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(54) Title: MEASURE OF THE DEGREE OF CRYSTALLINITY OF A POLYMER COATING ON A METAL SUBSTRATE

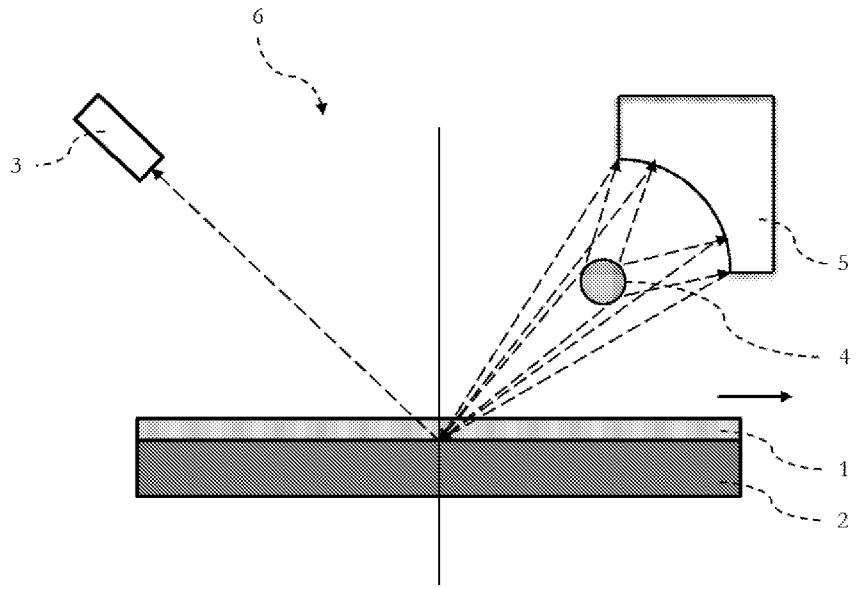

Figure 7

(57) Abstract: The present invention relates to a method and a measuring equipment of the degree of crystallinity of a polymer coating on a metallic substrate using a hyperspectral camera as well as representing or mapping said degree of crystallinity. An equipment for online measurement of crystallinity of polymers, according to the present invention comprising at least one hyperspectral camera, at least one lighting source, a polymer layer deposited on a substrate and means to convey said substrate, the lighting source and the hyperspectral camera being set-up in specular reflection towards said polymer layer.

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[Continued on next page]

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MEASURE OF THE DEGREE OF CRYSTALLINTY OF A POLYMER COATING ON A METAL SUBSTRATE

The present invention relates to a method and a measuring equipment of the degree of crystallinity of a polymer coating on a metallic substrate as well as representing or mapping said degree of crystallinity.

Applying a coating on a metal substrate enhance its properties such as corrosion resistance. Polymer coating films are usually laminated on a metal substrate then heated and eventually quenched. This quench, depending on the cooling speed applied, may hinder the formation of crystalline phase within the polymer, that will be partly in an amorphous state. The degree of crystallinity of the coating, which represents the proportion of polymer with a crystalline structure, influences greatly its properties. Thus, it is essential to assess the degree of crystallinity of such coatings to assure that the desired properties, requirements and specifications are met.

In the state of the art, the degree of crystallinity of a polymer coating on a metallic substrate is predominantly measured non-destructively using the Raman spectroscopy. This method is negatively impacted by some measurement conditions such as humidity, the chattering of the substrate, the medium between the substrate and the lighting or measuring devices, a variation in the distance between the sample and the measuring or lighting devices. Moreover, the lighting source used during a Raman spectroscopy generally heats the coating and degrades it, favouring the formation of crystalline phase. Furthermore, any light other than the lighting source impacts negatively the measurement precision. Consequently, the measured area needs to be protected from natural and exterior lights which is a major drawback for its industrial use.

Other techniques such as DRX or infrared spectroscopy can measure the degree of crystallinity of polymers but they are not applied on polymer coatings on a metallic substrate.

Besides, using the methods and equipment described in the state of the art, it is only possible to determine the crystallinity degree of a single spot along the substrate coating width. Depending on the technique used, those single spots are more or less spaced in function of the acquisition time, (from at least a dozen of seconds for the Raman spectroscopy to a fraction of second for the infrared spectroscopy) and the substrate speed. Figure 1 schematically illustrates the space between two consecutive measured spots depending on the measurement techniques (A: Raman spectroscopy, B and C: infrared spectroscopy, D and E: the present invention), each coloured spot represents a measured spot.

Consequently, there is a need to find a way to measure and represent the degree of crystallinity of a polymer coating, on the full width of such coating deposited on a metallic substrate, without degrading said coating and with a good precision of the measurement.

The purpose of this invention is to meet the aforementioned need.

