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(54) Title: MARKABLE POLYMER COMPOSITION AND MARKING PROCESS

(57) Abstract: The invention relates to a polymer composition that can be marked in one or more colours and that contains a polymer matrix and at least one prechromic compound which can be converted into at least two differently coloured conjugated compounds, each with a different increased conjugation length, by supplying energy. The invention also relates to an object entirely or partly made of said polymer composition, to a process for marking such an object in one or more colours and to a marked object thus obtained.



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## MARKABLE POLYMER COMPOSITION AND MARKING PROCESS

5                   The invention relates to a polymer composition which can be marked in one or more colours and which contains a polymer matrix and at least one prechromic compound. The invention also relates to an object entirely or partly made of said polymer composition, to a process for marking such an object in one or more colours and to a marked object thus obtained.

10                   Such a polymer composition is for example known from WO 98/19868. This publication describes a plastic composition containing at least three prechromic compounds which acquire their colour-forming power only after a colour-forming treatment, for example through illumination with UV light, and which may subsequently lose their colour-forming power under the influence of  
15   laser light. The at least three components may each be selectively bleached with the laser, so that a multi-colour image may be formed on a light substrate.

                  The drawback of the known method is that at least three different prechromic compounds must be present in the plastic composition to enable the application of a multi-colour marking or several markings in different  
20   colours. Another drawback is that the object's surface, at least the part where the marking is to be applied, must first be subjected to a colour-forming treatment, for example by means of irradiation with UV or IR laser light, after which the then differently coloured surface may be bleached to the desired colour or colours by (multiple) irradiation using for example VIS laser light, in the shape of the marking.

25                   The invention aims to provide a polymer composition that does not possess the aforementioned drawbacks, or possesses them to a lesser extent.

                  The inventors have surprisingly achieved this aim with a polymer composition containing at least one prechromic compound that can be converted into at least two differently coloured conjugated compounds, each with a different  
30   increased conjugation length, by supplying energy.

                  Within the context of the present application, a prechromic compound is defined as a colourless or only lightly coloured compound, which acquires a chromatic colour only after undergoing a colour-forming treatment. It may be a compound of low molar mass, but also an oligomeric or polymeric  
35   compound. The supply of for example energy to such a prechromic compound causes the compound to change into a modified compound of a (different) chromatic colour. This change in colour may be the consequence of the formation

of a conjugated system or of the expansion of a conjugated system. A conjugated system will expand when a larger number of atoms comes to form part of the system; this is also referred to as an increased conjugation length.

The prechromic compound in the polymer composition  
5 according to the invention differs from compounds that are used in the state of the art in that the supply of specific amounts of energy results in the conversion of a starting compound into at least two differently coloured conjugated compounds with different conjugation lengths. Coloured conjugated compounds with different conjugation lengths can be formed from a prechromic compound in different ways.  
10 The supply of energy may for example effect the separation of one or more groups from a chain, resulting in the formation of an unsaturated bond at the point where the group was attached to the chain, and hence the formation of a conjugated system or an increase in the size of a conjugated system. The more groups that are separated, the greater the system's conjugation length will be. A  
15 compound may for example already contain a number of alternating saturated and unsaturated bonds, with the compound's spatial configuration however being such as to allow insufficient overlap of the electron orbitals, precluding a conjugated system. The supply of energy to such a compound may cause its configuration to change so that a conjugated system does form.

20 The size of a compound's conjugated system generally influences that compound's absorption spectrum, and hence the perceived colour. As the conjugation length of a conjugated system increases, the absorption maximum, measured with the aid of a UV/VIS spectrophotometer, will generally shift to longer wavelengths. An example of this is the gradual formation of deep  
25 purple polyacetylene from a virtually colourless polyacetylene precursor under the influence of heat (A.L. Safir et al., *Macromolecules* 1993, 26, pp.4072-73). The prechromic compound is preferably converted step-by-step, by supplying specific amounts of energy, into at least two coloured conjugated compounds, the conjugation length of the conjugated compound increasing with every step. The  
30 advantage of this is that the formation of colour can be far better controlled.

