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(54) **Continuous or discrete sheet printing process for liquid crystals, thermochromic and/or photochromic materials**

(57) A continuous or discrete sheet printing process of dyestuffs is disclosed, said dyestuffs being selected from the group comprising liquid crystals, thermochromic and photochromic materials for displaying normally concealed wordings and/or figures and/or signs. The process is versatile in its various printing steps, the kind of dyestuff to be applied and the support to be printed. A label, card or sheet obtained by the process is also disclosed, for various applications of preservation, display of concealed messages, anticounterfeit, correct temperature for using products containing them and for promotional and advertising purposes.

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Description

[0001] The present invention relates to a continuous or discrete sheet printing process of dyestuffs selected from the group comprising liquid crystals, thermochromic or photochromic materials for displaying wordings and/or figures and/or signs that are normally concealed.

[0002] It is known that in view of the more and more sophisticated counterfeit of products it is necessary to develop anti-counterfeit techniques that are implemented in displaying messages that are normally hidden so as to allow buyers and sellers to identify the original products.

[0003] The need of markings adapted to identify the best preservation conditions of food or cosmetic products is also felt. Indeed according to the nature of the goods it may be required that a suitable marking, such as a colour, appears or disappears so as to indicate an environment adapted to cause product degradation or viceversa its best preservation condition.

[0004] Figures and signs of the above mentioned kind are also used to cover hidden messages, thus constituting also advertising or promotional media.

[0005] For the above mentioned requirements, some printing processes were developed in the past years, allowing to apply colesteric liquid crystals to labels.

[0006] It is well known that colesteric liquid crystals are substances changing colour through the entire range of the visible spectrum with the variation of temperature within a precise time interval that can be determined by a suitable variation of the composition of said liquid crystals.

[0007] In the document IT-A-1 094 343 a continuous printing process of microencapsulated liquid crystals on labels is disclosed, by carrying out continuously in the various stations of printing presses the following steps: printing a black background with an ink based on an organic solvent; printing the label wordings with an ink having a high evaporation speed; two cycles of silk screening application of microencapsulated liquid crystals, said steps being alternated with drying steps in corresponding ovens.

[0008] Although this innovative method gave optimal results and continues to be widely used, it requires however considerable attention and precision in its practical accomplishment, showing problems relating to stockage of liquid crystals and to the need of perfect timing in the drying steps so as to avoid a negative effect on the stability of liquid crystals.

[0009] An approach for solving the problems shown by the foregoing method is disclosed in Italian patent application 21260 A/90 relating to a process consisting of three printing stages: the first is a silk screening print of a black background by an ink in aqueous emulsion, allowing to avoid use of troublesome solvents for the subsequent printing step, consisting in silk screening printing of a layer of microencapsulated liquid crystals, while the last printing step is the silk screening overprint

of wordings or graphic symbols on labels so as to obtain a sandwich structure. However this process, even if it solves on the one hand the above mentioned problems, on the other hand requires that the above described structure is strictly respected, as it results not suitable for materials requiring printing conditions other than those for the liquid crystals.

[0010] For the various objects stated in the introductory part of this description, some dyestuffs were indeed developed showing different application requirements as they will be widely described hereinafter.

[0011] Among these materials the thermochromic dyestuffs are known in the art, consisting of special thermally sensitive substances enclosed in microcapsules having the features of appearing coloured under a determined temperature and becoming colourless above it, returning to the coloured stage when temperature goes again under the determined one. These colours are known under the name Thermocolor® and are marketed by Applicant. They show different shades, but above all they have the peculiar feature of having different intervals of temperature variations thus allowing versatility of use.

[0012] Photochromic dyestuffs are also known in the art, and they are sensitive to the light at the corresponding wavelengths and to the range of ultraviolet rays (UVA, UVB, UVC) namely that are normally transparent but under the action of the energy corresponding to the cited wavelengths they change their molecular structure by showing a colour and return to the colourless condition at the interruption of this energy source. Among these materials, those known in the trade with the indication Suncolor® marketed by Applicants, are well-known.