This object is achieved by providing a method according to claim 1. The method can also comprise any characteristics of claims 2 to 9. This object is also achieved by providing an apparatus according to claims 10 to 13.

Other characteristics and advantages of the invention will become apparent from the following detailed description of the invention.

To illustrate the invention, various embodiments will be described, particularly with reference to the following figure:

Figure 1 is a schematic representation of the measured area by the different techniques, A) Raman spectroscopy: A); Infrared: B) and C); the invention D) and E).

Figure 2 is a schematic representation of a first embodiment of a measuring equipment.

Figure 3 is a schematic representation of the intensity curves in function of the wavelength for two different coatings, one being 100% crystalline and the other being 100% amorphous.

Figure 4 is a schematic representation of the intensity curves in function of the wavelength for two different measurement conditions.

Figure 5 is a schematic representation of the distance travelled through the coating layer by a beam in function of the incident angle.

Figure 6 is an abacus linking the calculated ratio with the degree of crystallinity for an incident angle of 45° for a PET coating.

Figure 7 is a schematic representation of a second embodiment of a measuring equipment.

The invention relates to a process for mapping the crystallinity of a polymer coating 1 on a moving metallic substrate 2, the process repeating the following steps:

a) lighting a transversal area of said polymer coating 1 encompassing its full width W, with a polychromatic light including wavelengths in the infrared domain,

b) measuring with at least one hyperspectral camera 3,

- the light intensity $S_{impacted,\lambda\alpha}$ at a predetermined wavelength λα impacted by the degree of crystallinity of said coating in the infrared domain and
- the light intensity $S_{stable,\lambda\beta}$ at a predetermined wavelength λβ not impacted by the degree of crystallinity of said coating in the infrared domain

of at least two light beams (B1, B2) from said polychromatic light after reflection on said moving metallic substrate 2 on two different locations (L1, L2) within said transversal area,

c) determining at least an impacted absorbance A_{imp}, using said light intensity $S_{impacted,\lambda\alpha}$ at said predetermined wavelength λα impacted by the degree of crystallinity for each beam (B1, B2),

d) determining at least a stable absorbance A_{sta}, using said light intensity $S_{stable,\lambda\beta}$ at said predetermined wavelength λβ not impacted by the degree of crystallinity for each beam (B1, B2),

e) determining, for each beam (B1, B2), a ratio, R, equals to A_{imp}/A_{sta}

f) converting each ratio R to a degree of crystallinity,

g) mapping the degree of crystallinity of said polymer coating in said transversal area using said degree of crystallinity and said locations (L1, L2).

On the figures, only the light beams emitted by the polychromatic light emitter 4, reflected on the moving substrate and measured by the hyperspectral camera are represented. As illustrated in Figure 2, a polymer coating 1 deposited on a moving metallic substrate 2 is lighted at least in the infrared domain, from 700 nm to 0.1 mm, with a polychromatic light that can come from a polychromatic light emitter 4. The lighting is done in a way that a transversal zone encompassing the full width W of said polymer coating 1 is lighted.

Then a hyperspectral camera 3 measures the light intensity $S_{impacted,\lambda\alpha}$ at a predetermined wavelength λ_α in the infrared domain, that is impacted by the degree of crystallinity, as explained later. The measurement is done for at least two beams, e.g. B1 and B2, from the polychromatic light emitter 4 reflected by said moving metallic substrate 2 on at least two locations, e.g. L1 and L2. The locations are defined by the camera.

Then the hyperspectral camera 3 measures also the light intensity $S_{stable,\lambda\beta}$ at a predetermined wavelength λβ, in the infrared domain, not impacted by the degree of crystallinity. The measure is done for at least two beams, e.g. B1 and B2, from the polychromatic light emitter 4 reflected by said moving metallic substrate 2 on at least two locations, e.g. L1 and L2. The locations are defined by the camera.

As illustrated in Figure 3, in the frame of the present invention, a wavelength is affected by the degree of crystallinity when the intensity variation at this wavelength is superior or equal to 7% between a 100% crystalline coating and a 100% amorphous coating. A wavelength is not affected by the degree of crystallinity when the intensity variation at this wavelength is inferior to 7% between a 100% crystalline coating and a 100% amorphous coating.

Figure 3 exhibits two spectrums, one of a fully crystalline coating in optimal measurement condition (continuous line), one of a fully amorphous coating in optimal measurement condition (dot + dash). In the frame of the present invention, optimal condition means that the measurement is done on a metallic substrate without any polymer coating on it. Three wavelengths are noted (λ_1, λ_2 and λ_3). The wavelength λ_1 is considered as unaffected by the degree of crystallinity because its intensity is the same for the fully crystalline coating and for the fully amorphous coating. The wavelength λ_2 is also considered as unaffected by the degree of crystallinity as its wavelength intensity difference between the fully crystalline coating and the fully amorphous coating is smaller than 7%. The wavelength λ_3 is considered as affected by the degree of crystallinity as the wavelength intensity difference is bigger than 7%.