Prechromic compounds that are suitable for use in a polymer composition according to the invention, with it being possible to control the expansion of a conjugated system step-by-step, are for example compounds that contain protecting groups that may be separated from the prechromic compounds  
35 photochemically, thermally or with the aid of a different reactive compound, the separation of a protecting group resulting in the formation of a modified compound

with a conjugated system having a greater conjugation length.

When use is made of a compound containing protecting groups that can be thermally separated, the separation of the protecting groups may be effected by supplying energy in the form of heat or in the form of light, preferably laser light. Preferably, use is made of a prechromic compound whose protecting groups are not thermally removed at the temperature at which the polymer composition concerned is processed, but which may be converted with the aid of laser light.

When use is made of a prechromic compound containing protecting groups that can be photochemically separated, the separation of the protecting groups may be effected by supplying energy with the aid of a light source having the appropriate characteristics, preferably with the aid of laser light having the correct wavelength, etc.

When use is made of a prechromic compound containing protecting groups that can be separated with the aid of a reactant, for example an acid, a latent acid can, by supplying energy, be converted into an acid, which acid subsequently effects the separation of the protecting group.

The prechromic compound is preferably colourless, but a prechromic compound having a yellow colour, which means it exhibits absorption in the wavelength range up to approximately 500 nm, may also be used. Preferably, use is made of a prechromic compound with which the supply of energy ultimately results in the formation of a compound that colours cyan, i.e. that shows absorption in the wavelength range from approximately 600 to 700 nm. Compounds that colour cyan are generally compounds having a band gap of less than 2 eV. A band gap is defined as the difference in energy between the valence band and the conduction band. More preferably, use is made of a prechromic compound which may, after the supply of energy, be converted step by step into a compound having a band gap that will ultimately be smaller than 1.5 eV. This presents the advantage that for example the colours yellow, magenta and cyan may be created on a polymer composition containing such a prechromic compound by supplying energy. If these three elementary chromatic colours can be created, markings may in principle be obtained in any chromatic colour perceivable with the eye, for example via combinations of small, optionally overlapping, dots in these three colours.

Examples of prechromic compounds that may be used in the polymer composition according to the invention include oligomeric or polymeric

precursors of conjugated polymers, for example polyacetylene, polyisothianaphthene or the alternating copolymer of pyrrole and 2,1,3-benzothiadiazole.

An example is the thermal conversion of a virtually colourless polyacetylene precursor, for example poly(diethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate), into deep purple polyacetylene (A.L. Safir et al., *Macromolecules* 1993, 26, pp.4072-73). The group of poly(bis-thioalkylacetylenes) are also examples of polyacetylene precursors that may be converted into conjugated systems under the influence of energy, for example laser light (see for example J. Bargon and R. Baumann, *Microelectronic Engineering* 20, pp.55-72, 1993).

Good results have been obtained by using as the prechromic compound an alternating oligomer or polymer of N-Boc-pyrrole and 2,1,3-benzothiadiazole, as described by H.A.M. van Mullekom et al., *J. Chem. Soc.*, 1996, p.2163. In the case of this precursor the separation of the so-called Boc protecting group, i.e. t-butyloxycarbonyl group, from the nitrogen atom in the pyrrole unit may lead to the formation of a configuration with a conjugated system. This is due to the fact that, before the separation, the Boc groups prevent the formation of hydrogen bridges between the hydrogen atom attached to the nitrogen atom in the pyrrole and the nitrogen atoms of the 2,1,3-benzothiazole groups on either side of it. The formation of the hydrogen bridges changes the configuration, resulting in the formation of a conjugated system.

