(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
9 November 2006 (09.11.2006)

PCT

(10) International Publication Number
WO 2006/118889 A1

(51) International Patent Classification:
*G07D 7/12* (2006.01) *G07D 7/14* (2006.01)

(21) International Application Number:
PCT/US2006/015728

(22) International Filing Date: 25 April 2006 (25.04.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/676,262 29 April 2005 (29.04.2005) US

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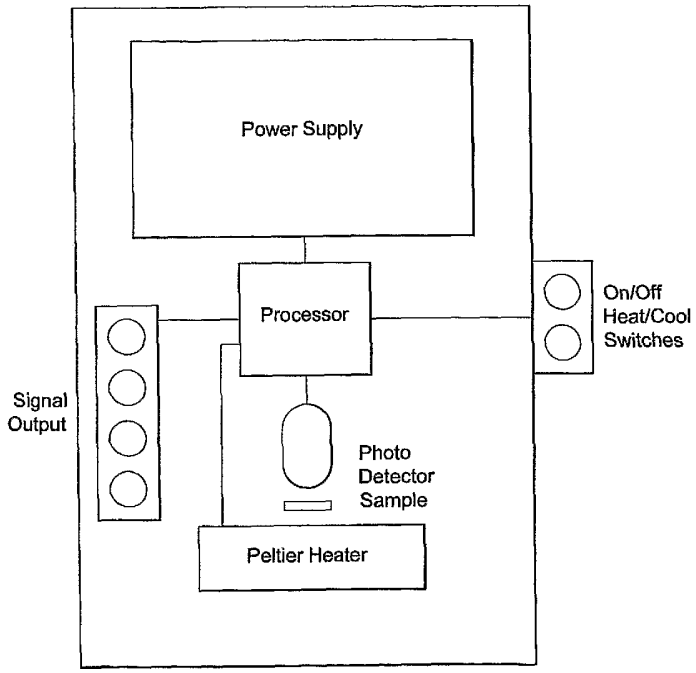
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) **Title:** METHOD FOR IDENTIFICATION OF PRODUCT FORGERIES




(57) **Abstract:** Methods of detecting forgeries and/or preventing forgery distribution are provided. The methods include providing a surface associated with an article; and providing a composition on the surface. The composition includes a chemiluminescent substance. The method further includes subjecting the article to a triggering source to elicit a chemiluminescent signal; and identifying unique information contained in the signal. The unique information is associated with the authentic article.

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# METHOD FOR IDENTIFICATION OF PRODUCT FORGERIES

## FIELD OF THE INVENTION

The invention relates to an article including a chemiluminescent substance. The invention further relates to methods and a device, which detect the presence of chemiluminescence for purposes of communicating information associated with the article. Useful applications of the invention include confirmation of the authenticity of an article or its contents, or conversely forgery detection.

## BACKGROUND OF THE INVENTION

Counterfeiting has become a global and highly profitable business. Counterfeiters don't have to cover research and development, marketing, and advertising costs, and most of the expense goes into making goods appear convincingly authentic, rather than making the goods perform well. Moreover, convicted counterfeiters often receive minimal fines.

It is estimated that up to 7% of global merchandise trade is illegal counterfeit merchandise. This is equivalent to about $512 billion in lost sales. Moreover, the problem is increasing. For example, growth of counterfeits are increasing by up to 30% annually.

Up to 10% of pharmaceuticals are estimated to be counterfeit. The packaging can look just like the real thing, and even the pills can look just like the real thing. Some of the pills may even contain some of the active ingredients. However, they can be counterfeit. In addition to the potential harm that can be caused to consumers of the counterfeits, distributors can be forced to pull millions of drug tablets from warehouses and pharmacy shelves nationwide.

Counterfeit products are not limited to pharmaceuticals. They can include any number of manufactured products, as well as natural products. For example, counterfeit products can include cigarettes, textiles, software and luxury goods.

Therefore, there is a need for methods to outwit the counterfeiters in the marketplace. Preferably, an article, such as an article of manufacture, would include a marker which is

imperceptible to the human eye and which is not present in the counterfeit. This would permit detection of counterfeiting or forgery.

## SUMMARY OF THE INVENTION

There are various embodiments of the invention discussed. Common to each is the use of a chemiluminescent composition which can be caused to emit one or more signals, the detection of which being indicative of information about the article associated with the chemiluminescent composition. In some embodiments, the presence of one or more signals *per se* may be an indication of information about the article. For example, a person using the invention would look for the presence of a chemiluminescent signal or emission as an indication that the article associated with the chemiluminescent composition (from which the signal was generated) was authentic or associated with one or more pieces of information or date relating to the article, as further described herein. In other embodiments, the light emission or emissions (signals) may be correlated with a key or code which translates the emission(s) into information about the product.

The chemiluminescent signals may vary in complexity and may produce various detection results which may directly or indirectly indicate the desired information about the article, as further described herein. Various detection devices, including devices which use software, may be employed to detect and/or interpret the results and/or display the information encoded in the signal(s) into an understandable format.

The present invention provides a method that includes providing a surface associated with an article; and providing a composition on the surface, wherein the composition includes at least one compound capable of producing a chemiluminescent signal alone or in combination with other reagents. The method further includes subjecting the article to a triggering source which elicits the chemiluminescent signal; and identifying unique information contained in the chemiluminescent signal, wherein the unique information is associated with the article.

