



Marking Plastics Substrates

5 The present invention relates to marking plastics substrates and in particular to marking plastics substrates using a thermal transfer printing process.

10 Printed markers comprising plastics substrates printed with indicia conveying data are known and widely used. For example printed plastics sheaths or flat strip tags are widely used for identifying electric cables. The known types of sheaths or strip tags are passed in unprinted "feedstock" form through conventional thermal transfer
15 printing apparatus in order to be marked with the required predetermined indicia. In conventional thermal transfer printing, pressure and heat are applied to a printing ribbon registering against the plastics feedstock, such that a print composition carried by the ribbon is
20 transferred to the feedstock. Conventionally, thermal transfer ribbons rely upon a wax or resin to transfer the dry ink onto the feedstock substrate.

25 This method of marking has inherent drawbacks; for example, the ink can be removed by means of heat, chemical action or abrasion. This can result in important printed markers becoming unreadable. Furthermore, over time, the action of ultra violet radiation on pigments in the ink can result in the mark fading.

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US patent number 5620508 describes a heat meltable solid ink comprising a mixture of carbon black and an oil-soluble dye bound together in a resin. Heat and pressure are applied to transfer the ink to a substrate. The oil-soluble dye acts as a disbursant so that the colouring agent on the resin are less likely to separate, and also improves the coating properties of the ink so as to provide a uniform ink layer on the substrate surface.

US patent number 4784905 describes a print carrier comprising a support layer on which is provided a thermal fusable ink layer. The thermal fusable ink layer consists of a carrier material, a colouring agent and an image gradation control agent, all contained in a fine porous resin material. The image gradation control agent is disbursed in the ink layer in the form of a network. Upon the application of heat, the colouring agent seeps from the network structure of the image gradation control agent, then seeps from the fine porous resin structure to gradually permeate a receiving sheet so that a transferred image is formed thereon. The image gradation control agent is not transferred to the receiving sheet with the colouring agent, but remains in the print carrier.

C.A. Bruce et al "thermally sensitive ribbon for laser transfer printing" IBM Technical Disclosure Bulletin, Volume 18, number 10, March 1976, page 3416 describes a laser transfer printing arrangement whereby a laser is used to transfer a heat sensitive formulation contained on a transparent substrate on to a surface. A very high print density can be achieved (with the minimum amount of energy

from the laser source) by incorporating into the formulation crystal violet dye, which is combined with other dyes to give a black image.

5 UK patent application number GB2083726A describes a process for creating a colour image of an object on a sheet of, for example, paper. The process involves analysing the object to obtain a set of signals which is representative of the shape and colour of the object and transferring a number of
10 dyes onto the sheet (according to the signals) from respective support layers by heating using a scanning laser.

European patent application number EP-A-0365222 discloses
15 an arrangement in which several donor sheets are used to sequentially apply dye to a substrate (using a flash gun). Each donor sheet comprises a number of colourants which are transferred to the substrate as a mixture.

20 US patent number 4661393 describes a heat transfer recording ink sheet comprising a substrate carrying an ink composition layer. When heat and pressure are applied to the ink sheet through a thermal printing head, the applied heat is transferred through the substrate to reach the ink
25 composition layer which melts and is thus transferred to a receiver sheet. The ink composition layer consists of a transfer component and a filling agent. The transfer agent consists primarily of a colouring agent carried by a supporting composition such as a resin and the filling
30 agent comprises organic or inorganic fine powders which act as a barrier to the migration and release of the transfer

component during transfer recording. The filling agent effectively limits the amount of colourant which is transferred to the receiver sheets, so that the ink sheet can be re-used.

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International patent application WO-99-11466 describes a black ink consisting of a black colour layer coated on a substrate, the black colour layer comprising a mixture of dyes and binders which together form a mark on a receptor
10 sheet in response to heat and pressure application.

The improvements have now been devised to marking plastics substrates.

15 A method of printing onto a plastics substrate, the method comprising the steps of:

- (i) providing a print carrier carrying a printing composition comprising first and second colourant materials; and
- 20 (ii) registering said print carrier against said substrate and applying heat and pressure thereto so as to transfer in a single step said printing composition, including both said first and second colourant materials, said substrate
25 characterised in that said printing composition is a unitary composition comprising said first and second colourant materials, and in that said first colourant material is arranged to penetrate into said plastics substrate to form a
30 substantially permanent mark below the surface of the substrate, and said second colourant

material is arranged to adhere to the surface of the substrate overlaying the substantially permanent mark.

