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(54) Title: PROCESS FOR THE MANUFACTURE OF A COLOUR-MARKED OBJECT ✓ (57) Abstract Process for the manufacture of a colour-marked object by irradiating the surface of the object with laser light, characterized in that the object, at least at the location where the marking is applied, consists of a plastic composition which contains at least three light-absorbing components which exhibit a maximum in their light absorption spectra at different wavelengths and lose their light-absorbing capacity under the influence of laser light, with the marking being applied in the form of matrix dots by irradiating the object's surface at the location of the matrix dots with laser light of such wavelength and intensity and for such duration that at least one of the light-absorbing components has wholly or partially lost its light-absorbing capacity.		Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> <i>In English translation (filed in Dutch).</i>

PROCESS FOR THE MANUFACTURE OF A COLOUR-MARKED OBJECT

5 The invention relates to a process for the manufacture of a colour-marked object by irradiating the surface of the object with laser light.

 Such a process is known from WO94/12352. That patent application describes a process whereby the
10 surface of an object is irradiated under arbitrarily chosen conditions such that a colour marking is obtained.

 A disadvantage of the known process is that the colours obtained are not freely chosen but are
15 achieved by chance. Moreover, the marking can be obtained in only a limited number of colours.

 The invention aims to provide a process that does not have the aforementioned disadvantages.

 Surprisingly, this is accomplished by that
20 the object, at least at the location where the marking is applied, consists of a plastic composition which contains at least three light-absorbing components which exhibit a maximum in their light absorption spectra at different wavelengths and lose their light-
25 absorbing capacity under the influence of laser light, with the marking being applied in the form of matrix dots by irradiating the object's surface at the location of the matrix dots with laser light of such wavelength and intensity and for such duration that at
30 least one of the light-absorbing components has completely or partially lost its light-absorbing capacity.

 In this way a marking can be obtained whose colour is determined freely, the marking may contain different
35 colours and markings in different colours can be obtained on the surface of the same plastic composition. Furthermore, the marking can even be obtained on the surface of the same plastic composition in a great many different colours.

A matrix dot has the colour of the light, that is absorbed by colour absorbing component, before the component has completely or partly lost its light absorbing capacity.

5 Light-absorbing components are understood to be components having a chromatic colour, such as dyes and pigments. Light-absorbing components are understood not to include white or black components such as titanium dioxide, chalk, barium sulphide, carbon black
10 or iron sulphide.

It is essential that the light-absorbing components do not lose or only hardly lose their light-absorbing capacity in normal daylight. For this reason, the light-absorbing components possess a colour
15 stability of at least 5, more preferably at least 7 and still more preferably more than 7 on the Wool scale (in accordance with DIN 54003).

Examples of suitable light-absorbing components are Irgalith® Rubine 4 BP, a magenta-
20 coloured pigment, Irgalith Blue LGLD, a cyan-coloured pigment, or Cromopthal® Yellow 6G and Cromopthal Yellow 3G, two yellow-coloured pigments. Incidentally, most light-absorbing components lose their light-absorbing capacity in whole or part on being irradiated with
25 laser light.

The process of the invention allows matrix dots to be applied onto the surface in a simple manner.

Irradiation with laser light of a particular wavelength reduces the light-absorbing capacity of a
30 preselected light-absorbing component and the surface on the irradiated sites will reflect the colour which is no longer absorbed by the component in question. The brightness of the reflected colour can be enhanced by increasing the intensity of the laser light or
35 extending the duration of irradiation.

A marking of a desired colour is formed by

applying a great many matrix dots on the surface.

It is also possible to apply matrix dots of different colours side by side on the surface. To an observer, the colour of the surface at the location of the matrix dots is a mixed colour because the colours of the matrix dots strike the eye as though they blend. This method of colour mixing, in which the colours to be mixed are located side by side, is called the partitive method. The mixed colour is determined by the ratio of the surface area of the matrix dots and the ratio of the brightness of the colours. In this way, a great many mixed colours can be formed.