The invention further provides a method that includes providing a surface associated with an article; and providing a composition on the surface at a predetermined location on the surface, wherein the composition comprises a dioxetane. This method further includes

subjecting the article to heat which elicits the chemiluminescent signal; and identifying unique information contained in a chemiluminescent signal, wherein the unique information is associated with the article.

Also provided is an article having associated therewith a surface to which is applied a composition. The composition includes at least one compound capable of producing a chemiluminescent signal, alone or in combination with other reagents, wherein unique information associated with the article is contained in the signal.

The present invention also provides a device for detecting forgery of an article. The device includes a heating source; and a detection element. The detection element detects light emitted by a chemiluminescent substance and converts the detected light into a detectable signal.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention provides methods which are useful for the rapid and cost-effective identification of product forgeries. In particular, the present invention uses chemiluminescence for forgery detection. Chemiluminescence is the generation of light by chemical reaction. Chemiluminescent substances may produce a chemiluminescent signal either alone or alone with other agents.

The use of chemiluminescence for forgery detection has many advantages. For example, many chemiluminescent substances are both stable and invisible to the naked eye. Also, chemiluminescent substances can be applied to a variety of surfaces, such as paper and polymeric surfaces. The chemiluminescent substances can be applied to surfaces, such as paper or cloth, by printing techniques. The chemiluminescent substance can be combined with existing dyes used for printing, or used separately. Moreover, a simple and portable device can be used to trigger and detect chemiluminescence. These and other advantages will be discussed in further detail below.

The present invention involves providing a surface associated with an article; and providing a composition on the surface of the article. The composition includes at least one compound which is capable of producing a chemiluminescent signal alone or in combination

with other reagents. The composition can further include reagents for the enhancement of the chemiluminescent signal.

The article including the chemiluminescent substance is subjected to a triggering source which elicits the chemiluminescent signal. The triggering source may be selected from the following: heat, light, chemical, pressure and combinations thereof. Unique information which is contained in or indicated by the chemiluminescent signal may then be identified. As mentioned above, the signal or signals may be correlated with a key or code which corresponds with data or information. This unique information is desirably associated with the authentic article and would therefore be indicative of the presence of an authentic article

In one desired embodiment, the chemiluminescent signal may be produced at a predetermined location on the surface. For example, a non-visible chemiluminescent substance(s) can be directly applied or printed on a secret location on labels or packaging. The location of the dry chemiluminescent material would preferably be difficult to detect. For example, in one embodiment the composition is invisible to the human eye.

Preferably, the composition of the chemiluminescent material will be difficult to reproduce by counterfeiters.

One purpose of the present invention is to determine the authenticity of a product by making, marking, or labeling the product or its packaging with substances which are chemiluminescent. These substances are routinely undetectable unless triggered by a special device designed for such a purpose. The device preferably both triggers and detects chemiluminescence. As described above, the chemiluminescent substances can be combined with normal ink (dyes), or be printed alone.

In one embodiment, the unique information contained in the chemiluminescent signal is encoded. The information needed to decode the unique information in the chemiluminescent signal can be known by the manufacturer of an authentic article. The decoding information can include the location of the applied composition on the surface of the article.

For example, the manufacturer can notify a customs inspector or a pharmacist that the article is authentic if a chemiluminescent signal is produced at a discrete location on the surface of an article. The composition may have been applied to the top left hand corner of a drug label. When the top left hand corner of the label is placed into a suitable detection device, and chemiluminescence is "triggered" by a device designed for this purpose, a chemiluminescent signal would be produced at the disclosed location on the label. This allows for authentication of the drug.

In the aforementioned example, the unique information obtained from a positive hit can be that of the manufacturer's name. However, the unique information can include other types of information as well. For example, in one embodiment the unique information includes at least one of the following: manufacturer's name, batch number, expiration date, characteristics of the article, lot number, a code and combinations thereof.

In one embodiment, the chemiluminescent substance(s) can be printed in the form of an identifying pattern, such as a bar code or characteristic image. The bar code/image can contain the unique information to identify the product. For example, the chemiluminescent composition applied to the surface of the article can consist of a plurality of light-emitting substances. In one embodiment, the composition includes chemiluminescent substances with different wavelengths. In a further embodiment, the composition includes chemiluminescent substances with different triggering temperatures. In yet another embodiment, the composition includes chemiluminescent substances with different decay rates.

In one particular example, an exact combination of different colors or wavelengths can encompass the unique information in the form of a code to identify the authentic product. In a more sophisticated example, an exact combination of chemiluminescent substances of different colors or wavelengths is applied in a particular pattern. Various combinations and patterns are possible, and the present invention is not limited in this regard.

The unique information contained in the code can be compared with information that has been provided about the article. For example, the comparison of the unique information with the provided information can indicate whether or not the article is authentic or a counterfeit. The information provided can be visible indicia. The provided information can be information on the article, on packaging for the article, on separate information provided

with the article, and combinations thereof. In one example, an inspector may come across drug bottles that include labels that look like the labels for an authentic drug from the manufacturer. However, when the label is subjected to triggering and detection, the inspector may discover that a chemiluminescent signal is absent. Moreover, even if a chemiluminescent signal is detected, it is possible that the drugs may still be counterfeit. In this instance, the code or particular image contained in a chemiluminescent signal can be important. For example, if the visible indicia on the label shows that the drugs are from Lot No. 10, the manufacturer can verify for the inspector that Lot No. 10 has associated with it a signal with an image including two circles and a triangle, for example. If the inspector finds that this particular image is not present in this signal, this is an indication that the article is not authentic.

