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(54) Title: MARKING OF PIPES

(57) Abstract: A method for the production of a machine readable marking on a plastics pipe, which comprises directing a laser onto a surface of the pipe whereby a machine readable marking is produced.



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MARKING OF PIPES

5 This invention relates to the marking of pipes, and more particularly to the application of markings to pipes to facilitate their identification, handling and further processing.

10 Plastics pipes are widely employed in the fluid distribution networks of, for example, the gas and water industries and in irrigation and sewage treatment. In addition, the telecommunications and electricity industries are increasingly deploying plastics pipes as ducting for cables. These industries specify very different properties for the plastics pipes in their networks and manufacturers are providing increasingly sophisticated products for specific end uses. In addition, the joining of these pipes, for example, by welding,
15 requires different regimes, depending on the pipe material, the manufacturer, and the welding method employed. It is important, therefore, that each pipe should carry the appropriate identification.

20 In the simplest case, plastics pipes are colour-coded. In the UK, for example, gas pipes are yellow, water pipes are blue, and sewage pipes are brown or black. Axial stripes are also applied to some pipes, for example, to indicate that the pipe is a composite or multilayer pipe. This enables buried pipes to be identified during subsequent excavations. There is, however, a limit to colour coding, and it cannot deal with the complex information required
25 to indicate, for example, part numbering, batch number, date of manufacture, specific welding conditions for pipe jointing, pressure rating and end use.

In French patent 2572326 there is described a welding protocol in which there is associated with the pipe an identification chart and a welding
30 machine is provided with means for reading the chart and for implementing a monitored heating programme, as a function of the chart parameters. Further welding methods in which the pipe is provided with a machine readable identification chart for implementing a welding cycle are disclosed in EP

272978 and US patents 5620625 and 4837424. The entire disclosures of these documents are incorporated herein by reference for all purposes.

5 Whilst such methods solve some problems, the durability and legibility of the machine readable markings is still questionable. Conventional methods of applying barcode markings, for example, by using adhesive paper or plastic film labels upon which the barcode markings are printed, or by printing directly onto the surface have not proved to be successful with plastics pipes, particularly polyolefin pipes. Furthermore ink marking is time-consuming and
10 there are complications associated with equipment maintenance and control of the print quality.

The present invention provides a method for the production of a machine readable marking on a plastics pipe, a novel plastics pipe adapted to
15 receive a machine readable marking, and a plastics pipe produced by the method.

In a first aspect the present invention provides a method for the production of a machine readable marking on a plastics pipe, which comprises
20 directing a laser onto a surface of the pipe whereby a machine readable marking is produced.

In a second aspect the invention provides a plastics pipe having an outer surface comprising a polymer material having dispersed therein a
25 marking additive, the presence of the marking additive providing an improvement in the ability of the surface of the pipe to receive a machine readable marking when a laser is directed thereon.

In accordance with a further aspect of the invention, the marking
30 additive is dispersed in only a minor portion of the outer surface of the plastics pipe, preferably in a longitudinally directed, more preferably an axially directed, stripe. A plastics pipe having an outer surface with a longitudinally directed stripe comprising a polymer material having dispersed therein a marking additive is also included within the invention.

In a third aspect, the present invention provides an apparatus for extruding a plastics pipe, the apparatus being provided with a laser and means for directing a beam from the laser onto the extruded pipe to produce a machine readable marking thereon.

Whilst the invention can be applied to a wide range of plastics pipes and to many different situations, it is particularly suitable for use with composite plastics pipes having an inner core and an outer removable protective layer, and will henceforth be more particularly described with reference thereto. It is to be understood, however, that the invention is not limited to such plastics pipes and can also be applied to pipes wherein the pipe wall is a single layer and to composite pipes wherein the outer layer is not removable.

Preferably the marking additive, where present, is dispersed solely in the outer removable protective layer of the composite plastics pipe.