Then, for each beam, at least an impacted absorbance is determined using said intensity $S_{impacted,\lambda\alpha}$ at the wavelength λ_α, impacted by the degree of crystallinity. The higher the intensity variation at a wavelength due to the degree of crystallinity, the more interesting it is to use such a wavelength for determining an impacted absorbance because the measurement will be more precise.

The impacted absorbance can be calculated, for example, using the following equation:

$A_{imp}=[(S_{impacted,\lambda\alpha}- D_{\lambda\alpha})]$,

where:

- $S_{impacted,\lambda\alpha}$ is the wavelength intensity impacted by the degree of crystallinity of the collected polychromatic light for a determined wavelength λ_α,

- $D_{\lambda\alpha}$ is the acquisition of the dark and represents the background noise for a determined wavelength λ_1. The dark corresponds to the noise, it is influenced by the camera temperature. Said dark is preferentially measured. It can be measured before the measurement or at regular time with an automatic shutter in the camera.

In the case where several impacted absorbances are determined for a same location along the coating width, a representative value, $Vs_{impacted}$, of them is determined. Preferably, the representative value can be the mean or the median of all the absorbances not impacted by the degree of crystallinity.

Then, for each beam, at least a stable absorbance is determined using said intensity $S_{stable,\lambda\beta}$ at the wavelength λβ not impacted by the degree of crystallinity. The lower the intensity variation at a wavelength due to the degree of crystallinity, the more interesting it is to use such a wavelength for determining an absorbance not impacted by the degree of crystallinity.

The stable absorbance can be calculated, for example, using the following equation:

$A_{sta}=[(S_{stable,\lambda\beta}- D_{,\lambda\beta})]$,

where:

- $S_{stable,\lambda\beta}$ is the wavelength intensity impacted by the degree of crystallinity of the collected polychromatic light for a determined wavelength λβ,

- $D_{\lambda\beta}$is the acquisition of the dark and represents the background noise for a determined wavelength λβ. The dark corresponds to the noise, it is influenced by the camera temperature. It can be measured before the measurement or at regular time with an automatic shutter in the camera.

In the case where several stable absorbances are determined for a same location along the coating width, a representative value, Vs_{stable}, of them is determined. Preferably, the representative value can be the mean or the median of all the absorbances not impacted by the degree of crystallinity.

Then, for each beam, a ratio R between the absorbance impacted by the degree of crystallinity and the absorbance not impacted by the degree of crystallinity is determined.

$R=[S_{impacted,\lambda\alpha}/ S_{stable,\lambda\beta}]$

In the case where representative values of the absorbance impacted by the degree of crystallinity and the absorbance not impacted by the degree of crystallinity are determined, the following ratio RV is calculated:

$RV=[Vs_{impacted}/ Vs_{stable}]$

Each ratio R or RV is linked to a degree of crystallinity.

In another embodiment, the impacted absorbance can be, for example, determined using the following equation:

$A_{imp2}=[(S_{impacted,\lambda\alpha}- D_{\lambda\alpha})/ (R_{i,\lambda\alpha}- D_{\lambda\alpha})]$,

where:

- $S_{impacted,\lambda\alpha}$ is the wavelength intensity impacted by the degree of crystallinity of the collected polychromatic light for a determined wavelength λ_{α},

- $R_{i,\lambda\alpha}$ is the wavelength intensity of the collected polychromatic light for a determined wavelength λ_α in optimal condition for a metallic substrate without coating on it

- $D_{\lambda\alpha}$is the acquisition of the dark and represents the background noise for a determined wavelength λ_1. The dark corresponds to the noise, it is influenced by the camera temperature. Said dark is preferentially measured. It can be measured before the measurement or at regular time with an automatic shutter in the camera.

In another embodiment, the stable absorbance can be, for example, determined using the following equation

$A_{sta2}=[(S_{stable,\lambda\beta}- D_{,\lambda\beta})/ (R_{i,\lambda\beta}- D_{,\lambda\beta})]$,

where:

- $S_{stable,\lambda\beta}$ is the wavelength intensity impacted by the degree of crystallinity of the collected polychromatic light for a determined wavelength λβ,

- $R_{i,\lambda\beta}$ is the wavelength intensity of the collected polychromatic light for a determined wavelength λ_β in optimal condition for a steel without coating on the surface

- $D_{\lambda\beta}$is the acquisition of the dark and represents the background noise for a determined wavelength λβ. The dark corresponds to the noise, it is influenced by the camera temperature. It can be measured before the measurement or at regular time with an automatic shutter in the camera.