It is noted that information about an authentic article may be transferred from a manufacturer location to a distributor location, such as a pharmacy, by any suitable means. As described above, this information may include the location of a signal on the surface of the authentic article. In one example, a pharmacist may receive by mail a package from the manufacturer including a sheet that indicates that for a given lot and batch number, the signal will be located on the bottom right hand corner of the label. The pharmacist may then take a bottle showing this lot number and batch number, and will use a device to determine whether a chemiluminescent signal is emitted at the discrete location where the manufacturer has specified. If the signal is not present at this location, the drug may be counterfeit, or is not from a specified lot.

The article for authentication can be an article of manufacture. In other embodiments, the article is a natural product. For example, the article can be a consumer good. The article can also be a drug or bioactive agent. Moreover, the article can be currency.

In one embodiment, the article can be selected from the following: foods, drinks, clothing, electronics, cigarettes, cosmetics, jewelry, computer hardware, computer software, mechanical parts, accessories and shoes. Accessories can include, but are not limited to, purses, wallets, belts, etc. However, the present invention is not limited to particular articles.

The surface associated with the article can include any number of surfaces. For example, the surface associated with the article can be selected from, but is not limited to, the

following: paper, plastic, metal, glass, a natural surface and combinations thereof. With respect to natural surfaces, these would include surfaces such as fruit peels, vegetable peels, animal skins, leather, fibers, etc. In one embodiment, the surface is selected from, but is not limited to, the following: surface of the article, a surface of a label on the article, a surface of a sheet of instructions or descriptions for the article, a surface of an accessory fitted to the article, a surface of a shipping document for the article, and a surface of a container used for shipping the article.

As described above, the composition on the surface of the article includes at least one compound that is capable of producing a chemiluminescent signal alone or in combination with other reagents. For example, the compound can be a photoactive indicator or precursor. In one embodiment, the compound is selected from the following: dioxetanes, dioxetane diones, dioxetane carboxylates, peroxyoxalates, oxalates, luciferins, endoperoxides, acridine, acridinium salts, luminols, phthalates, hydrazines, hydrazides, olefins, tetrapyrroles, porphyrins, metalloporphoryins, isoluminols, peroxy compounds, xanthines and combinations thereof.

In one preferred embodiment, the compound is a stable dioxetane, which can be directly applied to or incorporated within an article. An example of a suitable stable dioxetane for use with the present invention is 3-(2'-spiroademantane)-4-methoxy-4-(3"-hydroxy phenyl-1,2-dioxetane). The temperature at which chemiluminescent substances decay to produce light is unique to the chemiluminescent substance. For example, the aforementioned dioxetane can be triggered to decay to produce light at temperatures of about 60-65°C. As mentioned, a plurality of chemiluminescent substances with different trigger temperatures can encode information about the product.

As described above, it is also possible to produce a chemiluminescent signal by employing chemiluminescent precursors. For example, a stable dioxetane can be generated *in situ* by coating at least a portion of an article with an olefin reagent and a sensitizer. Subsequent to exposure of the coated article to light and oxygen, the sensitizer is promoted to an excited state, which allows for transfer of its excess energy to ambient oxygen, with the resultant formation of singlet oxygen. The singlet oxygen therein produced reacts with the olefin reagent to form a stable chemiluminescent dioxetane which when subjected to an appropriate triggering source, such as heat, decomposes to emit light on the article.

In one embodiment of the present invention, the triggering source to which the article is subjected is selected from the following: heat, light, chemical, pressure and combinations thereof. In another embodiment, the triggering and detection is performed in a dry state. In yet another embodiment, the methods of the present invention are performed non-enzymatically.

As described above, the methods of the present invention include the step of identifying unique information contained in the chemiluminescent signal. The unique information is associated with the article. In one embodiment, the identifying step includes capturing the chemiluminescent signal with a photoimaging device. Any number of photoimaging devices can be used. For example, in one embodiment, the photoimaging device can be selected from one of the following: X-ray film, photodiode, photomultiplying tube and Charge-Coupled Device (CCD) camera.

One device of the present invention that would be suitable for detecting forgery of an article includes a heating source; and a detection element. The detection element detects light emitted by a chemiluminescent substance and converts detected light into a detectable signal. Such a device can further include a processing unit. For example, a processing unit can include a programmed microprocessor which measures any deviations between information provided about the article, such as visible indicia, and unique information contained in the signal to determine if the article is a forgery. The device can also include a reader.

An example of a suitable detection element, which would be a light detecting device, is a photodiode. For example, if light is detected, the photodiode would send out a current. Certain photodiodes send out a current (i.e., detect) light between 380-555 nm. This type of photodiode detects bluish-green light, such as that emitted upon decomposition of the following dioxetane: 3-(2'-spiroademantane)-4-methoxy-4-(3"-hydroxy phenyl-1,2-dioxetane). A photodiode suitable for detecting bluish-green light is available from Epigap (Berlin, Germany). Other photodiodes (also available from Epigap) would be able to detect between 600-710 nm (red light). A suitable red emitting chemiluminescent material for use with a red photodiode is disclosed in U.S. Patent No. 5,965,736, which is incorporated herein by reference.