The preferred composite plastics pipes for use in the present invention have an outer protective layer that can be removed, for example, by peeling, in order to expose a clean, unoxidised surface of the inner core suitable for connection, for example, by electrofusion welding. Such pipes, and methods for their manufacture and use, are disclosed in GB 2297137, GB2297138, WO 04/016976, WO 04/016420 and WO 04/016421 the entire disclosures of which are incorporated herein by reference for all purposes.

Each of the layers of the composite plastics pipe can comprise any suitable thermoplastic polymeric material, consistent with the maintenance of the required end-use properties. Suitable polymeric materials include, for example, olefinically-unsaturated polymers and co-polymers, for example, polyolefins such as polyethylene, polypropylene, polybutene and polybutylene; ethylene and propylene co-polymers, for example, ethylene-vinyl acetate polymers, and propylene-vinyl acetate polymers; halogenated-vinyl polymers such as vinyl chloride polymers and co-polymers; polyamides,

for example, nylon 6, nylon 11 and nylon 66; polycarbonates; ABS polymers and ionomer polymers such as Surlyn (RTM).

5 The inner core of the pipe can comprise a polymeric material chosen to be compatible with the particular application, and especially with the fluid material to be conveyed by the pipe. For many applications polyethylene is the preferred material for the inner core. The grade of polyethylene chosen, that is to say, high density, medium density, low density, or linear low density, will depend upon the particular application. For example, suitable grades of
10 polyethylene for pressure pipe applications preferably meet the requirements of at least one of prEN 12201-1, prEN12201-2, prEN1555-1 and prEN1555-2.

Any suitable equivalent grade of polyethylene may, of course, also be used.
15

The outer protective layer of the composite plastics pipe is preferably formed from a polymeric material or a blend of polymeric materials having good mechanical and physical properties, especially toughness and low temperature impact strength, together with an ability to receive quantities of
20 stabilising materials, in particular UV stabilisers, sufficient to protect the underlying layer(s) and/or the inner core.

Preferred polymeric materials for the outer protective layer comprise propylene homo- and co-polymers, propylene block co-polymers, and
25 propylene random co-polymers.

The machine readable marking can take the form of an alphanumeric code imprinted on the surface of the product to indicate the date of manufacture, serial number, welding conditions etc. Preferably, however, the
30 laser marking comprises a machine readable chart, for example, a barcode. By "machine readable" in this specification is meant a marking, whether visible to the eye or not, which provides information encoded in a form which can be read or understood by a machine or computer and interpreted by hardware or software. In a preferred embodiment the machine readable marking can be

read by a reading device which provides information to further equipment, for example, to a display device, or operable equipment, for example, an electrowelding device. Preferably the reading device is a pen type reader (e.g. a bar code wand), a laser scanner, a CCD (Charge Coupled Device) reader and/or a camera-based reader.

Any suitable laser equipment can be used for producing the machine readable marking on the outer surface of the plastics pipe, for example, CO₂ lasers, for example, imaged-mask (stencil) pulsed CO₂ lasers, and dot matrix CO₂ lasers; yttrium aluminum garnet (YAG) lasers, for example, steered-beam laser writing yttrium aluminum garnet (YAG) lasers, and excimer lasers.

The laser marking method can comprise, for example, mask marking or beam deflected marking. In mask marking, a stencil of the desired mark is projected onto the pipe surface. The image of the stencil on the pipe is made using a lens. An extremely short impulse of light energy is directed onto the pipe surface. Suitable lasers for use in mask marking include, for example, pulsed TEA CO₂ lasers, pulsed Nd:YAG lasers and excimer lasers. In the beam deflected method, the laser is directed via two computer controlled galvanometer mirrors and a lens system to the pipe surface. The marking is made by directing the beam in the x and y directions. Suitable lasers for this method include, for example, CW CO₂ laser and CW (Q-switched) Nd:YAG lasers with around 532nm and 1064nm wavelengths.

The laser energy threshold for marking will of course depend on the polymer material and marking additive where present, but will normally be in the range of from 0.01 to 45 J/cm², preferably from 1 to 25 J/cm² and more preferably from 5 to 20 J/cm².