Such precursors of conjugated polymers have been described primarily with a view to obtaining electrically conductive polymers. Conversion of a precursor into a conjugated electrically conductive polymer through irradiation with laser light then presents the advantage that patterns for microelectronic circuits can then be created via (micro)lithographic techniques. The prime concern in such cases is obtaining favourable electrical properties of the polymer formed, colour formation not generally being an objective and in many cases even being undesirable. To obtain acceptable mechanical properties, necessary to produce for example flexible thin layers of polymer, besides good electrical properties, the polymer must have a specific minimum chain length or molar mass. Such mechanical properties are not necessary for the use of said precursors for conjugated polymers as prechromic compounds in markable polymer compositions. A minimum chain length is in the latter case determined by the light absorption spectrum, or by the size of the conjugated system. When the

conjugated compound has acquired a dark blue colour (cyan), the conjugation length need not increase any further. This will generally be the case at a much shorter chain length than is needed to arrive at the mechanical properties that are required for use as a conducting polymer in electronic applications. Preferably, the number of repeating units that may belong to a single conjugated system is therefore less than 100, more preferably less than 50, even more preferably less than 25 and most preferably less than 10. An oligomer or polymer will in general contain a single conjugated system consisting of successive repeating units. A polymer chain may however also contain several such conjugated systems.

The prechromic compound in polymer compositions according to the invention contains in a preferred embodiment according to the invention of an oligomer or polymer containing a specific maximum number of repeating units that can form part of a single conjugated system. The advantage of this is that the supply of a specific amount of energy ultimately leads to the formation of a single specific colour, associated with the maximum conjugation length. Different colours may then be obtained by supplying different specific amounts of energy in localized areas, so that colour blends can be observed. In such a case, by determining the formation of different coloured conjugated compounds, with conjugation lengths shorter than the maximum length, as a function of the supply of specific amounts of energy, a distinct relationship between the supplied amount of energy and the obtained colour may be obtained. In this way, a multi-colour marking in the desired colours may be obtained.

In another preferred embodiment the prechromic compound in the polymer composition according to the invention contains a mixture of oligomers or polymeric chains that differ in terms of the number of repeating units that can belong to a single conjugated system. This may be for example a mixture of oligomers of a specific chemical composition, but with a specific polydispersity. Such a polydispersity, or distribution of different chain lengths or molar masses, is often formed naturally during polymerisation. Thus, in such a mixture there are intermolecular differences in the maximum conjugation length and hence also intermolecular colour differences. The advantages of this are that the compound can be prepared in a simpler way, and that there are more possibilities of obtaining different colour blends by supplying a specific amount of energy.

As the polymer matrix, the polymer composition according to the invention in principle can contain any polymer or mixture of polymers known to those skilled in the art. Thermoplastic and thermosetting polymers, elastomers

and biopolymers may all be used. Suitable examples are given in for example WO 94/12352. Preferably, use is made of a polymer that can be processed at a temperature that is lower than the temperature at which the prechromic compound is converted into a coloured conjugated compound on supplying heat. For  
5 thermoplastic polymers, the processing temperature is the temperature at which the polymer is processed in the melt phase, for a thermosetting polymer it will often be the temperature at which the polymer composition is cured.

The polymer composition according to the invention can be prepared in any way known to those skilled in the art, for example by mixing the  
10 components with the aid of rolls, an injection-moulding machine, an extruder or another mixing or kneading apparatus. The prechromic compound may also be first mixed with a polymer in a relatively high concentration, after which the concentrate is mixed with the same or a different polymer until the desired final concentration is obtained. It is also possible to mix the components of the polymer  
15 composition in a solution, a suspension or an emulsion. Further, it is possible to add the prechromic compound already during the preparation of the polymer.

The polymer composition may also contain one or more of the usual additives, such as fillers and reinforcing agents, stabilisers, processing aids, flame retardants, dispersing agents, etc. The polymer composition may optionally  
20 also contain one or more other additives, for example pigments that are not sensitive to the energy supplied with a view to the application of the marking, to improve the colour or the intensity of the colour of the coloured conjugated compound formed.

The polymer composition according to the invention can also  
25 contain one or more additives for improving the absorption of laser light, which promotes the formation of coloured conjugated compounds or enables such formation when use is made of laser light of a wavelength at which no change in colour would normally occur. The laser light absorption of such an additive is preferably wavelength-selective.