The figure is a schematic representation of one embodiment of a suitable forgery detection device according to the present invention. The device may be a handheld device, if desired. Preferably, the device would include a light-tight enclosure, a power supply, a heating element and a detection element. In one example, the heating element includes Peltier heating elements that are capable of heating to temperatures of greater than 85°C. In one embodiment the detection element is a photodiode or photomultiplying tube. With reference to the figure, a sample, such as an article according to the present invention, is placed on the heating element in direct contact with the detection element (e.g., photodiode or photomultiplying tube). The sample will be heated, and chemiluminescence detected. Preferably, the heating element (e.g., Peltier element), would cool the heating surface for the next sample measurement.

In one desired embodiment, a method of the present invention includes providing a surface associated with an article; and providing a composition on the surface of a predetermined location on the surface, wherein the composition includes a dioxetane. The method further includes subjecting the article to heat, which elicits the chemiluminescent signal; and identifying unique information contained in the chemiluminescent signal, wherein the unique information is associated with the article.

As mentioned above, the methods of the present invention can include providing information about the article, and comparing the provided information with the unique information. The comparison of the unique information with the provided information indicates whether or not the article is authentic.

In situations where the chemiluminescent signal is produced at a predetermined location on the surface, this predetermined location may be known only to the manufacturer of the authentic article. The manufacturer would know other information, as well. For example, by knowing the exact dioxetane applied, the manufacturer would also know a suitable triggering temperature for that dioxetane, and a suitable detection element for that dioxetane (e.g., a suitable photodiode for detecting a dioxetane of a certain wavelength).

The chemiluminescent signal produced through decomposition of the dioxetane is captured with any suitable photoimaging device, such as those described above. These include, but are not limited to, photodiodes.

The unique information contained in the signal produced upon decomposition of the dioxetane may include any of the types of unique information described above. For example, unique information may include a manufacturer's name, batch number, expiration date, characteristics of the article, lot number, code and combinations thereof.

In order to outwit more sophisticated counterfeiters in the marketplace, it may be necessary to encode the unique information. The information to decode the unique information in the signal produced by decomposition of the dioxetane may be known only to the manufacturer of the authentic article. For example, the dioxetane may be an invisible marker, and only the manufacturer may know its location on the surface of the article. Moreover, only the manufacturer may know the exact composition applied to the article (for e.g., the exact dioxetane applied). Therefore, only the manufacturer would know suitable triggering/detection conditions.

Also, it may be necessary to apply the dioxetane or other chemiluminescent material in a particular pattern or image, which can be decoded by the manufacturer of the authentic article. With the methods of the present invention, it is also possible that the composition can be applied in the form of a bar code, which can be translated into a batch number, expiration date, etc. with the help of a programmed microprocessor and reader, for example.

Counterfeiting has become as profitable as trading illegal narcotics. The methods of the present invention are useful for detecting forgery of an article. The methods of the present invention are also useful for preventing forgery distribution. This is accomplished by providing an article having associated therewith a surface to which a chemiluminescent substance is applied.

In particular, the present invention provides an article having associated therewith a surface to which is applied a composition that includes at least one compound capable of producing a chemiluminescent signal. The signal is produced either alone or in combination with other reagents. The unique information associated with the article is contained in the signal. As described above, the unique information, when compared with information provided about the article (e.g., visible indicia), indicates whether or not the article is authentic.

For example, as described above, a counterfeiter can make the counterfeit product look like the real thing by providing visible indicia. Information provided by the counterfeiter could be on the article, on packaging for the article, and separate information provided with the article, and combinations thereof. However, the purpose of the methods and device of the present invention is to determine any deviations between the information provided by the counterfeiter and the unique information contained in the chemiluminescent signal to determine if the article is a forgery. The unique information contained in the signal on the surface of the provided article is the same as that described above. This information can be encoded, wherein the information needed to decode the unique information may be known only to the manufacturer of the authentic article. As already described, the information to decode the unique information can be the predetermined location of the chemiluminescent substance on the surface of the article, a pattern, an image, etc.

As described above, an article of the present invention can be an article of manufacture or a natural product. In one example, the article can be selected from a consumer good, a drug, a bioactive agent and currency. However, the article is not limited to these particular embodiments. Particular examples of articles are the same as those described above.

In addition to a stable dioxetane, any number of other photoactive indicators or precursors can be included in the composition that is on/in the article. Suitable examples of these are described above. The applied chemiluminescent composition can further include reagents for the enhancement of the chemiluminescent signal.

A variety of surfaces can be associated with the article. For example, a chemiluminescent substance can be applied or incorporated within paper, plastic, metal, glass, a natural surface and combinations thereof. The article surface can be a surface of the article, a surface of a label on the article, a surface of a sheet of instructions or descriptions for the article, a surface of an accessory fitted to the article, a surface of a shipping document for the article and a surface of a container used for shipping the article.

Stable chemiluminescent substances can be applied to various article surfaces, including paper and polymeric surfaces using printing or other techniques, such as spraying,

painting, dipping, etc. Once adhered to the surface, the dry chemiluminescent substance can be subjected to a triggering source to decompose. This elicits the chemiluminescent signal.

In one embodiment, the triggering source used on the article is selected from heat, light, chemical and combinations thereof. Examples of suitable chemicals that can be used to cleave protecting groups on stable dioxetanes are described in U.S. Patent No. 6,613,578 B1 to Moller, et al., which is incorporated herein by reference.

Preferably, the triggering source is heat, whereby a simple and portable device could be used to trigger and detect chemiluminescence. As described above, a suitable device for this purpose can include a heating source; and a detection element capable of detecting light emitted from the chemiluminescent substance and converting the detected light into a detectable signal.