The choice of laser marking method will depend upon the application. Mask marking generally provides higher marking speeds and, because the laser pulse duration is in the range of micro-second to nanosecond, the pipe to be marked does not need to be stationary. Beam deflected marking generally provides a bigger marking area. The marking area provided by mask

marking is, in contrast, small because of limited beam spot size and energy per pulse. Because the production of a mask is time-consuming, mask marking is more suitable for high-volume production without any change in the marking. In beam deflected marking, the patterns are produced by software and the method is therefore more flexible.

The laser marking method can include one or a combination of the following processes:

- (a) black carbonisation;
- (b) bleaching or changing the colour of a colorant in the polymer material;
- (c) physical modification of the surface finish;
- (d) scribing a shallow groove into the polymer material by vaporisation;
- (e) modification of the surface by melting.

Marking contrast can be achieved by surface material removal or colour change. When infrared lasers are used, marking contrast usually relies on thermal effects. When UV lasers, such as excimer lasers are used, marking contrast can be achieved through a photo-chemical transformation, that is to say, a colour change.

When a laser beam is focused on the surface of the polymer material, a variety of phenomena may occur to give rise to the machine readable marking.

(1) Vaporization

The laser beam is focused to a small spot, which greatly increases the energy density. When the energy is high enough, and the surface temperature is raised well above the melting point, the polymer material on which the beam is focused will vaporize. The efficiency of this vaporization process depends on the absorption of the wavelength of the laser radiation. In general, polymer materials absorb the 10.6 μm wavelength of a CO_2 laser very well. In many cases, the absorption is 100%. In the marking method, the energy densities are often high enough that the desired vaporization is completed in microseconds. A series of vaporized craters in a polymer surface usually

alters its appearance sufficiently to be visible if characters are formed. The marking contrast depends on the chemistry of the polymer material, its surface finish and its colour. A good marking edge resolution is normally achievable. The marking depth and width are readily controllable.

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(2) Softening/Melting

Polymer materials experience melting under infrared laser radiation, and ridges can be formed. Depending on the type of polymer material, different colours may appear. If the energy density exceeds the ignition point of the polymer material, carbonization occurs, which leads to black markings.

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(3) Layer removal/ablation

Layer removal/ablation is a form of controlled vaporisation. A thin layer of polymer material is vaporized exposing an under-layer of a different colour.

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(4) Colour change

At certain energy densities (below melting point), polymer materials can undergo chemical changes when exposed to laser radiation of a specific wavelength. The chemical change can be either a photo- or thermal-induced colour change, for example, an excimer laser induced photo-chemical colour change, or a CO₂ induced thermal-chemical colour change. The colour changes can be due to changes in chemical composition or in molecular structures.

20

25 In one preferred embodiment of the invention, a marking additive is dispersed in the polymer material in an appropriate amount to provide a colour change. In this specification, the term "marking additive" is intended to include any additive that will enhance the susceptibility of the polymer material to change colour, ablate or vaporise when acted upon by an incident laser beam. The presence of a marking additive is important for certain polymers such as polyethylene, polypropylene and polycarbonates, which do not mark well in their pure states. For such polymer materials, additives that increase the optical absorption coefficient of the polymer can improve the marking process simply by increasing the rate of temperature rise. By incorporating

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additives with high absorption and choosing the appropriate laser wavelength, enhanced markability can be achieved. Suitable additives can include, for example, inorganic fillers, flame retardants, UV inhibitors, pigments and stabilizers.

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In one particularly preferred embodiment, for example, a pigment is added that will undergo a colour change, or which can induce a colour change in the polymer material. Suitable pigments that can be used include inorganic pigments, for example: white TiO_2 , yellow iron oxide $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, black iron oxide Fe_3O_4 ; green chromium oxide (Cr_2O_3 and $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$); chrome orange $(\text{PbCrO}_4)_x \cdot (\text{PbO})_y$, cadmium yellow (mixed CdS/ZnS) and metallic pigments, for example, aluminium flakes. Suitable organic pigments that can be used include, for example: yellow di-chlorobenzidine derivatives; orange dianisidine derivatives; and red toluidine reds.