It is essential in this context that the centre-to-centre distance between the dots is small so that the eye cannot distinguish the individual matrix dots. Newspaper photos are coloured in this way also.

As is known from colour printing, very good results are achieved by applying matrix dots of at least three different colours on the surface. This is accomplished by irradiating the surface with laser light of at least three different wavelengths, in which process one of the at least three light-absorbing components wholly or partially loses its light-absorbing capacity at each wavelength. In this manner, the use of at least three colours allows a great many other colours to be formed by mixing the colours in the proper amounts.

Mixed colours can be achieved in a variety of fashions. Mixed colours can be achieved by, for example, varying the brightness of the colours of the matrix dots in relation to each other; by, for example, irradiating the matrix dots of a particular colour longer than other matrix dots. Alternatively, the ratio of the total area of the different colours can be varied in relation to each other by, for example, making one matrix dot larger than the other or by

forming more matrix dots of one colour than of the other colours. The matrix dots may be round or square but they may also be, for example, triangular or linear for example in order to fill the surface better or to
5 increase the total reflection of the surface.

A colour can be characterized in accordance with ASTM Standard E 308 by first measuring the tristimulus values of the colour and calculating therefrom the chromaticity coordinates that determine
10 the colour's location within the CIE D65 colour diagram (10° observer) as described in the aforementioned standard. Thus, the colour diagram is a graphic representation of all colours in the visible range.

The partitive mixing technique allows colours
15 to be formed which in the colour diagram lie in the area between the points representing the at least three different colours of the matrix points in the colour diagram. These points form the vertices of the area.

A method of the invention which allows even
20 more different colours to be obtained involves applying matrix dots so that they wholly or partially overlap. This colour mixing technique is referred to as subtractive blending.

Preferably, the colour of the surface is
25 determined by the subtractive mixing of at least three different coloured matrix points. The colour range evolving from subtractive mixtures is greater than in the case of partitive blending in that colours can be formed which in the colour diagram lie outside the area
30 between the points which represent the at least three different colours of the matrix points in the colour diagram.

The plastic composition may in principle contain any thermoset or thermoplastic or elastomer.
35 Plastics that the plastic composition mentioned in WO94/12352 can contain are particularly suitable.

Preferably, the light-absorbing components are so selected that the area between the points representing the at least three different colours of the matrix points in the colour diagram cover at least 10% of the area of the diagram.

Preferably, this area covers at least 30% of the diagram, more preferably at least 75% of the diagram.

The wavelength of the laser light with which the surface is to be irradiated in order for a predetermined light-absorbing component to lose its light-absorbing capacity can readily be determined by experiment.

Preferably, the wavelengths of the laser light with which the surface is irradiated are those at which the maximum occurs in the absorption spectrum of the light-absorbing component which is to lose its light-absorbing capacity. In this manner, very good selectivity and good brightness of the colours are obtained.

Preferably, the process of the invention is practised using one or more masks. Such masks are transmissive in those locations where the surface is to be irradiated and are not transmissive in those locations where the surface is not to be irradiated. Successive irradiation of the surface with different masks and with laser light of different wavelengths permits matrix dots of different colours to be applied on the surface rapidly and readily.

An advantage of this is that the size of the matrix dots is determined by the mask, not by the diameter of the laser beam, so that the surface may be irradiated with a large-diameter laser beam. As a result, irradiation will take less time.

Preferably, the process of the invention is practised with a variable mask.

Preferably, use is made of a mask produced by an LCD screen.

More preferably, use is made of a PDLCD (Polymer Dispersed Liquid Crystal Display) mask, which
5 has the added advantage that it does not absorb, but scatters, the non-transmitted laser beam, so that the mask does not become warm.