The examples below will show that the present inventors have established proof of principle. In particular, both nylon and paper samples have been coated with a composition including a chemiluminescent substance. The samples were stored at ambient temperature for about 3 months, evidencing the fact that the chemiluminescent substance was stable. The stable chemiluminescent substance was triggered using heat at a temperature of about 65°C. Detection of the chemiluminescent signal was achieved by exposure to Polaroid film 667. The result was that of a clear, bright chemiluminescent signal, which was present on the location on the sample to which the chemiluminescent substance had been directly applied. This illustrates that the methods and device of the present invention can unambiguously determine the authenticity of a product by making the product or the packaging with substances which are chemiluminescent.

The composition of the chemiluminescent material applied to the article will be difficult to reproduce by counterfeiters. For example, as described above, the composition can include a combination of chemiluminescent substances having different triggering temperatures and/or different wavelengths and/or different decay rates. Also, the location of the dry chemiluminescent material will be difficult to detect, since it will preferably be non-visible to the human eye. Also, the exact pattern, image, or code associated with the signal will be difficult to reproduce. The end result should be that counterfeiting of an article including such chemiluminescent substances should be kept at a pretty low level.

Other advantages of the present invention include the fact that the chemiluminescent substances can be easily applied in labels or packing using simple printing techniques. The chemiluminescent materials can be mixed with existing inks, or applied separately. Also, chemiluminescence can be triggered and detected using a simple portable device, which can even be handheld, such that it can be held directly next to a label for forgery detection, for example. All of the aforementioned advantages make the present invention not only useful to outwit the counterfeiters in the marketplace, but also make it practical for those whose job or desire it is to detect forgery of an article and prevent forgery distribution.

## EXAMPLES

**Example 1: Dioxetane created *in situ* on nylon polymer surface and on paper surface, triggered and detected with polaroid film.**

Nylon membrane, HYBOND N
Used olefin concentration of 10 mg/100 mL hexane
Used 1 $\mu$M DCMB in water
Triggered at 62°C
Detected by exposure to polaroid film 667 for 15 min.

1. Membrane soaked 30 s with olefin solution, dried, soaked 10 s DCMB solution
2. Membrane soaked 10 s DCMB, dried, soaked with 30 s olefin solution
3. Membrane soaked 10 s DCMB, dried, no olefin soaking

1, 2, and 3 above were irradiated 20 minutes with red LED cluster, 3.5 V

4. Membrane soaked 30 s with olefin solution, dried, soaked 10 s with DCMB solution
5. Membrane soaked 10 s with DCMB solution, dried, soaked 30 s with olefin solution

4 and 5 above not irradiated

Results:
1 positive; 2 positive; 3 negative; 4 negative; 5 negative

**Example 2: Dioxetane created *in situ* on Nylon/Glass interface, triggered and detected with Polaroid film.**

Glass slides (microscope cover slips)
Used 0.2 $\mu$L of 5$\mu$M DCMB
Used 0.2 $\mu$L water as control

spotted on glass slide, dried 30 minutes at 40°C

Paper or Nylon soaked in 10 mg olefin/100 mL Hexane solution for 30 seconds
Control paper and control nylon not soaked in olefin solution.

1. glass and paper "sandwiched" (pressed together) with glass slide, DCMB-side facing paper
2. glass and nylon "sandwiched" (pressed together) with glass slide, DCMB-side facing nylon
3. control paper "sandwiched" (pressed together) with glass slide, DCMB-side facing paper
4. control nylon "sandwiched" (pressed together) with glass slide, DCMB-side facing nylon

irradiated as in Example 1 for 20 minutes with red LED cluster, 3.5 V

Trigger at 62°C
Detected by exposure to polaroid film 667 for 15 min.

1 positive; 2 positive; 3 negative; 4 negative.

**Example 3: Dilution series of dioxetane created *in situ* on nylon polymer surface and on paper surface, triggered and detected with polaroid film**

Series of 1 μL spots of DCMB solutions in varying concentrations applied to surface, double spotted (two spots side-by-side), dried.
Nylon or membrane soaked in olefin solution (10 mg/100 mL hexane) for 2 seconds, dried.
Irradiated for 20 minutes using red LED cluster, 3.5 V.
Triggered at 62°C.
Detected by exposure to polaroid film 667 for 15 min.

Nylon
5 μM DCMB: positive
1 μM DCMB: positive
100 nM DCMB: positive
10 nM DCMB: negative
water: negative

Paper
5 μM DCMB: positive
1 μM DCMB: positive
100 nM DCMB: negative
10 nM DCMB: negative
water: negative

**Example 4: Lifetime Study. Triggering after 1 day, 5 days, 1 month, 2 months.**

Batch 1. Hybond N+, dipped 20 s in 1μM DCMB
Batch 2. Hybond N+, dipped 30 s in 1 μM DCMB
Batch 3. plain paper, dipped 2 minutes in 10 μM DCMB

Dried.
Soaked in olefin solution (10mg/100mL hexane) for 30 s.
Dried.
Irradiated for 20 minutes using red LED cluster, 3.5 V.
Stored at room temperature in ambient light.

Triggered at 62°C at various times.
Detected by exposure to polaroid film 667 for 15 min.

| | 1 day | 5 days | 30 days | 60 days |
|---|---|---|---|---|
| **Batch 1** | positive | positive | positive | positive |
| **Batch 2** | positive | positive | positive | positive |
| **Batch 3** | positive | positive | positive | positive |

**Example 5: Dioxetane applied on nylon polymer surface and on paper surface, triggered and detected with polaroid film.**

Nylon membrane, HYBOND N
Used dioxetane concentration of 10 mg/100 mL hexane
Triggered at 62°C
Detected by exposure to polaroid film 667 for 15 min.