15

The selection of the appropriate pigment, will depend, for example, on the polymer and its transparency to the laser light wavelength, the effect of the pigment on the polymer material properties, and the long term stability of the pigment. Organic pigments are often strong absorbers of visible light, and can be particularly effective. It is possible to obtain with certain pigments a polychromatic (both black and white) laser mark which exhibits two marking effects depending on the energy density of the laser namely:

- (i) bleaching of the pigment to allow the underlying polymer colour to show through; and
- (ii) carbonisation of the polymer.

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In another particularly preferred embodiment of the invention the laser markability of the polymer material is enhanced by the addition of an inorganic marking additive, for example, inorganic filler, for example, mica, carbon black, titanium dioxide, antimony trioxide, kaolin and aluminium silicate derivatives. A series of metal-oxide coated mica additives have recently been shown to allow good laser marks on previously unmarkable polyolefins using CO_2 and YAG lasers. These additives, sold by E Merck under the trade mark names AFFLAIR and LAZER FLAIR, give a pearlescent appearance.

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Pearlescence is an optical interference effect of white light interacting with the layered structure of mica platelets near the surface of the polymer material. Enhanced marking of the polymer material is probably not due to absorption by the mica, but rather due to trapping of the laser light near the surface to
5 cause thermal decomposition of the polymer material.

The amount of the marking additive that is dispersed in the polymer material will depend upon the nature of the additive and the polymer material. In general, however, the marking additive will be present in the polymer
10 material (or in that portion of the polymer material of the pipe that contains the marking additive) to an extent of from 0.1 to 20 percent by weight, based on the weight of the polymer material (or that portion of the polymer material of the pipe that contains the marking additive), preferably from 1 to 15 percent by weight, and more preferably from 1 to 10 percent by weight.

15 The depth of the laser marking will depend on the energy density, type of polymer material and the beam/material interaction time. In mask marking, the vaporization depth is typically a few microns to several tens of microns. In beam deflected laser marking, greater depth of penetration into the material
20 can be achieved, varying between a few microns to several tens of a millimeter. A further enhancement of the effect on the polymer material can be realized by the supply of gases such as oxygen or compressed air, which assist material removal.

25 The machine readable marking preferably has the maximum possible marking contrast. Marking contrast is the visual difference between the apparent brightness of the marked surface and unmarked surface of a workpiece. The sharpness or resolution of the marked edges also affects the marking contrast. This parameter is particularly important in marking bar
30 codes, as poor edge sharpness can cause the bar code reader to fail. High peak power or power density of the laser produces better edge resolution. The best marking results are obtained when there is a proper combination of pulse energy, pulse duration, and pulse repetition rate.

In yet another preferred embodiment of the invention, the marking additive is dispersed in a stripe, preferably a longitudinally directed stripe, and more preferably an axially directed stripe. Since some marking additives also fulfil other functions, for example, as fillers, stabilisers or pigments, for the avoidance of doubt it should be understood that the marking additive in this aspect of the invention is present only in a stripe on the outer surface of the plastics pipe. The stripe can be continuous or discontinuous and can extend all or part way along the length of the pipe. The width of the stripe can be constant or can vary, for example, along the length of the pipe. The stripe is preferably straight, although it could also form a spiral around the pipe. By restricting the marking additive to a stripe on the outer surface of the plastics pipe the additional costs of the additive can be kept to a minimum and the effect, if any, on the mechanical properties of the pipe can also be kept to a minimum. The width of the stripe will depend, to some extent, on the height of the machine readable marking, but is usually in the range of from 2 to 50 mm, preferably from 4 to 35 mm, and more preferably from 6 to 20 mm.

Composite pipes in accordance with the invention are produced on extrusion lines with multiple extruders and since it is already a requirement of some composite pipes that a longitudinal stripe of a different colour to the main body of the pipe is provided, the additional processing costs of including the marking additive in the stripe are very small.

