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(54) **Title:** USE OF BISMUTH OXIDES FOR LASER MARKINGS IN THERMOPLASTIC POLYURETHANE COMPOUNDS

(57) **Abstract:** A thermoplastic compound is disclosed. The compound is laser markable and made from thermoplastic polyurethane, a laser radiation opacifier substance, and optionally a colorant. The laser radiation opacifier comprises bismuth trioxide. The compound can be molded into durable plastic articles such as identification ear tags for domestic livestock that need identification via laser marking of symbols, numbers, or images.

WO 2006/065611 A1

# USE OF BISMUTH OXIDES FOR LASER MARKINGS IN THERMOPLASTIC POLYURETHANE COMPOUNDS

## CLAIM OF PRIORITY

**[0001]** This application claims priority from U.S. Provisional Patent Application Serial Number 60/635,833 bearing Attorney Docket Number 12004015 and filed on December14, 2004.

## FIELD OF THE INVENTION

**[0002]** This invention relates to thermoplastic polyurethane (TPU) compounds that contain bismuth oxide to assist in laser marking of the TPU compounds.

## BACKGROUND OF THE INVENTION

**[0003]** Laser marking is a well known and important means for quickly and cleanly inscribing plastic surfaces with identification marks, such as date codes, batch codes, bar codes or part numbers, functional marks, such as computer keyboard characters, and decorative marks, such as company logos. The most common laser marks are either a dark mark on a lighter colored background or a light mark on a dark colored background.

**[0004]** A light, dark or colored laser mark on a thermoplastic material may be produced by several different mechanisms or combination of mechanisms, depending on the resin and additives employed, the nature of any colored pigments, and the laser energy characteristics.

**[0005]** A dark marking has also been achieved by the use of additives that are colorless in the visible light spectrum but which change into a visible dark or black product when irradiated by laser light just outside the visible range, such as by a Nd:YAG (Neodymium doped Yttrium Aluminum Garnet)

laser (wavelength 1064 nm) or an excimer laser (wavelength 308 nm or 351 nm).

**[0006]** U.S. Pat. No. 4,816,374 (Lecomte) discloses the use of antimony oxide as a laser radiation opacifier substance in a polyurethane plastic material to satisfy French standard (number NF-T-54006) for abrasion in order to make and use ear tags for livestock animals.

**[0007]** However, it is not preferred to use heavy metals such as antimony in thermoplastic compounds for healthy and safety reasons. Indeed, antimony is still being studied regarding health problems that it might induce in mammals.

**[0008]** U.S. Pat. No. 6,214,917 (Linzmeier et al.) discloses thermoplastic polyurethanes as laser-markable plastics. The TPU's contain pigments having a coating of tin dioxide thereon, which coating is doped with 0.5-20% by weight of antimony, arsenic, bismuth, copper, gallium, germanium, or a corresponding oxide thereof.

**[0009]** U.S. Pat. No. 6,503,316 (Sakoske et al.) disclose a laser markable pigment and a laser markable compound containing that pigment, wherein the pigment is of the formula $Bi_xM_yO_z$, where M is at least one metal selected from Zn, Ti, Fe, Cu, Al, Zr, P, Sn, Sr, Si, Y, Nb, La, Ta, Pr, Ca, Mg, Mo, W, Sb, Ba, and Ce, x is from 0.3 to about 70, y is from about 0.05 to about 8, z is from about 1 to about 100, and the ratio of x to y is greater than 2. In other words, the laser markable compounds comprise Bi and at least one additional metal.

**[00010]** However, the use of the additional metal reintroduces the problems with metals such as antimony described above.

## SUMMARY OF THE INVENTION

**[00011]** What is needed is a laser radiation opacifier substance that can be used in a thermoplastic material without concern about the reasons that antimony and other heavy metallic compounds are currently disfavored.

**[00012]** The present invention has solved this problem in the art by providing bismuth oxide to serve as the laser radiation opacifier substance to be used in a thermoplastic material.

**[00013]** One aspect of the present invention is a thermoplastic compound, comprising: (a) thermoplastic polyurethane; (b) a laser radiation opacifier substance; and (c) optionally visible-spectrum colorant, wherein the laser radiation opacifier substance comprises bismuth oxide.

**[00014]** Another aspect of the present invention is a thermoplastic article made from the thermoplastic compound described above.

**[00015]** Another aspect of the present invention is the use of bismuth oxide as a laser radiation opacifier substance.