5 Also in accordance with the first aspect of the invention there is provided a print carrier carrying a releasable printing composition, which printing composition comprises a first and second colourant materials, said printing composition, including both said first and second colourant materials, being capable of being transferred in a single
10 step to a plastic substrate upon application of heat and pressure to said print carrier when it is registered against said substrate; characterised in that said first colourant material is arranged to penetrate into the
15 plastics substrate to form a substantially permanent mark below the surface of the substrate, and in that the second colourant material is arranged to adhere to the surface of the substrate overlaying the substantially permanent mark.

20 The invention enables a single stage printing process to be used to print a marking of predetermined configuration onto a plastics substrate comprising a sub-surface marking and corresponding surface printed marking simultaneously. The dual nature of the marking provides advantages in terms of
25 durability, particularly for use in harsh environments , or situations where the mark is liable to be subject to chemical action, or abrasion in the normal course of events or in cases of unauthorised tampering.

30 The invention is particularly suitable for use in providing plastics printed markers for identifying articles.

According to a second aspect the invention therefore provides a plastics printed marker comprising a plastics substrate having a printed mark formed by registering against said substrate a print carrier carrying a unitary printing comprising first and second colourant materials and applying heat and pressure thereto to release in a single step said printing composition from said print carrier comprising:

- (a) a first, sub-surface portion of a first colourant material penetrated into the substrate, and;
- (b) a second, surface portion of a second colourant material adhered to the surface of the substrate overlaying the sub-surface portion of the mark.

The printing composition carried by the print carrier comprises the first and second colourant materials and also, preferably, a plastics material facilitating binding with or penetration into the substrate. It is believed that a print carrier carrying such a printing composition is both novel and inventive per se, and thus provides a further aspect of the invention. This is particularly believed to be the case for such a print carrier for use in thermal transfer printing onto plastics substrates.

In one embodiment, the plastics material comprising the printing composition may be the same as the plastics material comprising the substrate.

In an alternative embodiment, the plastics material comprising the print composition may be different from the plastics material comprising the substrate. In this

instance, the plastics material transferred from the print carrier and bound with, or penetrated into, the substrate will be identifiable in the resulting printed marker, at least upon microscopic inspection.

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It is preferred that the plastics material carried by the print carrier comprises a thermoplastic material, such as PVC, a polyolefin or the like, more preferably, a homopolymer material.

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The printed marker according to the invention preferably comprises a plastics strip or length of plastics tubing (which tubing may be heat shrinkable or non-heat shrinkable). Where the printed marker is in the form of plastics tubing, it is preferred that the feedstock is in the form of flattened tubing. This facilitates ease of printing.

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It is preferred that the print carrier comprises a plastics film (desirably comprising polyester) preferably of a thickness substantially in the range 4-15 μ m (microns), more preferably approximately 6 μ (microns). The print carrier is capable of separating from the print composition it carries during the thermal transfer printing process. Desirably the print carrier is wound from a reel store.

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The print composition (or ink) carried by the print carrier is preferably touch dry. The first and second colourant materials are preferably relatively dark in colour and may for example be blue or black. The colourant materials may for example comprise dyes of suitable composition to ensure

that one penetrates the substrate and the other adheres to the surface of the substrate during the printing process.

5 One or other (or both) of the first and second colourant materials may comprise a mixture or composition of a plurality of dyes.

10 It is preferred that the printing composition comprises the colourant materials and the plastics material bound in a matrix material. The printing composition is preferably applied to the print carrier as a layer. The matrix material may, for example, comprise a relatively soft, high molecular weight material such as a wax or wax-like material.

15 The thermal transfer printer may be arranged to print any predetermined indicia mark upon the substrate.

20 The invention will now be further described in a specific embodiment by way of example only and with reference to the accompanying drawings in which:

Figure 1 is a plan view of a first embodiment of marked substrate according to the invention;

25 Figure 2 is a schematic sectional view of a prior art marked substrate;

Figure 3 is a schematic view of thermal transfer printing apparatus for operating the process of the invention; and

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Figure 4 is a schematic sectional view of a substrate marked in accordance with the invention.

