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(54) Title: THE USE OF MALONATES OR ALDONATES IN LASER IMAGING

(57) Abstract: A method for marking an object by directing a laser beam onto the areas of the object to be marked, wherein those areas at least comprise a malonate, gluconate or heptonate.



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THE USE OF MALONATES OR ALDONATES IN LASER IMAGING

Field of the Invention

This invention relates to the use of polysaccharides in laser imaging.

Background of the Invention

WO02/068205 discloses a material that reacts with a separate metal compound on irradiation with a laser, such that a reaction product of contrasting colour to the reactants is formed. This reaction product is used to form an image on an object, e.g. an edible object.

The reaction of WO02/068205 allows printing to be conducted with low maintenance costs, and avoids the need for solvents, emissions, debris and extraction. It allows on-line, non-contact coding, with reduced down-time. There is no need for the purchase or stocking of materials associated with printing. Adhesion problems and smudging can be avoided, and it is possible to code in damp conditions.

Summary of the Invention

The present invention is based on the ability of particular polysaccharide moieties to undergo internal reactions on irradiation with a laser, such that a reaction product of contrasting colour is formed. According to the present invention, a method for marking an object that comprises a malonate or gluconate, comprises directing a laser beam onto the areas of the object to be marked.

Depending on the nature of the components that are used, and the nature of the resulting reaction product, the product may be physiologically acceptable, or in other words edible. This means that the invention can be used in the marking of foodstuffs and pharmaceutical products such as tablets and pills.

Description of the Invention

In accordance with the invention, an object may comprise a malonate or gluconate moiety and a metal ion. On irradiation with a laser, this moiety may undergo an internal elimination reaction so as to form a reaction product *in situ* which is a colourant, dye or chromophore. Generally, the elimination reaction is a dehydration reaction (i.e. elimination of water), and usually the elimination reaction results in charring of the functional group.

Usually the object comprises a substrate and, coated thereon, a coating. In this instance, the moiety is preferably contained within the coating, as are any additional chemical additives.

The object or substrate upon which the image or mark is to be made can be a foodstuff, for example confectionary, eggs or fruit, or a pharmaceutical dosage unit such as a tablet or pill. If the object or substrate is intended for consumption or (if pharmaceutical) oral administration, then the moiety and reaction product are edible. Alternatively, the object or substrate can be paper, polymer film, card or board, plastic containers, or any other item capable of bearing a printed image.

The reaction product (i.e. the colourant, dye or chromophore) can be of greater colour intensity than the unreacted moiety, and preferably the unreacted moiety is substantially transparent or substantially colourless.

The polysaccharide includes groups, e.g. OH and COOH, that will undergo an internal elimination reaction with a metal ion. The metal ion is preferably a mono-, di- or tri-valent metal cation. Examples of preferred metal ions for use in the third embodiment include NH_4^+ , Li^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Sr^{2+} and Al^{3+} , where Na^+ is particularly preferred. Cu^{2+} is generally less preferred, since its salts may be highly coloured.

Alternatively, the metal ion may comprise a divalent transition metal cation, preferably from the first row of the Periodic Table. Examples of particularly preferable metal ions include Mn^{2+} , Co^{2+} , Fe^{2+} , Ni^{2+} and Cu^{2+} . Of these, Mn^{2+} and Co^{2+} are most preferable as their salts are generally relatively pale in colour, and Fe^{2+} is often least preferred since yellow aqueous ferrous ion solutions are sometimes readily darkened by atmospheric oxygen to ferric ion.

Alternatively, the functional group can form part of (or the moiety can comprise) a dicarboxylate. Examples of suitable dicarboxylates include 1,2-dicarboxylates (oxalates), 1,3-dicarboxylates (malonates), 1,4-dicarboxylates and 1,5-dicarboxylates, although 1,3-dicarboxylates (malonates) are preferred since they decompose to a dark oxide at a lower temperature than other dicarboxylate salts, thus facilitating dark laser image formation.