Advantages of these masks are that the desired mask can be computer-generated on the LCD
10 screen or PDLCD screen, whereupon the surface can be irradiated through the mask. Subsequently, a second mask is retrieved on the screen in the same position. This avoids possible positioning problems. Another advantage is that the various masks can be replaced
15 very rapidly.

Very good results are achieved if the process of the invention is practised with a laser device which simultaneously irradiates the object's surface with the aid of at least 3 masks positioned adjacent to each
20 other, with the masks being irradiated with laser light of different wavelengths in such a manner that the mask's images are projected onto the object's surface one over the other. The advantage is that the object's surface is irradiated with different masks in a single
25 operation. If in this procedure the masks are variable, an extra advantage is that different markings can be applied in very rapid succession. A set-up of the same kind is known from video projection.

The process can also be practised using a
30 controlled laser beam of variable intensity. This affords greater flexibility in terms of the shape of the object to be irradiated and the brightness of the colours.

Furthermore, a laser device with adjustable
35 wavelength is also most desirable inasmuch as it is then possible to irradiate the surface with laser light

of different wavelengths using a single laser device.

Preferably, the laser is capable of emitting light of the different wavelengths that match the maxima of the absorption spectra of the different
5 light-absorbing components. It is then possible to form all possible colours with a single laser device.

More preferably, use is made of a laser device in which at least 3 laser beams of different wavelengths are united in a single fibre, it being
10 possible to vary the intensity of each beam independently of the other beams. The advantage of this is that the object's surface can readily be irradiated with the aid of one combined laser beam which is capable of emitting all colours. This results in very
15 high flexibility as to the number of colours that can be selected and the shape of the marking to be applied.

Example I

A dry blend was prepared from 1897 parts by
20 weight of Ronfalin® SFA-34, an acrylonitrile-butadiene-styrene copolymer (ABS) supplied by DSM of the Netherlands, 100 parts by weight of Tiofine® R41, a titanium dioxide pigment supplied by Tiofine of the Netherlands, and 1 part by weight of Irgalith® Rubine
25 4BP, 1 part by weight of Irgalith Blue LGLD and 1 part by weight of Cromopthal® Yellow 6G, respectively magenta, cyan and yellow coloured pigments supplied by Messrs Ciba Geigy of the Netherlands.

The dry blend was melted in a ZSK®30 twin-
30 screw extruder supplied by Werner and Pfleiderer of Germany, kneaded at 260°C and granulated. The granulate was injection-moulded to plaques measuring 3.2*120*120mm in an Arburg Allrounder® 320-90-750 injection-moulding machine at a temperature of 240°C.
35 The coloured pigments in the plaques absorb visible light. The plaques were pale grey.

Markings were subsequently applied onto the surface by means of a laser set-up. Use was made of a tunable wavelength laser set-up (TMW laser set-up). The laser set-up contained a type EEO®-355 seeding laser, which was used as pump laser for a type GCR®-230/50 Nd:YAG laser. Furthermore, the laser set-up contained a type MOPO® 710 Optical Parameter Oscillator (OPO), which received the signal from the last-mentioned laser via a Frequency Doubling Optic (FDO). The set-up was supplied by Spercra-Physics of the USA.

The following laser settings were chosen:

Pulse width: 5 ns

Q-switching frequency: 30 Hz

dot diameter: 3 mm

writing speed: 10 mm/s

line spacing: 0.66 mm

focal length: +80 mm

A colour photo was applied onto the specimens by means of the aforementioned laser set-up by the method described below. A colour photo was broken down into a "red mask", a "green mask" and a "blue mask" (option: split channels RGB) by means of "Corel-Photoprint 5.0 for Hewlett Packard" of the Corel Corporation of the USA. These black/white masks were printed onto transparencies using a "Spectra Star™ GTx" colour printer of Messrs General Parametric Corporation of the USA. Position crosses were provided round the images for accurate positioning.