Figure 4 exhibits two spectrums, one of a fully crystalline coating measured in optimal measurement condition (S1), one of a fully crystalline coating measured in industrial measurement condition (S2) where the measurement conditions are degraded. Due to the different measurement condition, the industrial spectrum can be shifted towards lower or higher value. That is why a ratio of the absorbance calculated above, A_{imp2} and A_{sta2}, is preferably used to lower the impact of the measurement condition on the degree of crystallinity.

Then the degree of crystallinity of each beam, or location, is estimated by converting the ratio previously determined into a degree of crystallinity.

Advantageously, as illustrated in Figure 6, said ratio is converted to a degree of crystallinity using abacus. Preferably, the correlation of the abacus between the absorbance and the degree of crystallinity has been confirmed by other measurement method such as DRX, DSC or infrared spectroscopy, beforehand

A map or a visual representation of the coating degree of crystallinity is made using said previously determined degree of crystallinity and their associated location.

Because all the previously described steps are repeated and the metallic substrate is moving, the degree of crystallinity along the length of the coating polymer can be estimated. The resolution, number of measured spots in a defined area, in the length direction depends on the metallic substrate speed and the acquisition time of the hyperspectral camera. Lower is the speed and lower is the acquisition time, higher will be the resolution.

With the method according to the present invention, the degree of crystallinity of the full width of a polymer coating deposited on a metallic substrate can be measured and represented. Moreover, the degree of crystallinity is not influenced by the operating conditions, such as the chattering of the substrate and humidity, nor is the coating degraded by the lighting source. Furthermore, as illustrated in Figure 1, the resolution of the degree of crystallinity mapping is more precise compared to the state of the art techniques.

Advantageously, said method is repeated regularly so as to cover the full coating surface of said substrate. Preferably, the steps of the method are repeated as often as possible in order to obtain a degree of crystallinity map as precise as it can be.

Advantageously, said polymer coating is made of polyethylene terephthalate (PET).

Advantageously, said metallic substrate is made of steel. Such a substrate improves the measurement quality due to its low rugosity.

Advantageously, $\lambda\alpha$ is comprised between 8 and 12 micrometres. In an even preferred embodiment, $\lambda\alpha$ is comprised between 10.3 and 10.7 micrometres.

Apparently, some waves in those ranges are more impacted by the degree of crystallinity than in other ranges. Consequently, measuring the intensity of rays having such wavelengths enables a better estimation of the polymers degree of crystallinity.

Advantageously, said at least one hyperspectral camera measures the intensity of at least a wavelength comprised between 9.5 and 9.7 micrometres having its wavelength intensity not impacted by the degree of crystallinity. Using this range enables to have one of the most unaffected intensity by the crystallinity degree. In other words, the variation intensity in function

of the crystallinity degree is almost inexistent which permits to establish a good reference independently of the measurement condition.

Advantageously, the step b) is done on at least 30 locations within said transversal area. Doing the measures on at least 30 locations along the coating width increases the resolution of the crystallinity degree map. Thus, the probability to detect a default, where the crystallinity is different than the desired one is higher.

The invention also relates to an equipment 6 for online measurement of crystallinity degree of polymer coatings on a metallic substrate, comprising,

- at least one hyperspectral camera 3,
- at least one polychromatic light emitter 4,
- and means to convey said substrate,
- the polychromatic light emitter 4 and the hyperspectral camera 3 being set-up in specular reflection towards said substrate.

As illustrated in Figure 2, a polymer layer deposited on a substrate is conveyed, by conveying means such as rolls 5. The measurement equipment, composed of at least a lighting source 2 and at least one hyperspectral camera 1, is positioned above said polymer layer deposited on a substrate and means to convey said substrate (not represented). Said hyperspectral camera can record a spectrum of wavelength intensity for each pixel and is oriented in order to record the beams reflected on the polymer layer deposited on a substrate from the lighting source.

Advantageously, said hyperspectral camera 3 is oriented to make an angle comprised between 30° and 60°, preferentially between 40° and 50° and more preferably 45° with the metallic substrate. On one hand, as illustrated in Figure 5 by the 10° beam, smaller is the measurement angle, shorter is the distance passed by the beam through the coating and thus smaller is the intensity variation detected. On the other hand, as illustrated in Figure 5 by the 80° beam, higher is the measurement angle, longer it the distance passed by the beam through the coating and thus more sensible is the intensity variation detected to the substrate vibrations. Consequently, closer is the angle to 45°, better is the compromise between a sufficient intensity variation and a small vibration perturbation.

Advantageously, said polychromatic light emitter 4 is an infrared lighting source. Contrary to a LASER, an infrared lighting source is less prone to damage the coating because the power used is generally about 1 000 to 100 000 times lower than for the LASER lighting sources.

