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PLASTIC MARKING PROCESS

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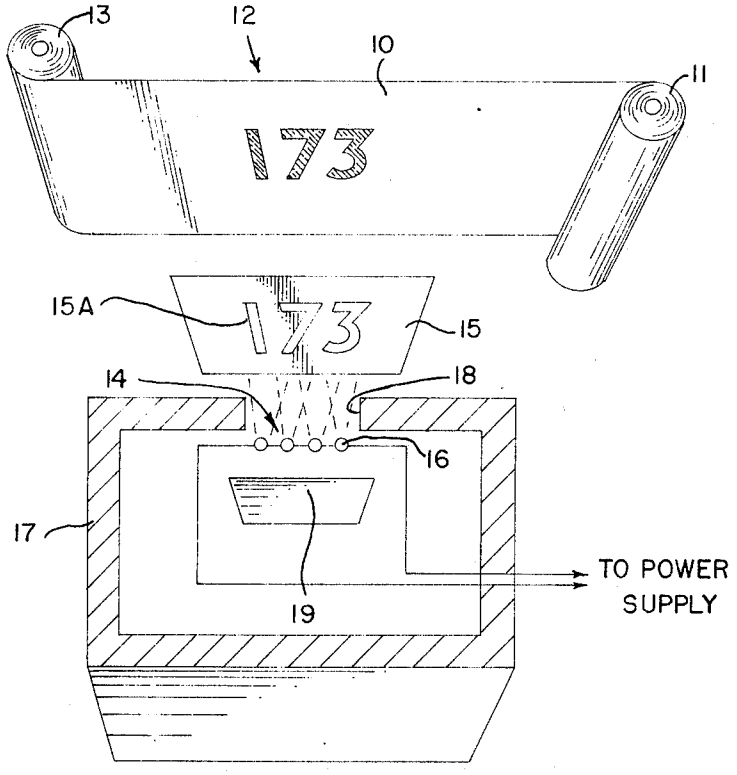

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PLASTIC MARKING PROCESS

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U.S. Cl. 96—45.1 8 Claims

ABSTRACT OF THE DISCLOSURE

A method for providing a code marking invisible in normal light on a plastic substrate exhibiting fluorescent properties wherein a source of intense optical radiation is impinged on the substrate through a stencil bearing the desired marking pattern, the radiation causing a change in the fluorescence of the substrate in the radiated area. The resultant marking is invisible in ordinary light, but visible under ultra-violet illumination.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to the marking of plastic substrates and more particularly relates to a means for marking a plastic material having fluorescent properties using optical radiation.

The prior art

In the packaging of materials in plastic containers, it is frequently desired to apply to the surface of the container some designation or code number which serves to indicate the source of the particular lot of material being packaged, the time or date when the particular material was packaged, or other information. Many times it is also desirable that the code or marking be invisible, as for example, where it is desired to follow the manufacturing history of the container without defacing the container.

Generally, the code marking is embossed on the plastic container surface by metal dies which is a time-consuming and expensive procedure.

SUMMARY OF THE INVENTION

The present invention provides a means of producing on a plastic substrate having fluorescent properties a marking invisible in ordinary light but which can be read when subjected to the proper selective light or energy wave length wherein an opaque stencil having an aperture pattern corresponding to the desired marking is placed between the substrate to be marked and a source of optical radiation, the substrate being so positioned that the aperture pattern of the stencil is in registration with the portion of the substrate on which it is desired to produce the invisible marking, whereupon the source of optical radiation is impinged on the substrate through the apertures of the stencil, the source of optical radiation transmitting sufficient energy to the substrate surface to cause a change in the fluorescence of the substrate exposed to the source of optical radiation.

DESCRIPTION OF THE DRAWING

In the accompanying figure is illustrated a schematic representation of an apparatus for projecting a source of optical radiation through an opaque stencil to produce a marking invisible in natural light but visible in ultraviolet light on the surface of a fluorescent plastic substrate.

