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Marking Plastics Substrates

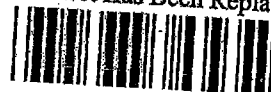
5 The present invention relates to marking plastics substrates and in particular to marking plastics substrates using a thermal transfer printing process.

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 printing apparatus in order to be marked with the  
15 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 transferred to the feedstock. Conventionally,  
20 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.

30 Improvements have now been devised to marking plastics substrates.

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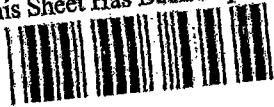


According to a first aspect, the invention provides a thermal transfer printing process for marking a plastics substrate, the process comprising applying heat and pressure to a print carrier registering against the substrate resulting in transfer of a printing composition carried by the print carrier to the substrate, the printing composition comprising a first pigmentation material arranged to bind to or penetrate into the plastics substrate to form a substantially permanent mark below the surface of the substrate, and a second pigmentation material arranged to adhere to the surface of the substrate overlaying the substantially permanent mark.

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 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.

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, the printed mark comprising:

- a) a first, sub-surface portion of a first pigmentation material bound to, or penetrated



into the substrate, and;

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

10           The printing composition carried by the print carrier  
              comprises the first and second pigmentation 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  
15           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.

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

25           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.

30           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.

5 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  
10 printing.

It is preferred that the print carrier comprises a plastics film (desirably comprising polyester) preferably of a thickness substantially in the range 4-15 microns,  
15 more preferably approximately 6 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.

20 The print composition (or ink) carried by the print carrier is preferably touch dry. The first and second pigmentation materials are preferably relatively dark in colour and may for example be blue or black. The  
25 pigmentation 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.

30 One or other (or both) of the first and second pigmentation materials may comprise a mixture or



composition of a plurality of dyes.

It is preferred that the printing composition comprises the pigmentation 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.

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

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;

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

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.

5 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  
10 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  
15 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,  
20 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  
25 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  
30 between 4-15 microns in thickness (preferably approximately 6 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 pigmentation 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 pigmentation 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 pigmentation 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:

- i) 50-70% by weight, first and second pigmentation materials. The first pigmentation 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  $C_{19}H_{14}N_6$  chemical name 1 H - pyrimidine, 2,3 - dihydro - 2,2 - dimethyl - 6 [(4 - (phenylazo) - 1 - naphthyl) azo]. The second pigmentation material comprises an amorphous black inert solid such as furnace black.

ii) 8-12% by weight low molecular weight homopolymer PVC.

iii) 15-20% by weight, releasing agent comprising a wax (stearic acid).

The constituents of the printing composition are milled together; the combined material is then layered onto the polyester film.

In use, the first pigmentation 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.

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.





Claims:

1. A thermal transfer printing process for marking a plastics substrate, the process comprising applying heat and pressure to a print carrier registering against the substrate resulting in transfer of a printing composition carried by the print carrier to the substrate, the printing composition comprising a first pigmentation material arranged to bind to or penetrate into the plastics substrate to form a substantially permanent mark below the surface of the substrate, and a second pigmentation material arranged to adhere to the surface of the substrate overlaying the substantially permanent mark.
2. A printing process according to claim 1, wherein the printing composition carried by the print carrier comprises the first and second pigmentation materials and also a plastics material facilitating binding with or penetration into the substrate.
3. A printing process according to claim 1 or claim 2, wherein the plastics material comprising the printing composition comprises plastics material substantially identical to the plastics material comprising the substrate.
4. A printing process according to claim 1 or claim 2, wherein the plastics material comprising the printing composition comprises material different from the plastics material comprising the substrate.





5. A process according to any preceding claim, wherein the plastics material carried by the print carrier comprises a thermoplastic material.
- 5 6. A process according to any preceding claim, wherein the plastics material carried by the print carrier comprises a homopolymer material.
- 10 7. A process according to any preceding claim, wherein the substrate comprises a plastics strip or length of plastics tubing.
8. A process according to any preceding claim, wherein the substrate is in the form of plastics tubing, the feedstock being in the form of flattened tubing.
- 15 9. A process according to any preceding claim, wherein the print carrier comprises a plastics film.
- 20 10. A process according to claim 9, wherein the print carrier comprises a polyester film.
11. A process according to any preceding claim, wherein the print carrier is of a thickness substantially in the range 4-15 microns.
- 25 12. A process according to any preceding claim, wherein the print carrier is of a thickness of approximately 6 microns.
- 30





13. A process according to any preceding claim, wherein the print carrier is capable of separating from the print composition during the thermal transfer printing process.
- b
14. A process according to any preceding claim, wherein the print carrier is wound from a reel store.
15. A process according to any preceding claim, wherein the print composition (or ink) carried by the print carrier is touch dry.
- 10
16. A process according to any preceding claim, wherein the first and second pigmentation materials are relatively dark in colour.
- 15
17. A process according to any preceding claim, wherein the pigmentation material comprises 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.
- 20
18. A process according to any preceding claim, wherein one or other (or both) of the first and second pigmentation materials may comprise a mixture or composition of a plurality of dyes.
- 25
19. A process according to any preceding claim, wherein the printing composition comprises the pigmentation materials and the plastics material bound in a matrix material.
- 30





20. A process according to claim 19, wherein, the matrix material comprises a relatively soft, high molecular weight material such as a wax or wax-like material.
- 5
21. A process according to any preceding claim, wherein the print carrier carries:
- 10 i) 50-70% by weight, first and second pigmentation materials;
  - ii) 8-12% by weight plastics material susceptible to binding with or penetrating into the substrate; and,
  - 15 iii) 15-20% by weight, releasing agent/matrix material.
22. A process according to claim 21, wherein the plastics material comprises a low molecular weight homopolymer PVC.
- 20
23. A process according to claim 21 or claim 22, wherein the releasing agent/matrix material comprises a wax material such as stearic acid.
- 25
24. A process according to any preceding claim, wherein the first pigmentation material comprises a first dye (a solvent violet) based on N - tetra, N - penta, N -
- 30 Lisea para-rosaniline hydrochlorides and a second dye (a solvent black) being an azo dye of formula  $C_{14}H_{24}$



N<sub>4</sub> chemical name 1 H - pyrimidine, 2,3 - dihydro - 2,2  
- dimethyl 6 [(4 - (phenylazo) 1 - naphthyl)  
azo].