1. Membrane soaked 30 s with dioxetane solution, dried
2. Membrane soaked 30 s with solution without dioxetane

Results:
1 positive; 2 negative

**Example 6: Dilution series of dioxetane applied on nylon polymer surface and on paper surface, triggered and detected with polaroid film**

Series of 1 μL spots of dioxetane solutions (10 mg/100 mL hexane) in varying concentrations applied to surface, double spotted (two spots side-by-side), dried.
Triggered at 62°C.
Detected by exposure to polaroid film 667 for 15 min.

Nylon
5 μM dioxetane: positive
1 μM dioxetane: positive
water: negative

Paper
5 μM dioxetane: positive
1 μM dioxetane: positive
water: negative

**Example 7: Lifetime Study. Triggering after 1 day, 5 days, 1 month, 2 months.**

Batch 1. Hybond N+, dipped 20 s in 1μM dioxetane (10 mg/100 mL hexane)
Batch 2. Hybond N+, dipped 30 s in 1 μM dioxetane (10 mg/100 mL hexane)
Batch 3. Plain paper, dipped 2 minutes in 10 μM dioxetane (10 mg/100 mL hexane)
Dried.
Stored at room temperature in ambient light.

Triggered at 62°C at various times.
Detected by exposure to polaroid film 667 for 15 min.

| | 1 day | 5 days | 30 days | 60 days |
|---|---|---|---|---|
| **Batch 1** | positive | positive | positive | positive |
| **Batch 2** | positive | positive | positive | positive |
| **Batch 3** | positive | positive | positive | positive |

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**WHAT IS CLAIMED IS:**

1. A method comprising:

providing a surface associated with an article;

providing a composition on the surface, wherein the composition comprises at least one compound capable of producing a chemiluminescent signal alone or in combination with other reagents;

subjecting the article to a triggering source which elicits the chemiluminescent signal; and

identifying unique information contained in the chemiluminescent signal, wherein the unique information is associated with the article.

2. The method of claim 1, wherein the chemiluminescent signal is produced at a predetermined location on the surface.

3. The method of claim 1, further including providing information about the article and comparing the provided information with the unique information.

4. The method of claim 3, wherein the comparison of the unique information with the provided information indicates whether or not the article is authentic.

5. The method of claim 3, wherein the providing information step includes providing the information on the article, on packaging for the article, on separate information provided with the article, and combinations thereof.

6. The method of claim 5, wherein the providing information step comprises providing visible indicia.

7. The method of claim 1, wherein the unique information comprises at least one of the group consisting of manufacturer's name, batch number, expiration date, characteristics of the article, lot number, a code and combinations thereof.

8. The method of claim 1, wherein the unique information contained in the chemiluminescent signal is encoded.

9. The method of claim 8, wherein the information to decode the unique information in the chemiluminescent signal is known by the manufacturer of the article.

10. The method of claim 1, wherein the article is an article of manufacture.

11. The method of claim 1, wherein the article is a natural product.

12. The method of claim 1, wherein the article comprises a consumer good.

13. The method of claim 1, wherein the article comprises a drug or bioactive agent.

14. The method of claim 1, wherein the article comprises currency.

15. The method of claim 1, wherein the article is selected from the group consisting of foods, drinks, clothing, electronics, cigarettes, cosmetics, jewelry, computer hardware, computer software, mechanical parts, accessories and shoes.

16. The method of claim 1, wherein the composition further comprises reagents for the enhancement of the chemiluminescent signal.

17. The method of claim 1, wherein the composition is invisible to a human eye.

18. The method of claim 1, wherein the composition is absent from a forged reproduction of the article.

19. The method of claim 1, wherein the composition comprises chemiluminescent substances with different wavelengths.

20. The method of claim 1, wherein the composition comprises chemiluminescent substances with different triggering temperatures.

21. The method of claim 1, wherein the composition comprises chemiluminescent substances with different decay rates.

22. The method of claim 1, wherein the at least one compound is selected from the group consisting of dioxetanes, dioxetane diones, dioxetane carboxylates, peroxyoxalates, oxalates, luciferins, endoperoxides, acridine, acridinium salts, luminols, phthalates, hydrazines, hydrazides, olefins, tetrapyrroles, porphyrins, metalloporphoryins, isoluminols, peroxy compounds, xanthines and combinations thereof.

23. The method of claim 1, wherein the surface associated with the article is selected from the group consisting of paper, plastic, metal, glass, a natural surface and combinations thereof.

24. The method of claim 1, wherein the surface is selected from the group consisting of a surface of the article, a surface of a label on the article, a surface of a sheet of instructions or descriptions for the article, a surface of an accessory fitted to the article, a surface of a shipping document for the article, and a surface of a container used for shipping the article.

25. The method of claim 1, wherein the triggering source is selected from the group consisting of heat, light, chemical, pressure and combinations thereof.

26. The method of claim 1, wherein the identifying step includes capturing the chemiluminescent signal with a photoimaging device.

27. The method of claim 26, wherein the photoimaging device is selected from the group consisting of X-ray film, photodiode, photomultiplying tube and Charge-Coupled Device (CCD) camera.

