycol 10 %

Vegetable oil 20 %

5 **[0024]** Possible variations in the ratio between the components may be necessary, depending on the used acrylic resin which may have slightly different features from supplier to supplier.

10 **[0025]** According to the present invention, the decalcomania manufacturing process is based on the CMYK system.

15 **[0026]** The primer activator liquid concerning each of the files of one of the four colors will be sprayed by the inkjet printer and pigmented one at a time, each one on the relevant primer previously coated on the sheet.

[0027] The manufacturing process comprises the following steps:

20 **[0028]** The first primer layer is laid on the transfer paper sheet using a hot laminator machine at a temperature of 60/120°;

25 **[0029]** The primer activator liquid of the file related, for example, to Cyan is transferred by means of the inkjet printer connected to a PC which has separated the overall image into four files, each one concerning one of the four colors; once the primer activator liquid has been transferred in the areas defined by the file of the Cyan color and as the ethanol has completely evaporated, there will be an adequate "tac" or tackiness in the sheet areas which have been covered by the activator liquid so as to make the powdered ceramic pigment adhere, which will be evenly and carefully spread over the entire sheet surface with the help of a soft brush, a cotton wad or a proper machine.

30 **[0030]** At this point, the powdered ceramic pigment will tend to stick only on the areas where the inkjet printer has deposited the primer activator liquid and the image will be gradually detected and perfectly visible in all its details.

35 **[0031]** Before the subsequent lamination step, the sheet will be perfectly cleaned by removing all the residual ceramic pigment in the white areas of the sheet using soft cotton, making sure that this is free from impurities so as to avoid scratching the just printed image and, at the same time, guarantee the proper sheet cleaning and allow the perfect adhesion of the subsequent primer during the hot lamination process.

40 **[0032]** The described processing steps

- Coating the primer on a release paper
- 50 - Laminating the primer on the sheet
- Printing the file related to the color being processed by means of the inkjet printer which transfers the primer activator liquid in the areas defined by the file
- Starting a drying process, if necessary
- 55 - Dusting with a ceramic pigment having a shade suitable for the file of the color being processed
- Cleaning the sheet

will be identically repeated also for the remaining three colors, magenta, yellow, black.

[0033] Once the process for the last color, for example black, has been completed and the primer has been laminated again, the sheet, if necessary, will be collodionized and dried for at least one hour, afterwards the decalcomania is ready to be applied and put in an oven at a temperature suitable for the type of pigment used.

[0034] The four CMYK colors may be indifferently transferred in the sequence which an operator considers more appropriate.

Claims

1. Components for manufacturing decalcomanias particularly suitable for ceramics and glass for temperatures up to 1300°, **characterized in** being composed of:

a) A primer to be applied on paper with a high release index consisting of:

- Acrylic resin for ceramic use;
- Plasticizer of the butyl glycol type loaded with plumbic, not plumbic or boric fluxes;
- Vegetable resin such as oil of turpentine or shellac;
- Silicone oil;

b) A primer activator liquid usable with a common inkjet printer composed of: ethanol or methanol, butyl glycol or propylene glycol, vegetable oil such as turpentine oil or another oil with adequate ricinoleic acid content.

c) A mixture of colophony and aromatic hydrocarbon dissolved by heating.

2. Components for manufacturing decalcomanias particularly suitable for ceramics and glass for temperatures up to 1300° according to claim 1, **characterized in that** the primer includes acrylic resin of the Mitsubishi BR 115 or 117 type, or others of the same family, with a percentage of acrylic resin and plasticizer of 30/70%, to which are added a vegetable resin such as turpentine or shellac in a 5% percentage, and silicone oil in a 0,1% percentage.

3. Components for manufacturing decalcomanias particularly suitable for ceramics and glass for temperatures up to 1300° according to claim 1, **characterized in that** the primer includes an acrylic resin of the Mitsubishi BR 115 or BR 117 type, or others of the same family, in a percentage of acrylic resin and plasticizer ranging from 30/70% to 70/30% up to a 1:1 ratio, to which have been added a vegetable resin such as turpentine or shellac in a percentage between 5 and 40%, and silicone oil in a percentage

ranging from 0,1 to 0,3%.

4. Components for manufacturing decalcomanias particularly suitable for ceramics and glass for temperatures up to 1300° according to claim 1, **characterized in that** the primer activator liquid is a mixture having the following percentages:

70% ethanol or methanol, 10% propylene glycol, 20% vegetable oil.

5. Components for manufacturing decalcomanias particularly suitable for ceramics and glass for temperatures up to 1300° according to claim 1, **characterized in that** the mixture of colophony and aromatic hydrocarbon has a ratio of the components ranging from 1:1 to 1:3, the components being dissolved at a temperature of 70/80°.