Alternatively, the functional group forms part of (or the moiety comprises) an anion having the partial formula -

$\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{COO}^{\ominus}$ -. Examples of suitable anions comprising this fragment are gluconates ($\text{HOCH}_2[\text{CH}(\text{OH})]_4\text{CO}_2^-$) and heptonates ($\text{HOCH}_2[\text{CH}(\text{OH})]_5\text{CO}_2^-$). Anions according to this embodiment can optionally be contained within a borate complex to form, for example, a boroheptonate salt, such that the functional group forms part of, or the moiety comprises, a boroheptonate salt. Typical boroheptonates contain 1 to 1.2% boron.

Based on the above information, other suitable functional groups, metal ions and intensity enhancers will be known, or can be readily chosen or tested for their suitability, by those of ordinary skill in the art.

It is within the scope of the invention that objects or substrates to be marked may be pre-wrapped, provided that the wrapping is transparent to the applied energy; in other words, film-wrapped tablets, foodstuffs or other such products can be printed by means of the present invention. Many commonly available wrapping films have been found to be transparent to IR laser energy, including PE, PP, PET, PVC, cellulose and cellulose acetate.

The space allocated on an object or substrate, or its wrapping, for the batch code, sell-by date, etc. is usually a small patch printed in a light colour to give good contrast to the (normally) black print. Using the system of the invention, this may be a white or lightly-coloured patch, which is printed with a laser-sensitive ink. On exposure to a threshold dose of laser energy, the ink changes colour to give the code. The patch may be printed down by a known printing technique, e.g. by flexo or gravure, as the packaging is made.

The object to be marked may be formulated with the additional components that allow marking. In a preferred embodiment, these components are formulated and used to coat a substrate. For application to the substrate, the material or materials used in this invention may be formulated in an aqueous or non-aqueous system, as a solution or dispersion achieved by, for example, ball milling. Typically, the materials are formulated in an aqueous system comprising ethanol or a water/ethanol mix. Preferably, the materials are formulated to include a binder, for example polyvinyl alcohol, acrylics, styrenics, cellulosics, polyurethanes. Optionally the formulation also includes IR absorbers.

Since it may determine the clarity of the marking that can be achieved, coating may be done more than once, if desired. Further, on top of the

coating, a protective layer of for example carnauba wax can be applied by a conventional coating process, provided the coatings are laser-markable through the protective layer, as is the case for carnauba wax.

The amounts of the components that are used in the invention can readily be chosen by one of ordinary skill, having regard to the intended use. For example, a coating composition may comprise 0.1 to 20% w/v of each component.

As indicated above, an image can be formed by the application of heat. Preferably, heat is applied locally, on irradiation with a laser. Suitable lasers include those emitting at high energy, including Nd-YAG lasers and CO₂ lasers, the latter typically at a wavelength of 10,600 nm. In many cases, it may be desirable to use a low-energy laser, such as diode laser, typically emitting light at a wavelength in the range of 800-1500 nm. In certain circumstances, this energy input may be insufficient to cause the desired reaction, and the composition to be irradiated then preferably comprises a suitable absorbent material.

Further additives that may be used are thus IR-absorbent materials, many of which are known. In general terms, any suitable such material may be incorporated, for the purposes of this invention, and can be chosen by one of ordinary skill in the art.

The laser can operate in either the dot matrix mode or continuous-wave, scribing mode. In this latter mode, improved quality of print can be obtained. Because of the low output of the laser, highly reliable, approaching maintenance-free, operation is offered. The system can operate in a scribe mode, and coding onto moving lines at up to 200 m/min is possible. For higher speeds than this, dot matrix printing is suitable.

The system can be used for coding through packing film, or coding into film laminates. A low-power laser ensures that puncturing does not occur.

The following Examples illustrate the invention.

Example 1

A solution of 2.74 g of manganese acetate tetrahydrate was prepared in deionised water (7 g). Separately, a solution of oxalic acid dehydrate (1.144 g) in deionised water (6 g) was prepared. The oxalic acid solution was added to the manganese acetate solution. A white precipitate of manganese

oxalate (a 1,2-dicarboxylate) formed immediately and was collected by filtration, washed with 3 x 5 g deionised water and dried at 55°C overnight.