[0013] An object of the present invention therefore is to provide a continuous or discrete sheet printing process that is versatile in connection with the various printing stages, the kind of dyestuff to be applied or support to be printed.

[0014] It is also an object of the invention to provide for a printing process allowing to use supports printed in environments with different temperatures.

[0015] The present invention attains the above objects by providing a continuous or discrete sheet printing process of dyestuff on the support characterized by the following steps:

a) printing the dyestuff and b) printing wordings and/or signs and/or figures, wherein:

1) if the dyestuff consists of liquid crystals, then phase a) occurs first and thereafter phase b) in case of printing continuous or discrete sheet paper, while for sheets of polymeric material or other transparent support either the sequence b-a or a-b may occur,

2) if the dyestuff is thermochromic, then the phases occur in the sequence b-a in case of

printing continuous or sheet paper, while for sheets of polymeric material or other transparent support either the sequence a-b or b-a may occur, or phase a) alone as wordings and/or signs and/or figures,

3) if the material is photochromic, then it occurs only phase a) as wordings and/or signs and/or figures.

[0016] The present invention will be now described in detail with reference to some embodiments as illustrative and non-limiting examples of the invention.

[0017] The printing process according to the present invention can be carried out at any speed on supports printed as continuous or discrete sheet by using flexographic, rotogravure, silk screening, typographic or offset printing machines, preferably silk screening and flexographic ones. Said support to be printed according to the invention may be a paper or polymeric material preferably selected from the group consisting of polyvinyl chloride, polyester and polypropylene. This support may be of any form and more particularly anyone selected among labels, cards, tags (even plastified) and sheets. The process according to the invention may also provide for a step of printing a background of one or more colours, more particularly when the dyestuff corresponds to the sign, wording or figure to be displayed under the action of the proper radiation. Said dyestuff may be chosen among liquid crystals, thermochromic materials like Thermocolor® and photochromic materials like Suncolor®.

[0018] The liquid crystals may be derivatives of cholesterol or other synthetic materials like the chiral-nematic ones, and for the purposes of the invention they are used in the form of microcapsules as they are well suited for being applied by means of printing processes.

[0019] In one embodiment of the invention the liquid crystals are the used dyestuff and in this case the process according to the invention, before the step of printing the wordings and/or signs and/or figures, provides for printing a black background on the continuous or discrete sheet of paper with low toxicity inks which are also scarcely aggressive to the subsequent steps of applying the liquid crystals, while in case of printing sheets of polymeric material or other transparent support, the liquid crystals are printed first and then the above mentioned black ink. The application of said ink may be effected at any desired speed by known silk-screening, flexographic, rotogravure or typographic printing machines and preferably by silk-screen machines carrying out several application layers.

[0020] In a second embodiment the process of this invention uses encapsulated thermochromic materials of the kind Thermocolor®. These materials are derivatives of pentylopyrroles or hexa-aryl-methane as non-limiting examples. The Thermocolor® materials are dyestuffs having a critical colour change range under which they are dark and above they are transparent.

This critical range, generally of several degrees, for instance eight degrees, may be comprised in a wide range of temperatures from below 0°C up to very high temperatures. According to the second embodiment it is possible first to print the wordings and/or signs and/or figures and then to apply the thermochromic material so that when the temperature reaches the colour change range, the material becomes transparent and the underlying wordings and/or signs and/or figures would be visible. In another case, the thermochromic material itself may constitute the wording or figure and therefore the support is not printed and the step of printing the wordings, signs and/or figures is coincident with the application of the thermochromic material. Preferably the process provides for the application of only one layer of thermochromic material.

[0021] In a third embodiment of the invention the invention, provides for the application of the photochromic material of the kind Suncolor®. These photochromic materials as non-limiting example, are derivatives of spiropyranes or indenone oxides which are visible when subjected to ultraviolet or visible spectrum radiation. For instance it is possible to make labels or cards in which the photochromic material takes a determined colour when exposed to solar light, which is compared with a reference scale indicating the various degrees of intensity of UV rays. The process of the invention thus provides for the application of said photochromic material only on portions of the label or card that should be visible under ultraviolet or solar source without needing any particular support to make detection of the hidden signs easier. This printing process provides for the application preferably of one layer only of photochromic material and the support may optionally be printed with background inks, if desired.