**[00016]** An advantage of the use of bismuth oxide in the thermoplastic compound is good opacifying power.

**[00017]** Another advantage of using bismuth oxide is the easy dispersion of that chemical into TPU compounds.

**[00018]** As used herein, "bismuth oxide" or "bismuth oxides" means bismuth trioxide ($Bi_2O_3$), bismuth pentoxide ($Bi_2O_5$), and any other oxide of bismuth known to exist. However, "bismuth oxide" or "bismuth oxides" does not include any bismuth oxide halide, such as bismuth oxychloride (BiOCl). or a bismuth metal oxide, such as $Bi_xM_yO_z$ where M is a metal.

**[00019]** Other features and advantages of the present invention will become apparent in the text below.

## EMBODIMENTS OF THE INVENTION

**[00020]** Thermoplastic Polyurethane

**[00021]** Thermoplastic polyurethane (TPU) is well known in the thermoplastic industry, whether aromatic-based TPU or aliphatic-based TPU. TPU is available from a number of commercial sources including Merquinsa Mercados Quimicos S.L. (Pearlthane™ and Pearlcoat™ grades); Bayer A.G. (Desmopan™ grades) and the like. TPU compounds can contain a variety of

optional additives to improve handling, processing, stability, durability, color, and the like. Any of these TPU compounds are suitable for use in the present invention.

**[00022]** For use in laser markable plastic articles, TPU is desired because it is a soft and flexible material particularly suited for identification tags for domestic livestock, etc.

**[00023]** It is within the scope of the present invention to blend the TPU with one or more other thermoplastic resins to alter the physical properties of the plastic article to be made from the compound of the present invention. Any thermoplastic polymer that is suitable for blending with TPU is useful in the present invention also for making a laser markable compound and article therefrom. Non-limiting examples of other polymers include polymers of ethylenically unsaturated monomers, such as polyethylene, polypropylene, polybutylenes, polystyrenes, poly (-methyl styrene), polyvinyl chloride, polyvinyl acetate, polymethyl methacrylate, polyethyl acrylate, polyacrylonitrile and the like; copolymers of ethylenically unsaturated monomers such as copolymers of ethylene and propylene, ethylene and styrene, and polyvinyl acetate, styrene and maleic anhydride; styrene and methyl methacrylate; styrene and ethyl acrylate; styrene and acrylonitrile; methyl methacrylate and ethyl acrylate and the like; and polymers and copolymers of conjugated dienes such as polybutadiene, polyisoprene, and polychloroprene.

**[00024]** The TPU can also be compounded optionally with thermosetting materials. Examples of thermosetting materials useful in this invention include synthetic butyl rubbers, synthetic isoprene rubbers, silicone RTV (room temperature vulcanizing) rubbers, styrene butadiene rubber, ethylene-propylene-diene rubber, acrylonitrile-styrene butatiene rubber and the like; saturated and unsaturated polyesters including alkyds and other polyesters; nylons and other polyamides; polyesteramides and polyurethanes; chlorinated polyethers, epoxy polymers, cellulose esters such as cellulose acetate butyrate, and the like.

**[00025]** Bismuth Oxides

**[00026]** The laser radiation opacifying substance need only comprise bismuth oxide, although it is within the scope of the invention to combine bismuth oxide with another laser radiation opacifying substance, such as BiOCl. It is preferable to use bismuth oxide alone.

**[00027]** Bismuth trioxide is often used as a replacement for lead oxides in food contacting articles. Thus, it is well understood by those skilled in the art that bismuth trioxide is considered benign for contact with mammals.

**[00028]** Bismuth trioxide is commercially available in major chemical-producing nations. For example, bismuth oxide is commercially available in France at the Pharmacie Centrale de France and in the United States of America at Pechiney Chemicals Division of Stamford, CT. BiOCl is also available commercially from these sources.

**[00029]** Optional Additives

**[00030]** In addition to conventional optional additives that may be present in the TPU, the compound of the present invention can optionally include colorants (pigments, dyes, or both) to provide a specific color, against with the laser-marking can be contrasted for easy reading of the information thereon. For avoidance of confusion, the use of titanium dioxide (or any other metallic pigment that doesn't contain any Bismuth) for improving color of the TPU compound should not be considered a bismuth metal oxide, as disclosed in U.S. Pat. No. 6,503,316 (Sakoske et al.). The titanium dioxide is a separate chemical discrete from the bismuth oxide also dispersed in the TPU.