6. Process for manufacturing decalcomanias particularly suitable for ceramics and glass which process comprises the use of the components of any one of claims 1 to 5, **characterized in that** said process includes:

- Separating the image, by means of a PC, into four files, each one pertaining to one of the four CMYK basic colors;
- Coating the primer on a release paper;
- Laminating the primer on the laminating release paper sheet;
- Transferring, by means of an inkjet printer connected to a PC, the primer activator liquid relative to the file of the color being processed on the laminating release paper,
- Starting a drying process, if necessary,
- Dusting with a ceramic pigment having a color corresponding to the file of the color being processed,
- Cleaning the sheet,
- Repeating the described operations in exactly the same way also for the remaining three colors, magenta, yellow, black.

Patentansprüche

1. Bestandteile für Herstellungs-Abziehbilder, die für Keramik und Glas bei Temperaturen bis zu 1300° besonders geeignet sind, **dadurch gekennzeichnet, dass** sie aus:

a) einer Grundierung, die mit einem hohen Freigabeindex auf das Papier aufgetragen werden soll und die aus:

- Akrylharz für Keramik Einsatz
- Plastifizierungsmittel von Butylglykol Typ

- beladen mit bleiernem, nicht bleiernem oder borartigen Schmelzmitteln
- Pflanzenharz wie Terpentinöl oder Schellack
 - Silikon Öl
- besteht;
- b) einem flüssigen Grundierung-Aktivator, der mit Injektionsdrucker benutzt werden kann und der aus: Ethanol oder Methanol, Butylglykol oder Propyläen-Glykol, Pflanzenöl wie Terpentinöl oder einem anderen Öl mit angemessenem Ricinolsäuren-Inhalt besteht;
- c) einer Mischung von Kolophonium und aromatischen Kohlenwasserstoff, die sich bei Hitze lösen, bestehen.
2. Bestandteile für Herstellungs-Abziehbilder nach Anspruch 1, die für Keramik und Glas bei Temperaturen bis zu 1300° besonders geeignet sind, **dadurch gekennzeichnet, dass** die Grundierung Akrylharz der Mitsubishi BR 115 oder 117, oder andere derselben Familie enthält, mit einem 30/70% Prozentanteil von Akrylharz und Weichmacher, denen man Pflanzenharz wie Terpentin oder Schellack in einem 5% Prozentsatz und Silikon Öl in einem 0,1% Prozentsatz hinzufügt.
3. Bestandteile für Herstellungs-Abziehbilder nach Anspruch 1, die für Keramik und Glas bei Temperaturen bis zu 1300° besonders geeignet sind, **dadurch gekennzeichnet, dass** die Grundierung Akrylharz der Mitsubishi BR 115 oder 117, oder andere derselben Familie enthält, mit einem Prozentanteil von Akrylharz und Weichmacher in einem Bereich von 30/70% zu 70/30% bis zu 1:1 Verhältnis, denen Pflanzenharz wie Terpentin oder Schellack in einem Prozentsatz zwischen 5 und 40%, und Silikon Öl in einem Prozentsatz von 0,1 bis 0,3% hinzugefügt worden sind.
4. Bestandteile für Herstellungs-Abziehbilder nach Anspruch 1, die für Keramik und Glas bei Temperaturen bis zu 1300° besonders geeignet sind, **dadurch gekennzeichnet, dass** die Grundierung-Aktivator-Flüssigkeit eine Mischung ist, die folgenden Prozentanteile hat:
- 70% Ethanol oder Methanol, 10% Propyläen Glykol, 20% Pflanzenöl.
5. Bestandteile für Herstellungs-Abziehbilder nach Anspruch 1, die für Keramik und Glas bei Temperaturen bis zu 1300° besonders geeignet sind, **dadurch gekennzeichnet, dass** die Mischung von Kolophonium und aromatischem Kohlenwasserstoff ein Verhältnis der Komponenten von 1:1 bis 1:3 hat. Die Komponenten werden bei einer Temperatur von

70/80° gelöst.