Referring to the drawings, Figure 1 shows "feedstock" in the form of a length of flattened heat-shrinkable plastics tubing 1 (or sheathing); following printing of a respective portion of the tubing 1 a marked indicium 2 is identifiable on the surface.

Referring to Figure 2, when applying conventional thermal transfer printing techniques, a layer of printed ink 3 adheres to the surface of tubing 1. It is possible intentionally, or accidentally, to remove the printed ink layer 3 from the underlying plastics tubing substrate 4 by abrasion, chemical action or degradation due to exposure to ultra-violet radiation.

The apparatus for printing of the tubing substrate 1 is shown in Figure 3 and generally designated 4. The apparatus comprises a drive roller 35 which draws feedstock tubing 1 from a reel store (not shown) to extend past a thermal printing head 36 of the apparatus. Simultaneously, a printer ribbon 38 is fed from a store of unused ribbon 39 extending past printing head 36, subsequently being wound of reel 40. In use, the printing head 36 is urged to press against flattened feedstock tube 1 sandwiching printer ribbon 38 therebetween, such that printer ribbon 38 is held in register with the feedstock tubing 1. In this way, the relevant indicia are marked on the tubing 1 as the print composition carried by the printer ribbon 38 is transferred to the surface of the flattened tubing 1.

Printer ribbon 38 comprises a polyester backing film between 4-15 μ m (microns) in thickness (preferably approximately 6 μ m (microns) in thickness), and which is arranged to release the printing composition under the applied pressure and heat of the thermal printer head 36. The print composition carried by the printer ribbon 38 is dry to the touch and comprises first and second selected colourant materials (such as respective dyes) and a thermoplastic material compatible with the material of the tubing 1 carried in a suitable matrix material, such as wax.

One of the colourant materials, and also the thermoplastic material, are selected to bind with the plastics material of the tubing substrate, or penetrate into the plastics material of the tubing substrate (for example by diffusion), upon application of the thermal transfer printing head. In this way, as shown most clearly in figure 4, a substantially indelible mark 7 in the required configuration of the indicia is formed at, or more preferably below, the surface of the substrate material (wall of tubing 1). The other of the colourant materials is selected to be printable on the surface of the plastics tubing 1 substrate, and not to penetrate significantly below the substrate surface. This provides a surface printed mark 3 overlaying the subsurface mark 7.

A suitable printing composition and matrix for performance of the invention has been found to be as follows:

- (ii) 50-70% by weight, first and second colourant materials. The first colourant material

comprises a first dye (a solvent violet) based on N - tetra, N - penta, N - Lisea para-rosaniline hydrochlorides and a second dye (a solvent black) being an azo dye of formula $C_{29}H_{24}N_6$ chemical name 1 H - pyrimidine, 2,3 - dihydro - 2,2 - dimethyl - 6 [(4 - (phenylazo) - 1 - naphthyl) azo]. The second colourant material comprises an amorphous black inert solid such as furnace black.

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- (ii) 8-12% by weight low molecular weight homopolymer PVC.
 - (iii) 15-20% by weight, releasing agent comprising a wax (stearic acid).
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The constituents of the printing composition are milled together; the combined material is then layered onto the polyester film.

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In use, the first colourant material binds with the PVC homo polymer material and penetrates the material of the plastics tube 1 to provide the subsurface mark 7. The second pigmentation material provides the surface printed mark 3 overlaying the subsurface mark 7.

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The invention provides a single stage printing process for printing a high quality and substantially indelible mark upon plastics substrates. The printed mark does not require fixing (which is often necessary with prior art techniques) and has good resistance to fading under ultra-violet radiation. The printer ribbon can be used with conventional thermal transfer printing apparatus.