Advantageously, said polychromatic light emitter 4 is a made of at least a metal or ceramic. Preferentially, the lighting source is a heated nickel chrome rod or a heated ceramic plate heated. Such a heating enables a higher emission of light in the infrared domain in which there are absorbance affected and unaffected by the degree of crystallinity. Depending on the heating temperature, the intensity of the emitted wavelengths varies. Preferably, said bar or ceramic are heated between 600°C and 800°C.

Advantageously, as illustrated in Figure 7, said equipment comprises a convex reflection mean 5 being positioned to reflect the light from the polychromatic light emitter 4 onto said substrate, said convex reflection mean 5 and the hyperspectral camera 3 being set-up in specular reflection towards said substrate. Such a device permits to concentrate the lighting intensity on an area, thus enabling a better and more precise measurement.

The reflecting device 5 is preferentially a convex mirror which permits to focus the beams on a small portion of the substrate length but on the whole substrate width. This reflective device is oriented in order to form an angle comprised between 20 and 80°, preferentially between 35 and 55°, between the reflected beam and the substrate plan. Said angle is preferably of 45°.

CLAIMS

1. A process for mapping the crystallinity degree of a polymer coating (1) of a moving metallic substrate (2), the process comprising the following steps:

   a) lighting a transversal area of said of said polymer coating (1) encompassing its full width W, with a polychromatic light including wavelengths in the infrared domain,

   b) measuring with at least one hyperspectral camera (3),

   - the light intensity $S_{impacted,\lambda\alpha}$ at a predetermined wavelength λα impacted by the degree of crystallinity of said coating in the infrared domain and
   - the light intensity $S_{stable,\lambda\beta}$ at a predetermined wavelength λβ not impacted by the degree of crystallinity of said coating in the infrared domain

   of at least two light beams (B1, B2) from said polychromatic light after reflection on said moving metallic substrate (2) on two different locations (L1, L2) within said transversal area,

   c) determining at least an impacted absorbance A_{imp}, using said light intensity $S_{impacted,\lambda\alpha}$ at said predetermined wavelength λα impacted by the degree of crystallinity for each beam (B1, B2),

   d) determining at least a stable absorbance A_{sta}, using said light intensity $S_{stable,\lambda\beta}$ at said predetermined wavelength λβ not impacted by the degree of crystallinity for each beam (B1, B2),

   e) determining, for each beam (B1, B2), a ratio, R, equals to A_{imp}/A_{sta}

   f) converting each ratio R to a degree of crystallinity,

   g) mapping the degree of crystallinity of said polymer coating in said transversal area using said degree of crystallinity and said locations (L1, L2).

2. The method according to claim 1, wherein the method is repeated regularly so as to cover the full coating surface of said substrate.

3. The method according to claim 1 or 2, wherein said polymer coating is made of PET.

4. The method according to anyone of claims 1 to 3, wherein said metallic substrate is made of steel.

5. The method according to anyone of claims 1 to 4, wherein $\lambda\alpha$ is comprised between 8 and 12 micrometres.

6. The method according to claim 5, wherein $\lambda\alpha$ is comprised between 10.3 and 10.7 micrometres.

7. The method according to anyone of claims 1 to 6, wherein step b) is done on at least 30 locations (L1, …, L30) within said transversal area.

8. The method according to anyone of claims 1 to 7, wherein said ratio R is converted to a degree of crystallinity using abacus.

9. The method according to anyone of claims 1 to 8, wherein said hyperspectral camera (3) is oriented to make an angle comprised between 30° and 60° with the metallic substrate.

10. An equipment (6) for online measurement of crystallinity degree of polymer coatings on a metallic substrate, comprising, at least one hyperspectral camera (3), at least one polychromatic light emitter (4), and means to convey said substrate, the polychromatic light emitter (4) and the hyperspectral camera (3) being set-up in specular reflection towards said substrate.

11. An equipment according to claim 10, wherein said polychromatic light emitter (4) is an infrared lighting source.

12. An equipment according to claims 10 or 11, wherein said polychromatic light emitter (4) is a made of at least a metal or ceramic.

13. An equipment according to anyone of claims 10 to 12, wherein said equipment comprises a convex reflection mean (5) being positioned to reflect the light from the polychromatic light emitter (4) onto said substrate, said convex reflection mean (5) and the hyperspectral camera (3) being set-up in specular reflection towards said substrate.