6. Verfahren für die Herstellung von Abziehbildern, das für Keramik und Glas besonders geeignet ist, und dessen Prozess den Einsatz der Bestandteile nach einem der Ansprüche von 1 bis 5 umfasst, **dadurch gekennzeichnet, dass** das Verfahren folgende Schritte umfasst:

- Trennung des Bildes in vier Files, durch einen PC. Jedes File betrifft eine der vier CMYK Grundfarben,
- Überzug des Abziehbildes auf Trennpapier;
- Laminieren des Abziehbildes auf Laminierung-Trennpapierblatt;
- Übertragen, durch Injektionsdrucker - verbunden mit einem PC - der Flüssigkeit des Grundierung-Aktivators auf das File der Farben und Verarbeitung auf Laminierung-Trennpapier;
- Wenn notwendig - Start eines Trocknung-Verfahrens;
- Bestäubung mittels eines Keramik-Pigments, indem es eine Farbe besitzt, die dem File der verarbeiteten Farbe entspricht,
- Reinigung des Blattes;
- Wiederholung der beschriebenen Verfahren in der genauen, gleichen Weise auch für die anderen drei Farben, Magenta, Gelb, Schwarz.

Revendications

1. Composants pour fabriquer des décalcomanies particulièrement appropriées pour céramique et verre pour des températures jusqu'à 1300°, **caractérisés en ce qu'ils sont constitués des éléments suivants:**

a) un apprêt à appliquer sur du papier à haut indice d'anti-adhésivité composé des éléments suivants:

- une résine acrylique pour usage céramique
- un plastifiant du type butylglycol chargé avec des fondants plombiques, non plombiques ou boriques;
- une résine végétale telle que l'huile de térébenthine ou la gomme-laque;
- une huile de silicone ;

b) un liquide activateur d'apprêt utilisable avec une imprimante à jet d'encre ordinaire composé des éléments suivants: éthanol ou méthanol, butylglycol ou propylène glycol, huile végétale par exemple huile de térébenthine ou autre huile avec une teneur discrète en acide ricinoléique

c) une mélange de colophane et d'hydrocarbure aromatique dissoutes à chaud.

2. Composants pour fabriquer des décalcomanies particulièrement appropriées pour céramique et verre pour des températures jusqu'à 1300° selon la revendication 1, **caractérisés en ce que** l'apprêt comprend une résine acrylique du type BR 115 ou BR 117 de la Mitsubishi, ou autres de la même famille, avec un pourcentage de résine acrylique et de plastifiant de 30/70%, à laquelle on ajoute une résine végétale telle que la térébenthine ou la gomme-laque dans un pourcentage de 5%, et de l'huile de silicone dans un pourcentage de 0,1%. 5
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3. Composants pour fabriquer des décalcomanies particulièrement appropriées pour céramique et verre pour des températures jusqu'à 1300° selon la revendication 1, **caractérisés en ce que** l'apprêt comprend une résine acrylique du type BR 115 ou BR 117 de la Mitsubishi, ou autres de la même famille, dans un pourcentage de résine acrylique et de plastifiant allant de 30/70% à 70/30% jusqu'à un rapport de 1:1, à laquelle on a ajouté une résine végétale telle que la térébenthine ou la gomme-laque dans un pourcentage entre 5 et 40%, et de l'huile de silicone dans un pourcentage allant de 0,1 à 0,3%. 15
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4. Composants pour fabriquer des décalcomanies particulièrement appropriées pour céramique et verre pour des températures jusqu'à 1300° selon la revendication 1, **caractérisés en ce que** le liquide activateur d'apprêt est un mélange avec les pourcentages suivants: 30

éthanol ou méthanol 70%, propylène glycol 10%, huile végétale 20%. 35

5. Composants pour fabriquer des décalcomanies particulièrement appropriées pour céramique et verre pour des températures jusqu'à 1300° selon la revendication 1, **caractérisés en ce que** la mélange de colophane et d'hydrocarbure aromatique présente un rapport des composants allant de 1:1 à 1:3, les composants étant dissous à une température de 70/80°. 40

6. Procédé pour fabriquer des décalcomanies particulièrement appropriées pour céramique et verre lequel procédé comprend l'usage des composants de l'une quelconque des revendications 1 à 5, **caractérisé en ce que** ledit procédé comporte les étapes consistant à: 45
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- décomposer l'image, au moyen d'un PC, en quatre fichiers, chacun concernant un des quatre couleurs de base CMYK;
- enduire un papier antiadhésif avec l'apprêt; 55
- laminer l'apprêt sur la feuille de papier antiadhésif à laminage,
- transférer, à l'aide d'une imprimante à jet d'en-

cre connectée à un PC, le liquide activateur d'apprêt concernant le fichier de la couleur en train d'être traitée sur la feuille de papier antiadhésif à laminage,
- si nécessaire, commencer un procédé de séchage,
- saupoudrer avec un pigment céramique ayant une couleur correspondante à le fichier de la couleur en train d'être traitée,
- nettoyer la feuille,
- répéter les opérations décrites exactement de la même manière aussi pour les trois couleurs restantes, magenta, jaune, noir.

REFERENCES CITED IN THE DESCRIPTION

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