- 5           25. A process according to any preceding claim, wherein  
the second pigmentation material comprises an  
amorphous black inert solid such as furnace black.
- 10           26. A process according to any preceding claim, wherein  
the printing composition is applied to the print  
carrier as a layer.
- 15           27. A process according to any preceding claim, wherein  
the thermal transfer printer is arranged to print a  
predetermined indicia mark upon the substrate.
- 20           28. A plastics printed marker comprising a plastics  
substrate having a printed mark, the printed mark  
comprising:
- 25               a) a first, sub-surface portion of a first  
pigmentation material bound to, or penetrated  
into the substrate, and;
- b) a second, surface portion of a second  
pigmentation material adhered to the surface of  
the substrate overlaying the sub-surface portion  
of the mark.
- 30           29. A plastics printed marker according to claim 28,  
wherein the substrate comprises a plastics strip.



30. A plastics printed marker according to claim 28, wherein the substrate comprises a length of plastics tubing.
- 5
31. A plastics printed marker according to any of claims 28 to 30, wherein the first and second pigmentation materials are relatively dark in colour.
- 10
32. A plastics printed marker according to any of claims 28 to 31, wherein one or other (or both) of the first and second pigmentation materials may comprise a mixture or composition of a plurality of dyes.
- 15
33. a print carrier carrying a releasable printing composition, which print composition comprises a first pigmentation material capable of binding to or penetrating into a plastics substrate, and a second pigmentation material capable of adhering to the
- 20
- surface of the plastics substrate.
34. A print carrier according to claim 33, wherein the printing composition carried by the print carrier comprises the first and second pigmentation materials
- 25
- and also a plastics material facilitating binding with or penetration into the substrate.
35. A print carrier according to claim 34, wherein the plastics material carried by the print carrier
- 30
- comprises a thermoplastic material.

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36. A print carrier according to claim 34 or claim 35,  
wherein the plastics material carried by the print  
carrier comprises a homopolymer material.
- 5 37. A print carrier according to any of claims 33 to 36,  
wherein the print carrier comprises a plastics film.
38. A print carrier according to claim 37, wherein the  
print carrier comprises a polyester film.
- 10 39. A print carrier according to any of claims 33 to 38,  
wherein the print carrier is of a thickness  
substantially in the range 4-15 microns.
- 15 40. A print carrier according to any of claims 33 to 39,  
wherein the print carrier is of a thickness of  
approximately 6 microns.
- 20 41. A print carrier according to any of claims 33 to 40,  
wherein the print carrier is capable of separating  
from the print composition during a thermal transfer  
printing process.
- 25 42. A print carrier according to any of claims 33 to 41,  
wherein the print carrier is wound in a reel store.
43. A print carrier according to any of claims 33 to 42,  
wherein the print composition (or ink) carried by the  
print carrier is touch dry.
- 30 44. A print carrier according to any of claims 33 to 43,



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

45. A print carrier according to any of claims 33 to 44,  
5 wherein one or other (or both) of the first and second pigmentation materials comprise a mixture or composition of a plurality of dyes.
46. A print carrier according to any of claims 33 to 45,  
10 wherein the printing composition comprises the pigmentation materials and the plastics material bound in a matrix material.
47. A print carrier according to claim 46, wherein, the  
15 matrix material comprises a relatively soft, high molecular weight material such as a wax or wax-like material.
48. A print carrier according to any of claims 33 to 47,  
20 wherein the print carrier carries:
- i) 50-70% by weight, first and second pigmentation materials;
  - 25 ii) 8-12% by weight plastics material susceptible to binding with or penetrating into a plastics substrate; and,
  - iii) 15-20% by weight, releasing agent/matrix  
30 material.





49. A print carrier according to claims 48, wherein the plastics material comprises a low molecular weight homopolymer PVC.
- 5 50. A print carrier according to claim 48 or claim 49, wherein the releasing agent/matrix material comprises a wax material such as stearic acid.
- 10 51. A print carrier according to any of claims 33 to 50, wherein the first pigmentation 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  $C_{20}H_{24}N_6$  chemical name 1 H - pyrimidine, 2,3 - dihydro - 2,2 - dimethyl - 6 [(4 - (phenylazo) - 1 - naphthyl) azo].
- 15 52. A print carrier according to any of claims 33 to 51, wherein the second pigmentation material comprises an amorphous black inert solid such as furnace black.
- 20 53. A print carrier according to any of claims 33 to 52, wherein the printing composition is applied to the print carrier as a layer.
- 25 54. A thermal transfer printing process substantially as herein described with reference to the accompanying drawings.
- 30 55. A printed plastics marker substantially as herein described with reference to the accompanying



drawings.

56. A print carrier substantially as herein described with reference to the accompanying drawings.

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