28. An article having associated therewith a surface to which is applied a composition comprising at least one compound capable of producing a chemiluminescent signal, alone or in combination with other reagents, wherein unique information associated with the article is contained in the signal.

29. The article of claim 28, wherein the unique information, when compared with provided information about the article, indicates whether or not the article is authentic.

30. The article of claim 29, wherein the provided information is information on the article, on packaging for the article, on separate information provided with the article, and combinations thereof.

31. The article of claim 29, wherein the provided information comprises visible indicia.

32. The article of claim 28, wherein the unique information comprises at least one of the group consisting of manufacturer's name, batch number, expiration date, characteristics of the article, lot number, a code and combinations thereof.

33. The article of claim 28, wherein the unique information is encoded.

34. The article of claim 33, wherein the information to decode the unique information in the chemiluminescent signal is known by the manufacturer of the article.

35. The article of claim 28, wherein the chemiluminescent signal is produced at a predetermined location on the surface.

36. The article of claim 28, wherein the article is an article of manufacture or a natural product.

37. The article of claim 28, wherein the article is selected from the group consisting of a consumer good, a drug, a bioactive agent and currency.

38. The article of claim 28, wherein the article is selected from the group consisting of foods, drinks, clothing, electronics, cigarettes, cosmetics, jewelry, computer hardware, computer software, mechanical parts, accessories and shoes.

39. The article of claim 28, wherein the applied composition further comprises reagents for the enhancement of the chemiluminescent signal.

40. The article of claim 28, wherein the at least one compound is selected from the group consisting of dioxetanes, dioxetane diones, dioxetane carboxylates, peroxyoxalates, oxalates, luciferins, endoperoxides, acridine, acridinium salts, luminols, phthalates, hydrazines,

hydrazides, olefins, tetrapyrroles, porphyrins, metalloporphoryins, isoluminols, peroxy compounds, xanthines and combinations thereof.

41. The article of claim 28, wherein the surface associated with the article is selected from the group consisting of paper, plastic, metal, glass, a natural surface and combinations thereof.

42. The article of claim 28, wherein the surface is selected from the group consisting of a surface of the article, a surface of a label on the article, a surface of a sheet of instructions or descriptions for the article, a surface of an accessory fitted to the article, a surface of a shipping document for the article, and a surface of a container used for shipping the article.

43. The article of claim 28, which when subjected to a triggering source, elicits the chemiluminescent signal.

44. The article of claim 43, wherein the triggering source is selected from the group consisting of heat, light, chemical, pressure and combinations thereof.

45. A method comprising:

providing a surface associated with an article;

providing a composition on the surface at a predetermined location on the surface, wherein the composition comprises a dioxetane;

subjecting the article to heat which elicits the chemiluminescent signal; and

identifying unique information contained in the chemiluminescent signal, wherein the unique information is associated with the article.

46. The method of claim 45, further including providing information about the article and comparing the provided information with the unique information.

47. The method of claim 46, wherein the comparison of the unique information with the provided information indicates whether or not the article is authentic.

48. The method of claim 45, wherein the identifying step includes capturing the chemiluminescent signal with a photoimaging device.

49. The method of claim 45, wherein the photoimaging device is selected from the group consisting of X-ray film, photodiode, photomultiplying tube and Charge-Coupled Device (CCD) camera.

50. The method of claim 45, wherein the chemiluminescent signal is produced at the predetermined location on the surface.

51. The method of claim 50, wherein the predetermined location is known by the manufacturer.

52. The method of claim 45, wherein the unique information comprises at least one of the group consisting of manufacturer's name, batch number, expiration date, characteristics of the article, lot number, code and combinations thereof.

53. The method of claim 45, wherein the unique information contained in the chemiluminescent signal is encoded.

54. The method of claim 53, wherein the information to decode the unique information in the chemiluminescent signal is known by the manufacturer of the article.

55. The method of claim 45, wherein the dioxetane is an invisible marker.

56. A method for detecting forgery of an article comprising the method of claim 1.

57. A method for preventing forgery distribution comprising the method of claim 1.

58. A method for detecting forgery of an article comprising the method of claim 45.

59. A method for preventing forgery distribution comprising the method of claim 45.

60. A device for detecting forgery of an article comprising:
a heating source;

a detection element, wherein the detection element detects light emitted by a chemiluminescent substance and converts the detected light into a detectable signal.

61. The device of claim 60, further comprising a processing unit.

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62. The device of claim 61, wherein the processing unit comprises a programmed microprocessor which measures deviations between information provided about the article and unique information contained in the signal to determine if the article is a forgery.