In a preferred method according to the invention, the machine readable marking is applied to the plastics pipe by an inline method wherein the laser is positioned downstream of the extruders and is directed onto the surface of the extruded pipe before it leaves the extrusion line. Of course this is not essential and it would also be possible to apply the machine readable marking to cut lengths of the plastics pipe in a separate laser marking step.

The laser marking method of the invention can produce permanent, high-quality marks at high-efficiency and low operating cost. The method can be operated at high speed and with a high reproducibility. It is easy to automate and to integrate into conventional extrusion lines.

An embodiment of a plastics pipe and method according to the invention will now be described, by way of example only, in the following Example:

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EXAMPLE

A plastics pipe manufactured by Uponor Limited and sold under the trade mark ProFuse was used for the present experiments. ProFuse comprises a core pipe, a protective skin layer and a stripe. The core pipe is made from un-pigmented PE 100 polyethylene material and is designed to meet all the requirements of the specific industry (other than pigmentation and marking). The protective skin layer is a polypropylene layer that is designed to adhere lightly to the core and to be removable when required, for example, for electrofusion jointing. The skin is pigmented to meet the industry requirements, dark blue for water, yellow for gas, and brown or black for sewage, and is stabilized for UV protection and light fastness. The stripe, made from the same polypropylene material as the skin, is pigmented brown and identifies the pipe as being multi-layered in both gas and water industries. All three materials are simultaneously extruded to produce a two-layer pipe with a longitudinal stripe.

A length of pipe was marked with manufacturer, batch and end use data using in-line laser marking. Comparison lengths were marked using respectively an inkjet printer and an indent marker.

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The laser method chosen was beam deflected laser marking. This method is characterised by the use of a galvanometer mirror to deflect a pulsed laser beam (CO₂) onto the surface of the pipe. The marked area is prescribed by using the mirror to control the Y-axis displacement of the beam and the longitudinal motion of the pipe to control its X-axis displacement.

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It was found that laser marking of the yellow-pigmented skin layer was adequate for identification, but marking on the blue-pigmented skin layer

lacked sufficient contrast. Laser marking of the brown stripe gave a barcode marking that was clear to the human eye but was not readable by a barcode wand. Addition of a marking additive such as LASERFLAIR in an amount of 2% by weight to the stripe gave very successful readable results.

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Comparison lengths of pipe marked by inkjet printing and indent marking gave inferior results and the methods were found to be time consuming, awkward and unreliable.

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The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

15

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the combination, except combinations where at least some of such features and/or steps are mutually exclusive.

20

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

25

The invention is not restricted to the details of the foregoing embodiments. The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

30

CLAIMS

1. A method for the production of a machine readable marking on a
5 plastics pipe, which comprises directing a laser onto a surface of the
pipe whereby a machine readable marking is produced.
2. A method according to claim 1, wherein the plastics pipe has an outer
10 surface comprising a polymer material having dispersed therein a
marking additive, the presence of the marking additive providing an
improvement in the ability of the pipe surface to receive a machine
readable marking when a laser is directed thereon.
3. A method according to claim 1 or 2, wherein the marking additive is
15 dispersed in only a minor portion of the outer surface of the plastics
pipe.
4. A method according to claim 2 or 3, wherein the marking additive is
20 dispersed in a longitudinally directed stripe.
5. A method according to claim 4, wherein the stripe is axially directed.
6. A method according to any one of the preceding claims, wherein the
25 plastics pipe is a composite plastics pipe having an inner core and an
outer removable protective layer.
7. A method according to claim 6, wherein a marking additive is dispersed
solely in the outer protective layer.
- 30 8. A method according to claim 6 or 7, wherein the inner core of the
plastics pipe comprises polyethylene.