[0022] It is therefore clear that in all the above described cases the process of the present invention is very simple as it requires at most two printing stages avoiding compulsory structures preventing to modify the process according to the requirements of the various dyestuffs to be applied. The present invention allows also to carry out the dyestuff application at any desired moment, even on preprinted supports.

[0023] The process according to the invention provide also that the above described liquid crystals and the thermochromic materials may be applied on the same support, namely the possibility of printing them one on the other or one beside the other, so as to obtain structures with special effects. The application on the same support may also be effected with two or more thermochromic materials having a different critical colour change range. Moreover it is possible to apply a finishing upper layer making more brilliant and apparent the effect created by the underlying dyestuff.

[0024] A typical composition comprising various dyestuffs may also include additives such as for instance stabilizers, UV-absorbers and alcoholic solvents.

[0025] From the foregoing detailed description it is

clear that many variations, substitutions and additions may be resorted to the process of invention without departing however from its scope as defined in the appended claims.

Claims

1. Continuous or discrete sheet printing process of dyestuff on a support characterized by the steps of a) printing the dyestuff and b) printing of wordings and/or signs and/or figures, wherein:

1) if the dyestuff consists of liquid crystals, then phase a) occurs first and thereafter phase b) in case of printing continuous or discrete sheet paper, while for sheets of polymeric material or other transparent support either the sequence b-a or a-b may occur,

2) if the dyestuff is thermochromic, then the phases occur in the sequence b-a in case of printing continuous or sheet paper, while for sheets of polymeric material or other transparent support either the sequence a-b or b-a may occur, or phase a) alone as wordings and/or signs and/or figures,

3) if the material is photochromic, then it occurs only phase a) as wordings and/or signs and/or figures.

2. Process according to claim 1, characterized by the step of previous printing a background before effecting phase b).

3. Process according to any of claims 1 and 2, characterized in that, if the dyestuff consists of liquid crystals, then the process before step b) in case of printing continuous or discrete sheets of paper, provides for a step of printing a black or dark background, while in case of printing sheets of polymeric material or other transparent support, said process provides for printing first the liquid crystals and then said black or dark background.

4. Process according to any of the preceding claims, characterized in that the printing steps are alternated with drying steps

5. Process according to claim 1 characterized in that the printing steps are carried out by machines selected from the group comprising flexographic, silk-screening, rotogravure, typographic and offset machines.

6. Process according to claim 5, characterized in that the printing machines are silk-screening and flexographic machines.

7. Process according to any of the preceding claims,

characterized in that the support is a paper or polymeric material, said polymeric material being preferably selected from the group comprising polyvinylchloride, polyester and polypropylene.

8. Process according to claim 1 characterized in that the liquid crystals are esters derivatives of cholesterol or other synthetic substances.

9. Process according to claim 1 characterized in that the thermochromic materials are derivatives of pentylpyrroles or hexaarylmethane such as those marketed under the name Thermocolor®.

10. Process according to claim 1 characterized in that the photochromic materials are derivatives of spiropyranes or indenone oxide and with critical variation range in the wave range of visible or ultraviolet light, such as those marketed under the name Sun-color®.

11. Process according to any of the preceding claims, characterized in that the liquid crystals and the thermochromic materials are printed on the same support, one on the other or one beside the other.

12. Process according to any of the preceding claims, characterized in that thermochromic materials with different colour change range are printed on the same support.

13. Process according to claim 1 characterized in that the composition containing the dyestuffs comprises stabilizers, UV-absorbers and alcoholic solvents.

14. Label, card or sheet obtained by the process according to any of claims 1-12.

15. Use of label, card or sheet according to claim 14 as an anti counterfeit device, indicator of preservation conditions, indicator of correct use temperature and promotional and advertising medium.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 99 20 0063

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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A	GB 1 332 185 A (XEROX CORP) 3 October 1973 (1973-10-03) * page 3, line 122 - page 4, line 9 *	1,14,15	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B41M G03C C09K
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		4 October 1999	Markham, R
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 20 0063

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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04-10-1999

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