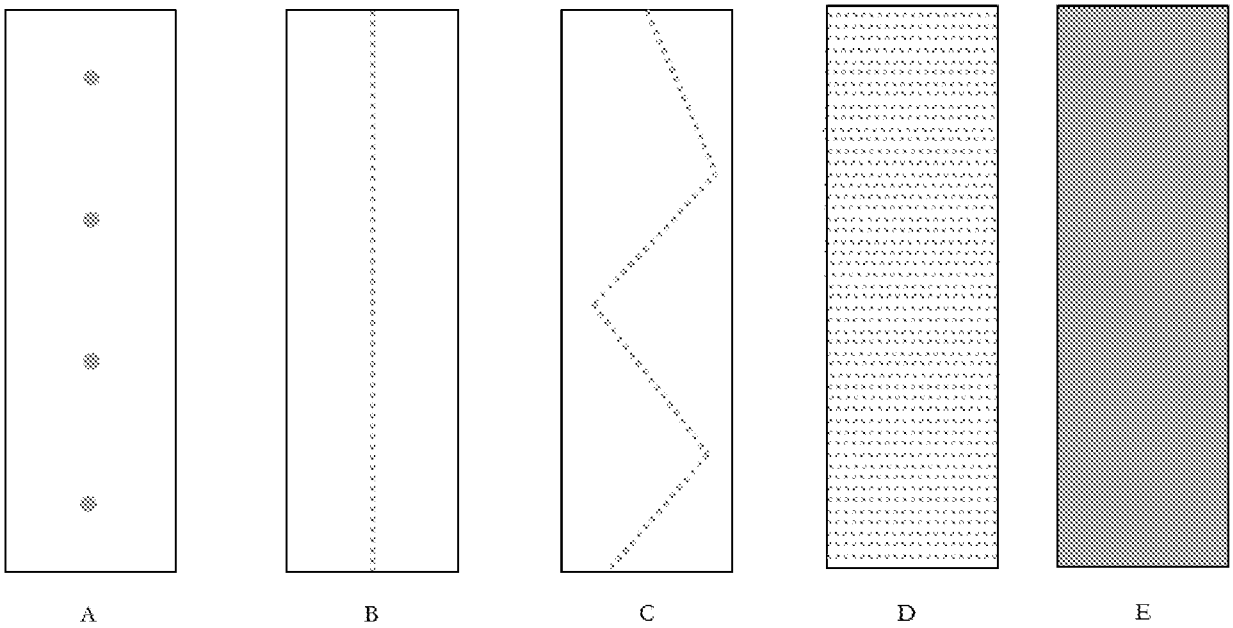

FIGURE 1

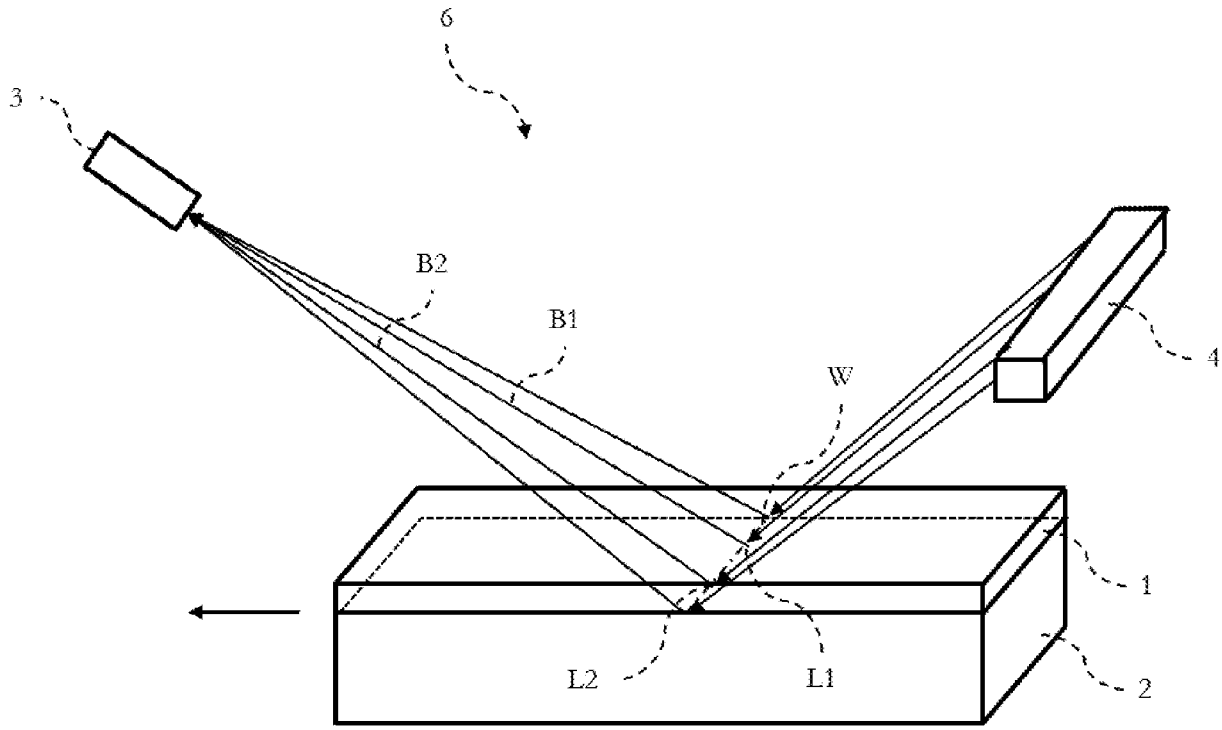

FIGURE 2

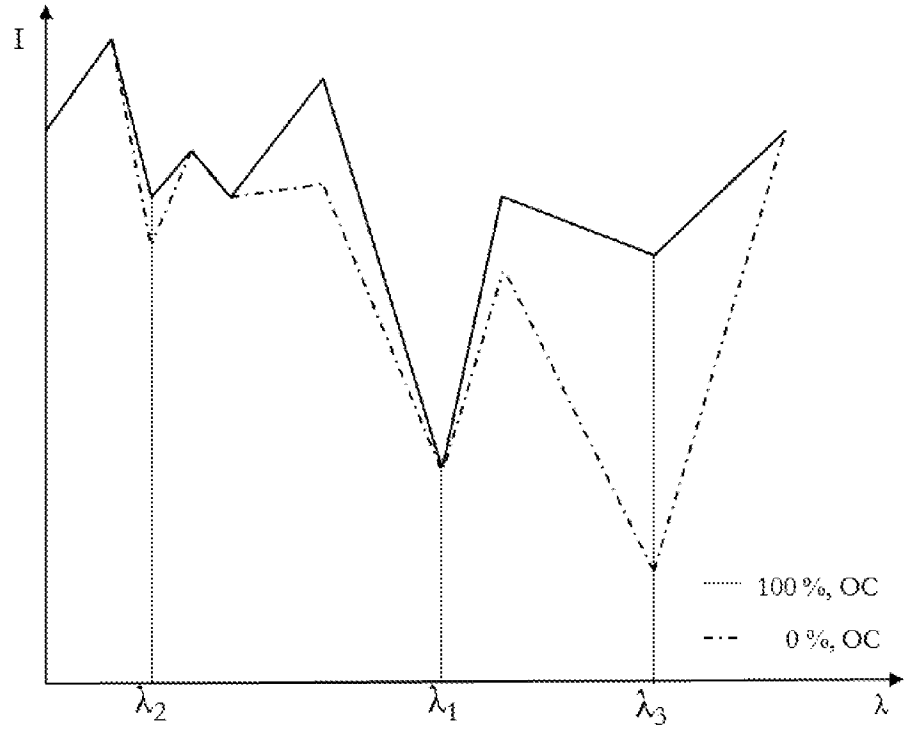

Figure 3

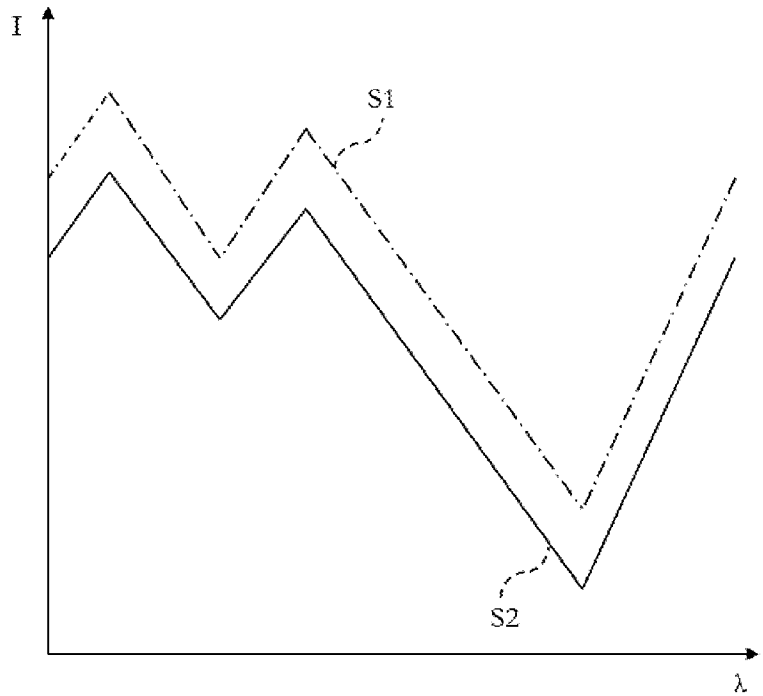

Figure 4

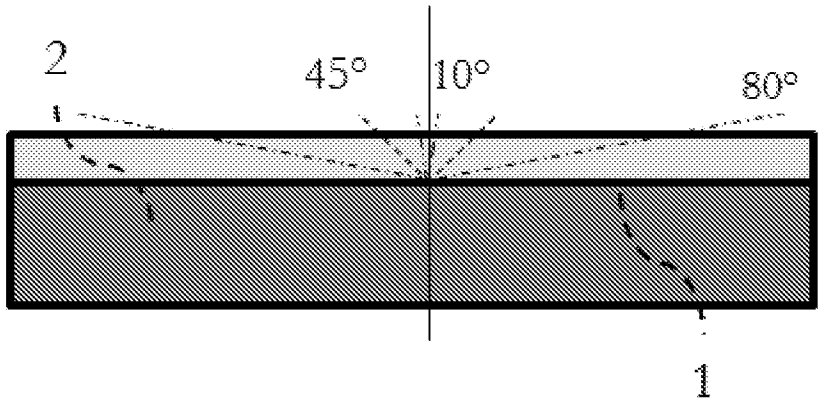

Figure 5

Figure 6

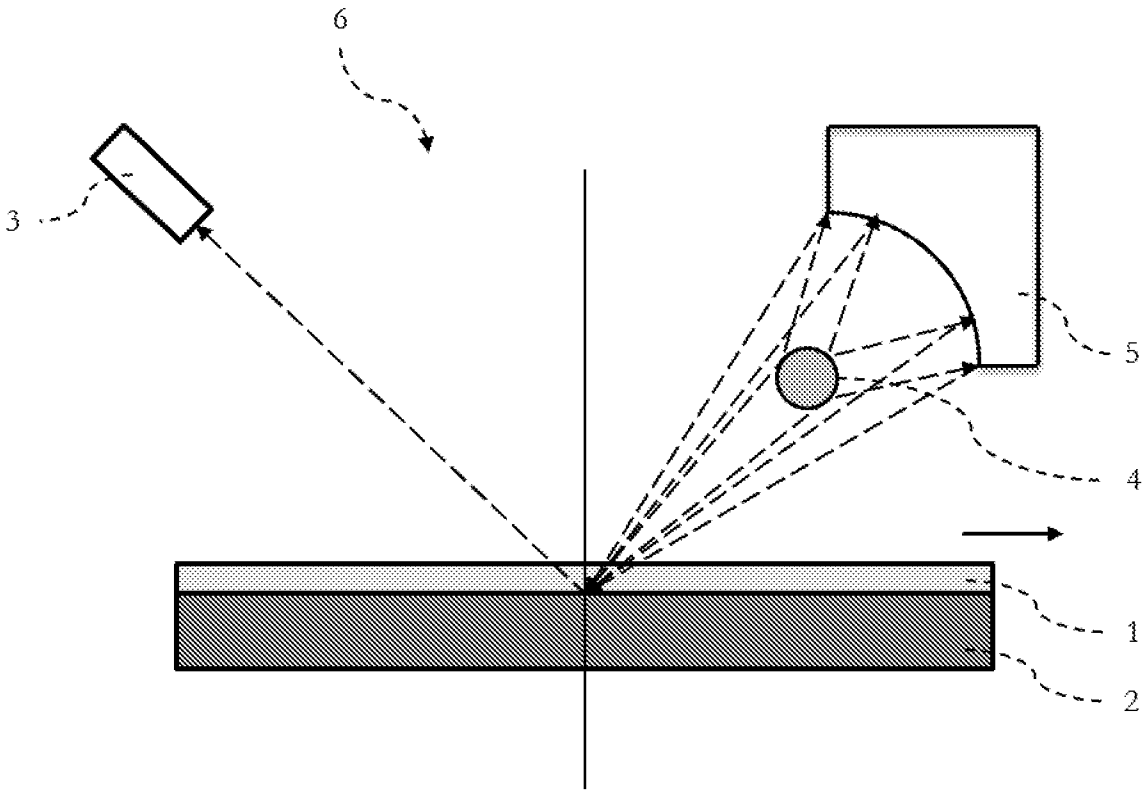

Figure 7

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/060438

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N21/35 G01N21/3563 G01J3/42
ADD.

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)
G01N G01J

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 practicable, search terms used)
EPO-Internal, WPI Data, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	RYAN GOSSELIN ET AL: "On-line prediction of crystallinity spatial distribution across polymer films using NIR spectral imaging and chemometrics methods", CANADIAN JOURNAL OF CHEMICAL ENGINEERING, vol. 86, no. 5, 27 September 2008 (2008-09-27), pages 869-878, XP055612135, US, CA ISSN: 0008-4034, DOI: 10.1002/cjce.20098 pages 871-877	1-13
Y	WO 2015/195746 A1 (INNOPIX INC [US]) 23 December 2015 (2015-12-23) paragraphs [0410] - [0412]	1-13

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
12 August 2019	23/08/2019

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Meacher, David

2

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/060438

C(Continuation). 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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