9. A method according to any one of claims 6 to 8, wherein the outer protective layer comprises a propylene homo- or co-polymer, a propylene block co-polymer, or a propylene random co-polymer.
- 5 10. A method according to any one of the preceding claims, wherein the machine readable marking comprises a barcode.
11. A method according to any one of the preceding claims, wherein the machine readable code can be read by a pen type reader, a laser
10 scanner, a CCD reader and/or a camera-based reader.
12. A method according to any one of the preceding claims, wherein the laser is a CO₂ laser, an yttrium aluminum garnet (YAG) laser, or an excimer laser.
- 15 13. A method according to any one of the preceding claims, wherein the laser marking method comprises mask marking, or beam deflected marking.
- 20 14. A method according to any one of the preceding claims, wherein the laser energy is in the range of from 1 to 25 J/cm².
15. A method according to any one of the preceding claims, wherein the laser marking method comprises one or more of:
25 (a) black carbonisation;
(b) bleaching or changing the colour of a pigment in the polymer material;
(c) physical modification of the surface finish;
(d) scribing a shallow groove into the polymer material by vaporisation;
30 (e) modification of the surface by melting.
16. A method according to any one of claims 2 to 15, wherein a pigment is added to the polymer material that will undergo a colour change, or that

can induce a colour change in the polymer material when acted upon by a laser.

- 5 17. A method according to claim 16, wherein the pigment is an inorganic pigment.
- 10 18. A method according to claim 17, wherein the pigment is white TiO_2 , yellow iron oxide $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, black iron oxide Fe_3O_4 ; green chromium oxide (Cr_2O_3 and $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$); chrome orange $(\text{PbCrO}_4)_x \cdot (\text{PbO})_y$, cadmium yellow (mixed CdS/ZnS) or a metallic pigment.
- 15 19. A method according to claim 16, wherein the pigment is an organic pigment.
- 20 20. A method according to claim 19, wherein the pigment is a yellow di-chlorobenzidine derivative; an orange dianisidine derivative; or a red toluidine red.
- 25 21. A method according to any one of claims 2 to 20, wherein the marking additive comprises inorganic filler.
- 26 22. A method according to claim 21, wherein the inorganic filler comprises mica, carbon black, titanium dioxide, antimony trioxide, kaolin, or an aluminium silicate derivative.
- 30 23. A method according to any one of claims 2 to 22, wherein the marking additive is present in the polymer material (or is that portion of the polymer material of the pipe that contains the marking additive) to an extent of from 0.1 to 20 percent by weight.
24. A method according to claim 4 or 5, wherein the width of the stripe is from 2 to 50 mm.

25. A method according to any one of the preceding claims, wherein the pipe is produced on an extrusion line with multiple extruders and the machine readable marking is applied to the pipe by an in-line method wherein the laser is positioned downstream of the extruders and is directed onto the surface of the extruded pipe before it leaves the extrusion line.
26. A method according to any one of the preceding claims substantially as described in the Example.
27. A method for the production of a machine readable marking on a plastics pipe by laser treatment substantially as hereinbefore described.
28. A plastics pipe having an outer surface comprising a polymer material having dispersed therein a marking additive, the presence of the marking additive providing an improvement in the ability of the surface of the pipe to receive a machine readable marking when a laser is directed thereon.
29. A plastics pipe according to claim 28, wherein the marking additive is dispersed in only a minor portion of the outer surface of the plastics pipe.
30. A plastics pipe according to claim 29, wherein the marking additive is dispersed in a longitudinally directed stripe.
31. A plastics pipe according to claim 30, wherein the marking additive is dispersed in an axially directed stripe.
32. A plastics pipe according to any one of claims 28 to 31, wherein the plastics pipe is a composite plastics pipe having an inner core and an outer protective layer.