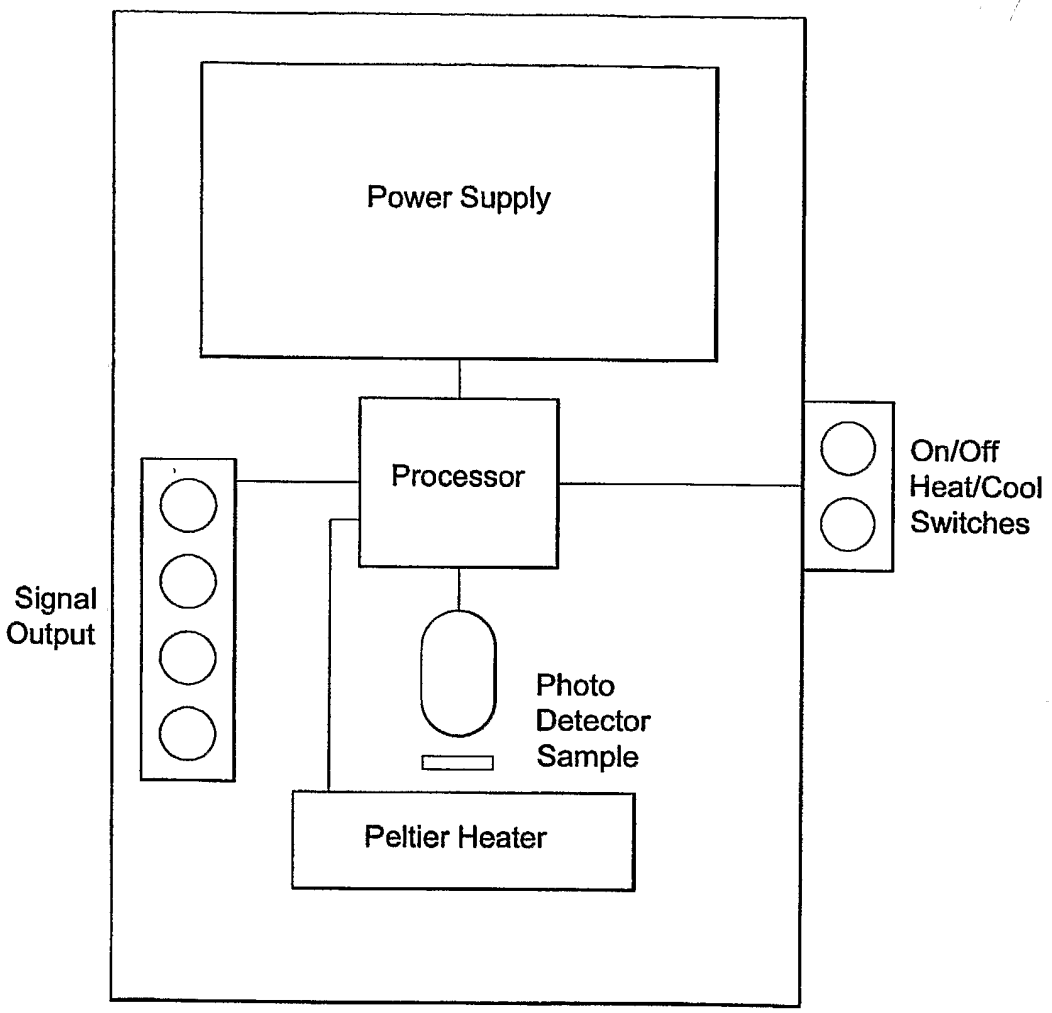
Power Supply
Processor
On/Off
Heat/Cool
Switches
Signal
Output
Photo
Detector
Sample
Peltier Heater

FIG. 1

# INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/015728

A. CLASSIFICATION OF SUBJECT MATTER
INV. G07D7/12 G07D7/14

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)
G07D

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 | US 2002/105654 A1 (GOLTSOS WILLIAM) 8 August 2002 (2002-08-08) paragraphs [0012] - [0015] paragraphs [0030] - [0040] paragraphs [0044] - [0055] figures 1,8,9 | 1-62 |
| X | WO 2004/040504 A (LAMBERT, CLAUDE; HACHIN, JEAN-MICHEL) 13 May 2004 (2004-05-13) page 2, line 5 - page 3, line 31 page 6, line 26 - page 7, line 12 page 8, line 19 - page 9, line 12 page 11, lines 12-28 figures 1-4 | 1-62 |

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

[X] See patent family annex.

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 14 September 2006 | 21/09/2006 |

| Name and mailing address of the ISA/ | Authorized officer |
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# INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/015728

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | US 5 289 547 A (LIGAS ET AL)<br>22 February 1994 (1994-02-22)<br>column 2, line 58 - column 5, line 40<br>column 8, lines 5-40<br>column 10, lines 24-59<br>column 11, lines 25-52 | 1-62 |
| X | EP 0 430 810 A (ARJOMARI-PRIOUX S.A)<br>5 June 1991 (1991-06-05)<br>column 2, line 7 - column 3, line 52<br>column 5, lines 36-44<br>column 6, lines 21-26<br>column 6, lines 49-57<br>column 7, lines 33-46<br>figures 3,5 | 1-62 |
| X | US 2004/106205 A1 (STEVENSON NIGEL R ET AL) 3 June 2004 (2004-06-03)<br>paragraphs [0046] - [0055]<br>paragraphs [0059], [0060], [0063]<br>paragraphs [0068] - [0070]<br>figures 2,3 | 1-61 |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2006/015728

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| US 2002105654 A1 | 08-08-2002 | NONE | |
| WO 2004040504 A | 13-05-2004 | AU 2003288342 A1 | 25-05-2004 |
| | | BR 0315825 A | 13-09-2005 |
| | | CA 2504155 A1 | 13-05-2004 |
| | | CN 1714373 A | 28-12-2005 |
| | | EP 1556837 A2 | 27-07-2005 |
| | | FR 2846445 A1 | 30-04-2004 |
| | | JP 2006505033 T | 09-02-2006 |
| | | MX PA05004522 A | 23-11-2005 |
| | | US 2006054825 A1 | 16-03-2006 |
| US 5289547 A | 22-02-1994 | NONE | |
| EP 0430810 A | 05-06-1991 | NONE | |
| US 2004106205 A1 | 03-06-2004 | US 2003030558 A1 | 13-02-2003 |