Subsequently, the "blue mask" was fitted onto the aforementioned plaques and irradiated with the laser at a wavelength of 450 nm. Next, this mask was removed and replaced with the "green mask", which was accurately positioned over the image obtained with the "blue mask". This "green mask" was irradiated with laser light having a wavelength of 530 nm. Lastly, the "red

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mask" was fitted and irradiated with laser light having a wavelength of 650 nm. On completion of this last irradiation an indelible colour photo had been obtained in the plastic, the colour range of which photo was
5 comparable with that of the original.

Example II

A lacquer consisting of 65.0 parts by weight of Uracron® 474 CY, a hydroxyfunctional resin supplied
10 by DSM Resins of the Netherlands, 20.8 parts by weight of Tolonate® HDT EV 412, supplied by Hüls of Germany, 0.6 part by weight of dibutylindilaureate supplied by Aldrich of Belgium, 10.0 parts by weight of Kronos® CL 220, 1.2 parts by weight of Cromoptal® Yellow 3G, a
15 yellow pigment supplied by Ciba Geigy of the Netherlands, 1.2 parts by weight of Paliogen® Red L 3910 HD, a red pigment supplied by BASF of the Netherlands and 1.2 parts by weight of Orasol® Blue GN a blue colorant supplied by Ciba Geigy of the
20 Netherlands was prepared in a beaker by vigorous stirring. The lacquer was applied onto an aluminium sheet to a film thickness of 50 micrometres. The lacquer film had a grey hue. Markings were made in the lacquer film as described in example I.

25 The laser settings for this experiment were:
pulse width: 5 ns
Q-switching frequency: 30 Hz
dot diameter: 3 mm
writing speed: 25 mm/s
30 line spacing: 0.66 mm
focal length: +40 mm

C L A I M S

1. Process for the manufacture of a colour-marked
5 object by irradiating the surface of the object
with laser light, characterized in that the
object, at least at the location where the marking
is applied, consists of a plastic composition
which contains at least three light-absorbing
10 components which exhibit a maximum in their light
absorption spectra at different wavelengths and
lose their light-absorbing capacity under the
influence of laser light, with the marking being
applied in the form of matrix dots by irradiating
15 the object's surface at the location of the matrix
dots with laser light of such wavelength and
intensity and for such duration that at least one
of the light-absorbing components has completely
or partially lost its light-absorbing capacity.
- 20 2. Process according to claim 1, characterized in
that the colour of the surface is formed by the
subtractive mixing of at least three different
coloured matrix points.
3. Process according to claim 1, characterized in
25 that the colour of the surface is formed by
partitive mixing of the colours of the matrix
dots.
4. Process according to any one of claims 1, 2 or 3,
characterized in that the light-absorbing
30 components are so selected that the area between
the points representing the at least three
different colours of the matrix points in the
colour diagram cover at least 10% of the area of
the diagram.
- 35 5. Process according to any one of claims 1-4,
characterized in that the wavelengths of the laser



light with which the surface is irradiated are those at which the maxima occur in the absorption spectra of the different light-absorbing components.

- 5 6. Process according to any one of claims 1-5, characterized in that the process of the invention is practised with the aid of one or more masks.
7. Process according to any one of claims 1-6, characterized in that the process of the invention
- 10 is practised with the aid of a variable mask.
8. Process according to claim 6, characterized in that the mask is produced by an LCD screen.
9. Process according to claim 6, characterized in that use is made of a variable PDLCD (Polymer
- 15 Dispersed Liquid Crystal Display) mask.
10. Process according to any one of claims 1-9, characterized in that the surface is irradiated with a laser device which simultaneously irradiates the object's surface with the aid of at
- 20 least 3 masks positioned adjacent to each other, with the masks being irradiated with laser light of different wavelengths in such a manner that the mask's images are projected onto the object's surface one over the other.
- 25 11. Laser device characterized in that at least 3 laser beams of different wavelengths are united in a single fibre, it being possible to vary the intensity of each beam independently of the other beams.