33. A plastics pipe according to claim 32, wherein a marking additive is dispersed solely in the outer protective layer.
34. A plastics pipe according to claim 32 or 33, wherein the inner core of the plastics pipe comprises polyethylene.
35. A plastics pipe according to any one of claims 32 to 34, wherein the outer protective layer comprises a propylene homo- or co-polymer, a propylene block co-polymer, or a propylene random co-polymer.
36. A plastics pipe according to any one of claims 28 to 35, wherein the machine readable marking comprises a barcode.
37. A plastics pipe according to any one of 28 to 36, wherein a pigment is added to the polymer material that will undergo a colour change or that can induce a colour change in the polymer material when acted upon by a laser.
38. A plastics pipe according to claim 37, wherein the pigment is an inorganic pigment.
39. A plastics pipe according to claim 38, wherein the pigment is white TiO_2 , yellow iron oxide $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, black iron oxide Fe_3O_4 ; green chromium oxide (Cr_2O_3 and $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$); chrome orange $(\text{PbCrO}_4)_x \cdot (\text{PbO})_y$, cadmium yellow (mixed CdS/ZnS) or a metallic pigment.
40. A plastics pipe according to claim 37, wherein the pigment is an organic pigment.
41. A method according to claim 40, wherein the pigment is a yellow di-chlorobenzidine derivative; an orange dianisidine derivative; or a red toluidine red.

42. A plastics pipe according to any one of claims 28 to 41, wherein the marking additive comprises inorganic filler.
43. A plastics pipe according to claim 42, wherein the inorganic filler comprises mica, carbon black, titanium dioxide, antimony trioxide, kaolin, or an aluminium silicate derivative.
44. A plastics pipe according to any one of claims 28 to 43, wherein the marking additive is present in the polymer material (or is that portion of the polymer material of the pipe that contains the marking additive) to an extent of from 0.1 to 20 percent by weight.
45. A plastics pipe according to claim 30 or 31, wherein the width of the stripe is from 2 to 50 mm.
46. A plastics pipe according to any one of claims 28 to 45, having a machine readable laser marking applied thereto.
47. A plastics pipe having a machine readable laser marking applied thereto substantially as herein before described.
48. A plastics pipe having a machine readable laser marking applied thereto when produced by method according to any one of claims 1 to 27.
49. An apparatus for extruding a plastics pipe, the apparatus being provided with a laser and means for directing a beam from the laser onto the extruded pipe to produce a machine readable marking thereon.
50. An apparatus according to claim 49, wherein the apparatus comprises an extrusion line with multiple extruders and the laser is positioned downstream of the extruders and is directed onto the surface of the extruded pipe before it leaves the extrusion line.

51. An apparatus according to claim 49 or 50, wherein the laser is a CO₂ laser, an yttrium aluminum garnet (YAG) laser, or an excimer laser.

5 52. An apparatus according to any one of claims 49 to 51, wherein the laser beam directing means comprises a mask, or beam deflecting means.

10 53. An apparatus according to any one of claims 49 to 52, substantially as hereinbefore described.

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INTERNATIONAL SEARCH REPORT

International application No

T/GB2005/004810

A. CLASSIFICATION OF SUBJECT MATTER

B41M1/30 B41M5/24 B41M5/26 B41M5/36 B29C47/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B41M B29C B23K B29D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 100 61 062 A1 (BEIERSDORF AG) 23 August 2001 (2001-08-23) column 1, lines 18-22 column 2, lines 26-37, 43, 47-51 column 3, lines 37-61	1-48
X	US 6 746 724 B1 (ROBERTSON JOHN A ET AL) 8 June 2004 (2004-06-08) column 3, lines 1-10, 18-25 column 3, line 58 - column 4, line 35 column 4, lines 56-65 column 5, lines 40, 41, 46-49, 52	1-7, 10-48
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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