30 The amount of prechromic compound added to the polymer composition according to the invention will depend on the desired intensity of the colours, and may vary within a wide range. The polymer composition according to the invention preferably contains 0.005 - 10 mass percent prechromic compound, more preferably 0.01 - 5 mass percent and even more preferably 0.05 - 1 mass  
35 percent prechromic compound (total of the one or more prechromic compounds relative to the total mass of the polymer composition).

The polymer composition according to the invention can be processed into an object consisting entirely or partly of the polymer composition by techniques known to those skilled in the art, for example by injection-moulding or extrusion, or by applying a coating to an object by for example spin-coating.

- 5 Allowance must then however be made for the stability of the chosen prechromic compound to prevent the risk of all or part of it being converted already during the production of the object.

- 10 In a preferred embodiment all or part of an object is covered with a coating containing the polymer composition according to the invention, which has optionally cured at room temperature.

- The invention also relates to a process for marking an object consisting entirely or partly of the polymer composition according to the invention in one or more colours by supplying specific amounts of energy to the polymer composition to convert the prechromic compound into at least one coloured conjugated compound with an increased conjugation length. Preferably, the prechromic compound is converted into at least two coloured conjugated compounds, each with a different increased conjugation length. Even more preferably, the prechromic compound is converted into at least three coloured conjugated compounds, each having a different increased conjugation length. The advantage of this is that any other desired colour may be obtained by mixing the at least three colours. Good results are obtained when the prechromic compound may be converted into conjugated compounds that are yellow, magenta and cyan.
- 15  
20

- Energy may be supplied in different forms, for example in the form of heat or in the form of light, for example laser light. Heat may be supplied by pressing for example a heated object, like a stamp in the form of the marking, onto a surface consisting of the polymer composition according to the invention, or by pressing hot needles onto the surface, with the pattern of the pinpoints created by the needles forming a marking, which marking may comprise a single chromatic colour if all the needles have the same temperature or which marking may comprise several colours if the employed needles have different temperatures. The amount of energy supplied by contacting the object with a heated object depends on such factors as the object's temperature and the contact time.
- 25  
30

- Energy may also be supplied in a localized area by means of irradiation with laser light. The advantage of this is that the amount of energy supplied can be accurately controlled via the wavelength and the intensity of the
- 35

laser light, the duration of irradiation the surface and the type of laser used.

The specific amount of energy to be supplied in order to obtain a specific conjugation length, and hence a specific colour, depends on the type of prechromic compound used, on the polymer that forms part of the polymer composition and on any other additives that may optionally form part of the polymer composition. Those skilled in the art will easily be able to experimentally determine the relation of the amount of energy to be supplied and the colour obtained for a given polymer composition. The laser parameters, such as wavelength, intensity, pulse duration, pulse length, pulse frequency, total irradiation time and the like, required to obtain a specific desired colour in a specific polymer material can for example be determined by producing specimens from the material and irradiating them at various different laser settings beforehand. The energy density can also be varied within certain limits by creating a converging beam with the aid of a lens placed in the laser beam. The greater the difference between the distance from the moulded part to the lens and the focal distance, the lower the density will be. This yields a table of colours obtained at each of the laser settings. From then onwards the laser settings required to irradiate an object of that polymer composition to create any desired colour can be determined with the aid of the table. This can be entirely or partly automated with a computer.

In a preferred embodiment of the method according to the invention, an object consisting entirely or partly of the polymer composition according to the invention is irradiated with a laser beam. In this way, matrix dots can be applied to the object's surface. A marking of one or more specific colours is obtained by applying a large number of matrix dots of different colours to the surface, for example the three chromatic colours yellow, magenta and cyan. An observer will perceive the colour of the surface in the area of the matrix dots as a blend colour, because the colours of the matrix dots will not be seen individually with a naked eye. The colour of the blend depends on the ratio of the area of the matrix dots and the ratio of the brightness of the colours. A large number of different colours can thus be created. Of importance in this context is that the centre-to-centre distance between the individual matrix dots is so small that the eye cannot perceive the individual matrix dots. Such a process for applying a multi-colour marking is for example described in patent application WO 98/19868.