Referring to the figure, a plastic substrate **10** which exhibits fluorescence in filtered ultraviolet light is transportable from supply roll **11** past a marking station indicated by the arrow **12** to be taken up on take-up roll **13**. The fluorescent plastic substrate **10** is sensitive to the optical radiation from a source **14** which is directed thereon through stencil **15** having aperture pattern **15A** corresponding to the marking which is desired to be printed on the surface of the substrate **10**.

The stencil **15** is placed adjacent to the moving substrate **10** in a position at which the aperture pattern **15A** is in registration with the portion of the substrate **10** at which it is desired to mark the substrate as it passes through the marking station **12**.

The source of optical radiation **14** is illustrated diagrammatically as one or more lamps **16** with series current distribution connections thereof which are located in close proximity to the moving substrate **10**. The lamps **16** are housed in an opaque base **17** having an opening **18** and a reflector **19** to reflect light rays from which the optical radiation is projected to the stencil **15**. The lamps **16** are electrically connected to a power supply which furnishes high voltage direct current for energizing the lamps.

The lamps **16** will be understood to be such as will radiate any suitable form of optical radiation which will furnish an amount of energy which is effective to cause a change in the fluorescence of the fluorescent plastic substrate.

For example, the lamp **16** can be formed from a tube or envelope made of fused quartz which contains an inert gas such as xenon or krypton under reduced pressure. Such lamps emit a high energy continuous spectrum light when energized.

The wavelengths of the light emitted by the lamp **16** are both in the infra-red and ultra-violet range and include as well, wavelengths of some or all the light in the intermediate or visible spectrum. Ultraviolet light having wavelengths ranging from 4000 angstroms, for example, to a lower limit of 1800 angstroms, which is the limit for the transmission of ultra-violet light through quartz, is particularly desirable for the purpose of the present invention and a light source of the type described is particularly efficient in producing an abundance of light between these wavelengths.

The source of optical radiation **14** may be operated continuously with exposure controlled by means of a suitable shutter or of the instantaneous discharge or flash type which may be operated intermittently as required for exposure.

PREFERRED EMBODIMENTS

The areas of the plastic substrate marked by exposure to the optical radiation are invsible in ordinary light but exhibit a fluorescence different from the fluorescent color of the unexposed areas of the fluorescent substrate in accordance with the pattern of the apertures in the stencil when viewed in ultraviolet light. The visual impact of the marking results from the contrast developed between the initial background and the changed fluorescent areas and can be readily identified. The change in fluorescence in the radiated area can be either significantly more or less fluorescence or fluorescence of a significantly different color or wave length.

There are many polymeric materials known to the art which exhibit fluorescence in filtered ultraviolet light. For example, when viewed in ultraviolet light, synthetic resins such as phenol-formaldehyde resins have an intense blue-violet fluorescence, thiourea-formaldehyde resins have a bluish-white fluorescence, cellulose-acetate has a faint bluish-white fluorescence, cellulose-nitrate has a yellow-brown fluorescence, polyacrylic acid has an intense blue fluorescence, polybutadiene has a bright violet fluorescence, polystyrene has a blue-violet fluorescence, chlorinated rubber has a pale light blue fluorescence, polyvinylacetate has a white-blue fluorescence, polyvinylalco-

hol has a white fluorescence, polyvinylchloride has a blue-green fluorescence, and epoxy resins exhibit a light blue flourescence.

The fluorescence of common plastics in filtered ultraviolet light may be found in the "Handbook of Plastics" by H. R. Simonds and C. Ellis van Ostrand, 1943, Table 107.

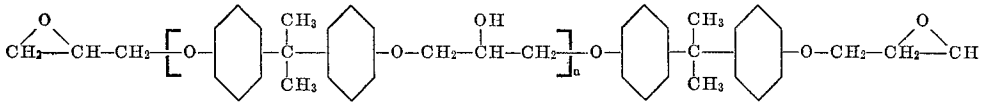
The amount of optical radiation transmitted through the stencil will be dependent upon the voltage and energy from a suitable source. Generally, the amount of the optical energy emitted by the radiation source sufficient to cause a change in the fluorescence of the fluorescent plastic substrate may vary from about 1 to about 6 joules per square centimeter of substrate surface.

Various sources of optical radiation may be employed, such as xenon-filled flash tubes, argon-filled flash tubes, mercury-vapor flash tubes, or xenon, argon or mercury-vapor continuous radiation tubes.