4.52 g of manganese acetate tetrahydrate was dissolved in 10 g deionised water. Separately, 1.96 g malonic acid was dissolved in 1.5 g deionised water. The solutions were mixed. On standing overnight, a precipitate of manganese malonate hydrate (a 1,3-dicarboxylate) formed which was collected by filtration and washed with 3 x 2 g deionised water. The precipitate was then dried at 55°C overnight.

The manganese oxalate (2 g) and the manganese malonate (2 g) were mixed with Texicryl 13-011 polymer emulsion (4.8 g each). Both products were milled for 3 h using steatite balls, and then coated independently on MWV card using a 2.5 rated wire coating bar (RK coaters) and dried using warm air.

Each coating was exposed imagewise using a CO₂ scribing laser. Manganese oxalate gave no laser imaging activity; by contrast manganese malonate gave legible brown images at 5 W and 8 W laser power. The results indicate that the malonates are more reactive to the CO₂ scribing laser than the oxalates.

Example 2

A 20% by weight solution of sodium heptonate dihydrate (Croda) in deionised water was coated to card manufactured by MeadWestvaco Corporation using a 2.5 rated wire coating bar supplied by RK Coaters. The coating was dried using a warm air to give a colorless layer and then imaged using a CO₂ scribing laser. Legible dark brown alphanumeric images were obtained at powers between 3 and 5 W.

Example 3

A 20% by weight solution of sodium boroheptonate (Croda) in deionised water was coated to card manufactured by MeadWestvaco Corporation using a 2.5 rated wire coating bar supplied by RK Coaters. The coating was dried using warm air to give a colorless layer and then imaged using a CO₂ scribing laser. Legible black-brown alphanumeric images were obtained at powers between 3 and 5 W.

CLAIMS

1. A method for marking an object by directing a laser beam onto the areas of the object to be marked, wherein those areas at least comprise a malonate or compound having the partial formula - $\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{COO}^{\ominus}$.
2. A method according to claim 1, wherein the object comprises a metal malonate.
3. A method according to claim 2, wherein the metal is sodium.
4. A method according to claim 2, wherein the metal is a divalent transition metal cation.
5. A method according to claim 2, wherein the metal is Mn^{2+} , Co^{2+} , Fe^{2+} , Ni^{2+} , Cu^{2+} or a mixture thereof.
6. A method according to claim 1, wherein the compound is a gluconate.
7. A method according to claim 1, wherein the compound is a heptonate.
8. A method according to claims 6 or 7, wherein the compound comprises a monovalent, divalent or trivalent metal cation, or a mixture thereof.
9. A method according to claim 8, wherein the cation is NH_4^+ , Li^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Sr^{2+} , Al^{3+} or mixtures thereof.
10. A method according to claims 6 to 9, wherein the functional group is contained within a borate complex.
11. A method according to any preceding claim, wherein the object is a pharmaceutical or foodstuff, and the reaction product is physiologically acceptable.
12. A method according to any preceding claim, wherein the object comprises a substrate and, coated thereon, a coating comprising the malonate or gluconate.
13. A method according to claim 12, wherein the substrate is a tablet or pill and the coating comprises a pharmaceutical agent.
14. A method according to any preceding claim, wherein the object is wrapped or covered in a filmic material.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
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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 A61K

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.
X	GB 2 135 466 A (PILOT INK CO. LTD.) 30 August 1984 (1984-08-30) claim 1 page 2, line 56 - line 57 page 2, line 62 page 8, line 26	1-5, 12
X	US 2003/157433 A1 (KODAK POLYCHROME GRAPHICS LLC) 21 August 2003 (2003-08-21) claim 16 sentence 1, paragraph 162 - sentence 3 table 2 ----- -/-	1, 6, 8, 9, 12

☒ 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
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

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