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Claims:

1. A method of printing onto a plastics substrate (1), the method comprising the steps of:

5 (i) providing a print carrier carrying a printing composition comprising first and second colourant materials; and

10 (ii) registering said print carrier against said substrate and applying heat and pressure thereto so as to transfer in a single step said printing composition, including both said first and second colourant materials, said substrate characterised in that said printing composition is a unitary
15 composition comprising said first and second colourant materials, and in that said first colourant material is arranged to penetrate into said plastics substrate(1) to form a substantially
20 permanent mark below the surface of the substrate (1), and said second colourant material is arranged to adhere to the surface of the substrate (1) overlaying the substantially permanent mark.

25 2. A print carrier (38) carrying a releasable printing composition, which printing composition comprises a first and second colourant materials, said printing composition, including both said first and second
30 colourant materials, being capable of being transferred in a single step to a plastic substrate

(1) upon application of heat and pressure to said print carrier (38) when it is registered against said substrate (1); characterised in that said first colourant material is arranged to penetrate into the plastics substrate (1) to form a substantially permanent mark below the surface of the substrate (1), and in that the second colourant material is arranged to adhere to the surface of the substrate (1) overlaying the substantially permanent mark.

3. A method of printing process or a print carrier (38) according to claim 1 or claim 2 respectively, wherein the printing composition carried by the print carrier (38) comprises the first and second pigmentation materials and also a plastics material facilitating binding with or penetration into the substrate (1); preferably wherein the plastics material comprising the printing composition comprises:
plastics material substantially identical to the plastics material comprising the substrate; or
plastics material substantially different from the plastics material comprising the substrate.

4. A method of printing or a print carrier (38) according to any respective preceding claim, wherein the plastics material carried by the print carrier comprises a thermoplastic material (preferably a homopolymer material).

5. A method of printing or a print carrier (38) according to any preceding claim, wherein:

- 5 i) the print carrier (38) comprises a plastics film, preferably wherein the print carrier comprises a polyester film; and/or
- ii) wherein the print carrier is of a thickness substantially in the range 4-15 μ m (microns), preferably of approximately 6 μ m (microns).

10 6. A method of printing or a print carrier (38) according to any preceding claim, wherein the print carrier (38) is capable of separating from the print composition during the thermal transfer printing process; and/or wherein the print carrier (38) is wound from a reel

15 store; and/or

 wherein the print composition (or ink) carried by the print carrier (38) is touch dry; and/or

 wherein the first and second colourant materials are relatively dark in colour; and/or

20 wherein one or other (or both) of the first and second colourant materials may comprise a mixture or composition of a plurality of dyes; and/or

 wherein the printing composition comprises the colourant materials and the plastics material bound in

25 a matrix material, the matrix material preferably comprising a relatively soft, high molecular weight material such as a wax or wax-like material.

7. A method of printing or a print carrier (38) according to any respective preceding claim, wherein:

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- (i) the colourant material comprise dyes of suitable composition to ensure that one penetrates the substrate and the other adheres to the surface of the substrate during the printing process; and/or,
- (ii) the substrate (1) comprises a plastics strip or length of plastics tubing (the feedstock preferably being in the form of flattened tubing).

8. A method of printing or a print carrier according to any preceding claim, wherein:

the print carrier (38) carries:

- (i) 50-70% by weight, first and second colourant materials;
- (ii) 8-12% by weight plastics material (preferably comprising a low molecular weight homopolymer PVC) susceptible to binding with or penetrating into the substrate (1); and,
- (iii) 15-20% by weight, releasing agent/matrix material (preferably comprising a wax material such as stearic acid); and/or

the second colourant material comprises an amorphous black inert solid such as furnace black; and/or, the printing composition is applied to the print carrier (38) as a layer.

9. A plastics printed marker comprising a plastics substrate (1) having a printed mark formed by registering against said substrate (1) a print carrier (38) carrying a unitary printing composition comprising first and second colourant materials and applying heat and pressure thereto to release in a single step said printing composition from said print carrier (38) , the printed mark comprising:

(a) a first, sub-surface portion of a first colourant material penetrated into the substrate, and;

(b) a second, surface portion of a second colourant material adhered to the surface of the substrate overlaying the sub-surface portion of the mark.

10. A plastics printed marker according to claim 9, wherein the substrate (1) comprises a plastics strip; and/or

wherein the substrate (1) comprises a length of plastics tubing,

preferably wherein the first and second colourant materials are relatively dark in colour.