To illustrate the manner in which the process of the present invention may be carried out, the following examples are given. It is to be understood, however, that the examples are for the purpose of illustration and the invention is not to be regarded as limited to any of the specific materials or conditions recited therein.

Example I

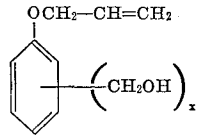
To a tinplate surface was applied at a dry film weight of 3.5 mg./in.^{2} a coating solution composed of 21.93% of an epoxy resin commercially available from the Shell Chemical Company under the tradename EPON 1007 represented by the formula:



wherein n is an integer indicating repeating units, the epoxy resin having the following physical properties:

Melting point—125°–135° C.
Viscosity at 25° C. (measured in 40 wt. percent butyl carbitol)—18–28 poises
Epoxide equivalent (measured in 75 wt. percent xylene)—2000–2500

7.32% of a mixture of allyl ethers of mono-, di- and trimethylol phenols having the following structure:



wherein x is an integer of 1 to 3 commercially available from the General Electric Company under the tradename GE 75108 Methylon; 0.30% of a polyvinyl butyral resin having a molecular weight of about 50,000 commercially available from Shawinigan Resin Company under the tradename Butavar B–76, and 0.45% phosphoric acid, the above components dissolved with 70% Cellosolve acetate.

The coating solution was baked 10 minutes to a cured film at 400° F. When examined under ultraviolet illumination using a Raytech Hand Illuminator, the coating had a light blue fluorescence at 3200 to 4000 AU and a light violet fluorescence at 2800 AU.

An aluminum stencil having an aperture pattern having a numerical design was placed between the epoxy resin substrate and a source of optical radiation which emitted a high energy light of a continuous spectrum. The source of optical radiation was a flash emitted by an array of four series connected xenon-filled quartz flash tubes. The flash emitted had a duration of approximately 150 microseconds and was energized by a 980 watt-second pulse of energy delivered by a 160 microfarad bank of capacitors charged to 3500 volts. The amount of radiant energy transmitted to the substrate by this flash was 3 joules/cm.^{2} of substrate surface.

The flash tubes were spaced ¾ inch apart and a polished metal reflector was mounted in contact with the back surface of the flash tubes to reflect the light rays onto the epoxy resin substrate. The coated surface was also spaced one inch from the plane of the flash tubes.

The coated plate was examined under daylight conditions and no marking could be observed on the coated plate. However, when the coated plate was examined under ultraviolet illumination, the numerical marking was observed on the coating surface which stood out due to the contrast in fluorescence between the light blue fluorescence in the non-flashed area and the relative non-fluorescence in the flashed area.

The clarity of the printed image was measured by determining the intensity of visible light which would just extinguish the image. This is defined as the voltage applied to a 100 watt projector lamp placed 15 inches distance at a 10° incident angle from the sample. A simple nomograph was used to convert actual voltage over a range from 20 to 140 volts to a corrected range of from 0 to 100 volts. The numerical marking had an extinction voltage of 35.

The marked sample was then immersed in water at 160° F. for 20 minutes. A slight loss in clarity of the mark was observed, although the mark was still readable in ultraviolet light at 3200 to 4000 AU and below 2800 AU.

Example II

The procedure of Example I was repeated with the exception that small amounts of organic fluorescent materials were added to the coating formulation. More intense markings were observed in ultraviolet light than with the unmodified coating formulation when the coating surface was irradiated in accordance with the procedure of Example I. The fluorescent materials added to the coating formulation of Example I, their concentrations, and the extinction voltages of the markings in ultraviolet light are recorded in the table below.

TABLE

Fluorescent material	Amount of Fluorescent material added to coating formulation (phr.)[1]	Extinction voltage
4-methyl-7-diethylamino coumarin	0.5	68
4-methyl-7-diethylamino coumarin	0.05	38
Sodium fluorescein	0.05	42

[1] Parts per 100 parts resin solids.

Only slight losses in marking clarity were observed after immersion of the above irradiated samples in water at 160° F. for 20 minutes.