The process according to the invention makes it possible to

write directly on the surface in the form of lines or dots by using a laser, optionally a pulsed laser, with a writing head or to use masks. In a preferred embodiment one or more masks are used in the production of objects bearing one or more coloured markings according to the invention. These masks are transparent in the places where the surface is to be irradiated and are non-transparent in places where the surface is not to be irradiated. An advantage of this is that the size of the matrix dots is determined by the mask and not by the laser beam, so that the surface can be irradiated with a laser beam having a large diameter. Irradiation will consequently take less time and additionally a high resolution will be obtained. Preferably, the process according to the invention is carried out with the aid of a variable mask.

The invention also relates to a marked object obtained with the process according to invention. Examples of such objects are information carriers such as posters, signboards, identity, credit or cash-point cards, (parts of) utilitarian objects, etcetera. The objects can carry one or more monochromatic markings of different colours, but also one or more multi-coloured markings.

The invention will now be elucidated with reference to several examples without being limited thereto.

#### Examples I – III and Comparative Experiment A

Plates 1 to 4 were produced as follows: 500 mg of Lexan® PC105, a polycarbonate marketed by General Electric Plastics (NL), was dissolved in 10 ml of CHCl<sub>3</sub> to form a homogeneous transparent solution (solution A). Next, 10 mg (0.014 mol) of the prechromic compound 4,7-bis[5-(2,1,3-benzothiadiazol-4-yl)-N-t-Boc-pyrrole-2-yl]-2,1,3-benzothiadiazole (precursor B), synthesized as described by Van Mullekom et al. in Chem. Commun., 1996, pp. 2163-2164, was dissolved in 5 ml of solution A. This led to the formation of a light yellow, homogeneous, transparent solution (solution C). Solution C was used to apply a homogeneous polycarbonate film containing precursor B to a glass plate with the aid of a spin-coating technique. To this end a clean, dry glass plate was placed on a PM101 DT-R48S photo-resist spinner supplied by Headway Research Inc. (US), after which the entire glass surface was coated with solution C. The glass plate was then spun for 10 seconds at a speed of 650 rpm, followed by 20 seconds at 4000 rpm. The glass plates thus obtained were homogeneously coated, transparent and of a light yellow colour.

Example I

Plate 1 was placed on a plate heated to approximately 220°C. After about 5 minutes the entire plate was found to have turned blue and it retained this colour after cooling (absorption maximum at approximately 597 nanometres)

Example II

A temperature gradient was created across plate 2 by bringing one end into contact with a plate heated to about 220°C, while the opposite end was supported outside the plate and hence remained at room temperature. A discolouration was immediately observed at the side of the plate heated to 220°C, which gradually shifted towards the side remaining at room temperature. When the discoloured zone had moved halfway across the glass plate, the latter was removed from the heated plate and cooled to room temperature. A colour gradient from yellow to orange to red to purple to blue was observable parallel to the applied temperature gradient (in the direction in which the temperature increased).

Example III

Plate 3 was irradiated with a CO<sub>2</sub> laser in a number of areas using the following laser settings:

- a pulse frequency of 5000Hz
- a wavelength of 10.6 micrometres
- an intensity of approx. 1 W/mm<sup>2</sup>
- a dot diameter of approx. 5 mm.

Three different areas were irradiated for 5, 10 and 15 seconds, respectively, which caused the light yellow colour to change to pinkish red, purple and blue, respectively.

Comparative Experiment A

Plate 4 was produced analogously to plates 1 up to and including 3 except that solution A, instead of solution C, was used in the spin-coating step. Plate 4 was homogeneously coated, transparent and colourless and was used as a reference. Plate 4 was irradiated under the same conditions as plate 3. No changes in colour or surface gloss were observed on plate 4. Irradiation for a greater length of time results in brown markings due to degradation of the polymer.

#### Examples IV-VI

Plates 5 to 7 were made as follows. Commercial-grade solvents were used.

Varnish D was prepared using 58.5 mass % Uralac® SN820X-70, a saturated polyester resin in xylene produced by DSM Resins (NL), 23.9 mass% Uramex®MF 822 B, an amino-resin crosslinker from DSM Resins (NL), 8.0 mass% Solvesso 100, a solvent containing a mixture of hydrocarbons, 4.8 mass% n-butanol, and 4.8 mass% methoxypropylacetate (mpa).