27 March 2006

Date of mailing of the international search report

07/04/2006

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No

T/GB2005/004810

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 710 570 A (QUANTUM CHEMICAL CORPORATION) 8 May 1996 (1996-05-08) page 2, line 11 page 3, line 11 - page 4, line 3 page 4, lines 7-21 page 4, line 43 - page 7, line 36 -----	1-48
X	US 2004/013969 A1 (DELP REINER ET AL) 22 January 2004 (2004-01-22) paragraphs [0001], [0002], [0004] paragraphs [0011] - [0043] -----	1-48
X	US 6 007 929 A (ROBERTSON ET AL) 28 December 1999 (1999-12-28) column 2, line 66 - column 5, line 65 -----	1-7, 10-48
X	DE 40 01 856 A1 (CIBA-GEIGY AG, BASEL, CH) 2 August 1990 (1990-08-02) page 4, line 18 - page 5, line 65 page 6, lines 2-10 -----	1-7, 10-48
Y	WO 2004/016421 A (UPONOR INNOVATION AB; THE IMPERIAL COLLEGE OF SCIENCE, TECHNOLOGY AND) 26 February 2004 (2004-02-26) page 4 - page 5 page 8 - page 10 page 11 - page 12 -----	28,47-53
Y	US 4 085 521 A (NEUROTH ET AL) 25 April 1978 (1978-04-25) column 4, lines 3-15; figure 1 -----	49-53
Y	WO 95/24317 A (DSM N.V; AAGAARD, OLAV, MARCUS) 14 September 1995 (1995-09-14) page 6, line 6 page 7, line 17 - page 8, line 19 -----	1-53
Y	EP 0 669 365 A (NIPPON KAYAKU KABUSHIKI KAISHA) 30 August 1995 (1995-08-30) page 3, line 39 - page 4, line 5 page 5, line 29 - page 6, line 17 -----	1-53
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Y	WO 98/56594 A (M.A. HANNACOLOR) 17 December 1998 (1998-12-17) page 6, line 9 - page 10, line 2 -----	28, 47-49,53

INTERNATIONAL SEARCH REPORT

International application No
T/GB2005/004810

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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US 6746724	B1	08-06-2004	NONE	
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WO 9856594	A	17-12-1998	AU 8055498 A CA 2293571 A1 MX PA99011421 A US 6627299 B1 US 6022905 A US 6017972 A US 5977514 A	30-12-1998 17-12-1998 11-06-2002 30-09-2003 08-02-2000 25-01-2000 02-11-1999

Box No. VIII (iv) **DECLARATION: INVENTORSHIP** (only for the purposes of the designation of the United States of America)
The declaration must conform to the following standardized wording provided for in Section 214; see Notes to Boxes Nos. VIII, VIII (i) to (v) (in general) and the specific Notes to Box No. VIII (iv). If this Box is not used, this sheet should not be included in the request.

**Declaration of inventorship (Rules 4.17(iv) and 51bis.1(a)(iv))
for the purposes of the designation of the United States of America:**

I hereby declare that I believe I am the original, first and sole (if only one inventor is listed below) or joint (if more than one inventor is listed below) inventor of the subject matter which is claimed and for which a patent is sought.

This declaration is directed to the international application of which it forms a part (if filing declaration with application).

This declaration is directed to international application No. PCT/..... (if furnishing declaration pursuant to Rule 26ter).

I hereby declare that my residence, mailing address, and citizenship are as stated next to my name.

I hereby state that I have reviewed and understand the contents of the above-identified international application, including the claims of said application. I have identified in the request of said application, in compliance with PCT Rule 4.10, any claim to foreign priority, and I have identified below, under the heading "Prior Applications," by application number, country or Member of the World Trade Organization, day, month and year of filing, any application for a patent or inventor's certificate filed in a country other than the United States of America, including any PCT international application designating at least one country other than the United States of America, having a filing date before that of the application on which foreign priority is claimed.

Prior Applications: GB 0427788.5

I hereby acknowledge the duty to disclose information that is known by me to be material to patentability as defined by 37 C.F.R. § 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the PCT international filing date of the continuation-in-part application.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Inventor's Signature: Jeremy Bowman Date: 21 Dec 2005
(The signature must be that of the inventor, not that of the agent)

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Residence:
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Mailing Address:

Citizenship:

Inventor's Signature: Date:
(The signature must be that of the inventor, not that of the agent)

☐ This declaration is continued on the following sheet, "Continuation of Box No. VIII (iv)".