Example III

The procedure of Example I was repeated with the exception that a coating composition composed of 19.2% of a vinyl chloride/vinyl acetate copolymer containing 87 mole percent vinyl chloride and 13 mole percent vinyl acetate, 12.3% of a heat stabilizer composition and 68.5% organic solvent was applied to tinplate and baked for 8 minutes at 325° F.

The flashed sample, when exposed to ultraviolet light under 2800 AU had a dark blue fluorescence in the flashed area and a light yellow fluorescence in the non-flashed area. The marking was clearly readable and had an extinction voltage of 33.

Example IV

An epoxy/vinyl chloride copolymer was prepared by reacting one mole of vinyl chloride with 0.248 mole of glycidyl crotonate at 80° C. using 0.2 mole percent of benzoyl peroxide catalyst.

At 28% conversion, a copolymer containing 28.6% glycidyl ester and 40.2% chlorine was obtained. The intrinsic viscosity of the copolymer was 0.187 poise at 30° C. Forty grams of the copolymer were dissolved in a mixture of 51 grams of toluene and 9 grams of isopropanol along with one gram of Versamide 125 which is a condensation product of a polymerized fat and a polyamine of the type described in U.S. Patent 2,379,413.

The coating composition was applied to a tinplate surface and baked 8 minutes at 325° F. Cured coated samples were marked in accordance with the procedure of Example I over the range of 2.5 to 4.0 kilovolts. The amount of energy transmitted to the substrate over this range was 1.5 to 3.5 joules/cm.^{2}.

None of the samples exhibited a print visible in normal light but all exhibited a clearly readable coaded image under ultraviolet light. At 3200–4000 AU, the coded image was a non-fluorescent marking on an overall fluorescent background. At 3.5 kilovolts, i.e., at 3.0 joules/cm.^{2} of substrate surface, image visibility under ultraviolet light was excellent, as evidenced by extinction voltage of 75 volts.

The markings on the samples were found to be extremely stable, as there was no sognificant alteration of the coded image when the flashed samples were exposed to water at 160° F. for 20 minutes or exposed to room illumination, that is, a cool, white fluorescent lamp and stored in the dark for over 6 months.

Example V

A film, about 4 mils thick, which was cast from a copolymer containing 86% vinyl chloride, 13% vinyl acetate, and 1% maleic acid, was irradiated at 4.0 kilovolts, 1250 joules, following the procedure of Example I using a reflective metal surface to backup the film. The amount of energy transmitted to the substrate was 3.5 joules/cm.^{2}. An examination of both sides of the films indicated that the marking could be read from either side of the film.

What is claimed is:

1. A process for producing a marking invisible in natural light but visible in ultraviolet light on a plastic substrate exhibiting fluorescent properties in filtered ultraviolet light which comprises the steps of positioning an opaque stencil having an aperture pattern corresponding to the desired marking between the substrate to be marked and a source of optical radiation so that the aperture pattern is in registration with the portion of the substrate on which it is desired to produce the marking, impinging the source of optical radiation on the substrate through the apertures of the stencil, the source of optical radiation transmitting sufficient energy to the substrate surface to cause a change in the fluorescence of the substrate in the areas exposed to the source of optical radiation, the change in fluorescence being discernible only in ultraviolet light.

2. The process of claim **1** wherein the plastic substrate is comprised of an epoxy resin.

3. The process of claim **1** wherein the substrate is a copolymer containing vinyl chloride.

4. The process of claim **1** wherein the substrate is a vinyl chloride/vinyl acetate copolymer.

5. The process of claim **1** wherein the substrate is a vinyl choride/vinyl acetate/maleic acid terpolymer.

6. The proces of Example I wherein the source of optical radiation is a flash lamp which emits a high-energy, continuous spectrum light.

7. The process of Example 1 wherein the source of optical radiation is a xenon-filled quartz tube.

8. The process of claim **1** wherein the source of optical radiation transmits to the substrate an amount of energy in the range of about 1 to about 6 joules/cm.^{2} of substrate surface.

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Simonds et al., Handbook of Plastics, Table 107, (1943).

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U.S. Cl. X.R.

117—33.5; 161—33, 164, 412; 204—159.2, 159.14