TiO<sub>2</sub> paste E was prepared from a concentrated grinding-type resin that was diluted with a diluting resin. The concentrated grinding-type resin was prepared from: 500 g of Kronos® 2059, a titanium dioxide, 200 g of Uralac® SN820X-70, 75 g of xylene/mpa 2/1, 40 g of Solvesso 100 and 2 g of K-disperse 152, a pigment dispersant from King Industries (UK). The diluting resin was prepared from: 85 g of Uralac® SN820X-70, 50 g of butyl glycol and 48 g of Solvesso 100.

Paste E was bead-ground using 200 g of glass beads. The particle size of the TiO<sub>2</sub> pigment in the ultimately obtained paste E was smaller than 12 micrometres.

0.0203 g of precursor B was dissolved in 5 drops of CH<sub>2</sub>Cl<sub>2</sub>. To this were then successively added 0.512 g of TiO<sub>2</sub> paste E, 0.554 g of varnish D and 1 drop of a 1% solution of BAY silicon oil OL-17 in xylene. The mixture was mixed with the aid of a contact mini-shaker/vortex (Tamson, NL) and then applied to a glass plate (approx. 10x10x0.3 cm) in a thin layer with the aid of a 150 micrometre doctor blade (Tamson, NL). The glass plate had been cleaned with isopropanol before the application of the solution. The glass plate and the substrate were heated in an oven for eight hours at 100°C. The cured coating was light yellow, opaque and had a glossy surface (approx. 10x7 cm).

#### Example IV

Plate 5 was irradiated with the aid of a frequency-doubled Nd-YAG laser (532 nm) supplied by Haas of Germany. The following settings were selected: intensity 1.4 W; pulse frequency 3kHz; writing speed 254 mm/s; writing density 300 dpi dot diameter approx. 80 micrometres. In the irradiated area the light yellow colour turned bright blue. In this way a matt blue square measuring about 3x3 mm was obtained.

Example V

Plate 6 (identical to plate 5) was irradiated with the aid of an Nd-YAG pumped, tunable OPO laser (Lambda Physik, of Germany). The following laser settings were selected: wavelength 421 nm, pulse frequency 1 kHz, intensity 500 mW, writing speed 24 mm/s. Only the distance from the plate to the focus of a lens placed in the beam (focal distance = 200mm) was varied. A block measuring 10 x 10 mm was written.

Distance between the plate and the focus 108 mm: in the irradiated area the light yellow colour turned pinkish red. The gloss of the surface was not affected. The settings mentioned above were used to write twice in the same area elsewhere on the varnish. A darker shade of pinkish red was obtained than after the single writing session. Three and four irradiation sessions in the same area resulted in an identical shade of pinkish red, which was a little redder than after two writing sessions.

The distance from plate 6 to the focus was then reduced, causing the energy density to increase. The block was written once. Results:

83 mm out of focus: in the irradiated area the light yellow colour turned pinkish red; as a result of better focussing, the laser's writing pattern was visible, which was not the case at 108 mm out of focus.

68 mm out of focus: in the irradiated area the light yellow colour changed into purple lines with pink edges.

58 mm out of focus: in the irradiated area the light yellow colour changed into very dark blue lines with pinkish red edges.

Example VI

Plate 7 (identical to plates 5 and 6) was irradiated with laser light of 676 nm from the aforementioned Nd-YAG pumped OPO laser. The plate was 108 mm out of focus, the writing speed was 12 mm/s. In the irradiated area the light yellow colour changed into a shade that appeared green to the eye.

CLAIMS

1. Polymer composition which can be marked in one or more colours and which contains a polymer matrix and at least one prechromic compound, characterised in that the prechromic compound can be converted into at least two differently coloured conjugated compounds, each with a different increased conjugation length, by supplying energy.
2. Polymer composition according to Claim 1, characterised in that the prechromic compound can be step by step converted into at least two differently coloured conjugated compounds by supplying energy, the conjugation length of the conjugated compound increasing with each step.
3. Polymer composition according to Claim 1 or 2, characterised in that the prechromic compound can be converted into at least two coloured conjugated compounds by supplying energy in the form of laser light.
4. Polymer composition according to Claim 1 or 2, characterised in that the prechromic compound can be converted into at least two coloured conjugated compounds by supplying energy in the form of heat.
5. Polymer composition according to any one of Claims 1-4, characterised in that the band gap of the coloured conjugated compound is smaller than 2 eV.
6. Polymer composition according to Claim 5, characterised in that the band gap is smaller than 1.5 eV.
7. Polymer composition according to any one of Claims 1-6, characterised in that the prechromic compound is a precursor of an alternating oligomer or polymer of pyrrole and 2,1,3-benzothiadiazole.
8. Polymer composition according to Claim 7, characterised in that the prechromic compound is an alternating oligomer or polymer of N-Boc-pyrrole and 2,1,3-benzothiadiazole.
9. Polymer composition according to any one of Claims 1-6, characterised in that the prechromic compound is a precursor of a polyisothianaphthene.
10. Polymer composition according to any one of Claims 1-6, characterised in that the prechromic compound is a precursor of a polyacetylene.
11. Polymer composition according to any one of Claims 1-10, characterised in that the prechromic compound is an oligomer or polymer containing at

- least 10 successive repeating units which may belong to a single conjugated system.
12. Polymer composition according to Claim 11, characterised in that the composition contains a prechromic compound that contains a mixture  
5 oligomers or polymeric chains that differ in terms of the number of successive repeating units that can belong to a single conjugated system.
13. Polymer composition according to any one of Claims 1-12, characterised in that the polymer composition contains between 0.01 and 5 mass% of the prechromic compound (total of the one or more prechromic  
10 compounds relative to the total mass of the polymer composition).
14. Polymer composition according to any one of Claims 1-13, characterised in that it also contains an additive for improving the colour or colour intensity of the coloured conjugated compound formed.
15. Polymer composition according to any one of Claims 1-14, characterised in that it also contains an additive for improving the absorption of the  
15 laser light.
16. Polymer composition according to Claim 15, characterised in that the additive has wavelength-selective absorption of the laser light.
17. Object entirely or partly produced from the polymer composition  
20 according to any one of Claims 1-16.
18. Object entirely or partly provided with a coating containing the polymer composition according to any one of Claims 1-16.
19. Process for marking an object according to Claim 17 or Claim 18 in one or more colours, wherein a specific amount of energy is supplied to the  
25 polymer composition, as a result of which the prechromic compound is converted into at least one coloured conjugated compound with an increased conjugation length.
20. Process for marking an object according to Claim 17 or Claim 18 in one or more colours, in which specific amounts of energy are repeatedly  
30 supplied to the polymer composition, as a result of which the prechromic compound is converted into at least two differently coloured conjugated compounds, each with a different increased conjugation length.
21. Process according to Claim 19 or Claim 20, characterised in that the specific amount of energy is supplied through irradiation with laser light,  
35 the laser conditions being selected in accordance with the desired increase in conjugation length of the prechromic compound.

22. Process according to any one of Claims 19-21, characterised in that one or more masks are used in the process.
23. Process according to any one of Claims 19-20, characterised in that the specific amount of energy is supplied in the form of heat by contacting the object with an object of a specific temperature, the conditions being selected in accordance with the desired increase in conjugation length of the prechromic compound.
24. Marked object obtained with the process according to any one of Claims 19-23.
25. Marked object containing two or more coloured conjugated compounds derived from a prechromic compound, each with a different increased conjugation length.

## INTERNATIONAL SEARCH REPORT

Application No

PCT/NL 01/00531

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B41M5/26 B41M5/28 G03C1/73 G03C7/46 C08K5/46  
C08K5/3415 B41M5/34

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)

IPC 7 B41M G03C C08K

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, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages                                                         | Relevant to claim No. |
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents :

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\*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

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\*&amp;\* document member of the same patent family

Date of the actual completion of the international search

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| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
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