**[00031]** For ease of handling, the colorants are often delivered in the form of colorant concentrates for dilution or "letdown" into the compound at the mixer or extruder. Colorant concentrates are commercially available from PolyOne Corporation in North America, Europe, and Asia. (www.polyone.com)

**[00032]** Non-limiting examples of pigment colors are red, orange, yellow, and green in the lighter hues so that the dark image of laser marked information can be seen in considerable contrast.

**[00033]** Table 1 shows the acceptable, desirable, and preferred concentrations of the TPU (alone or with other thermoplastic or thermosetting polymers), non-metallic bismuth compound(s), and optional pigment(s).

**Table 1 -- Range of Ingredients**

| Ingredient (Weight Percent) | Acceptable Range | Desirable Range | Preferred Range |
|---|---|---|---|
| TPU or TPU with other polymer(s) | 85-99.5% | 90-97% | 93-96% |
| Bismuth Oxide | 0.5-15% | 3-10% | 4-7% |
| Colorant | 0 -5% | 0 -5% | 0-5% |

**[00034]** Method of Compounding

**[00035]** The compound of the present invention can be mixed using any conventional mixing equipment, including without limitation high speed mixers and extruders. Preferably, a twin-screw extruder is used at melt-mixing temperatures and speeds to provide excellent dispersion of the non-metallic bismuth compound and optional colorant therein. More preferably, after the polymer is melted, the bismuth oxide and additives are added via a side feeder.

**[00036]** Mixing temperatures can range from about 180°C to about 260°C, and preferably from about 200°C to about 220°C.

**[00037]** Mixing speeds can range from about 50 to about 1000, and preferably from about 150 to about 300550 revolutions per minute.

**[00038]** As an alternative to adding solids via a side feeder to the polymer melt in the extruder, the ingredients can be fully premixed using a low/high speed mixer operating at about 25°C temperature and about 500rpm mixing speed.

**[00039]** The extruded product can be formed into pellets for subsequent molding or extrusion operations.

USEFULNESS OF THE INVENTION

**[00040]** TPU compounds of the present invention are particularly suitable for laser marking where durability is important. For example, cattle identification tags are exposed to all of the environmental elements that the cattle endure, as well as conditions created by the cattle such as rubbing against trees, posts, etc. Agriculture regulations, such as French Standard No. NF-T-54006 must be satisfied in order for laser markable identification ear tags can be used in an agricultural environment in France.

**[00041]** Laser marking of the TPU compounds of the present invention can use any of the lasers reported in U.S. Pat. No. 6,503,316 (Sakoske et al.), such as neodymium:yttrium aluminum garnet (Nd:YAG) lasers, carbon dioxide ($CO_2$) lasers, diode lasers, excimer lasers and the like.

**[00042]** As reported in Sakoske et al., typical YAG lasers emit light in the near-infrared spectrum at wavelengths of 1064 nm. Such lasers typically have continuous power outputs of from about 1 to about 50 watts, and can be operated in a pulsed mode at typical peak powers of from about 1 watt to about 45 kilowatts. For pulsed mode operation, frequencies of from about 1 to about 64,000 pulses/second may be used.

**[00043]** As reported in Sakoske et al., typical $CO_2$ lasers emit light in the far-infrared region of the spectrum, with intensity spikes at wavelengths of 9.8 and 10.6 microns. Such $CO_2$ lasers typically operate at a continuous output power of from about 1 to about 40 watts.

**[00044]** As reported in Sakoske et al., the size of the laser spot that impinges the substrate is typically greater than 0.1 micron in diameter, preferably from about 40 to about 500 microns, and more preferably from about 50 to about 125 microns. The speed at which the laser beam travels across the surface of the substrate preferably ranges from 0 to about 254 cm/second, more preferably from about 5 to 50 cm/second for most thicknesses and compositions. The laser beam may be projected with a seam overlap of 0 to 100 percent, preferably from about 10 to about 90 percent for many applications.

The laser parameters are controlled in order to provide sufficient localized heating of the bismuth-containing compound, while avoiding unwanted damage to the substrate.

**[00045]** As reported in Sakoske et al., the laser beam, the movement of which can be controlled by a computer, may be used to create discrete symbols or designs or, alternatively, may be serially indexed across the surface of the substrate to create multiple symbols or designs at the same time. For example, a word may be created by separately making each letter of the word with the laser, or by rastering the laser across the entire word to form all of the letters at the same time. A single laser beam may be used for marking in accordance with the present invention. Alternatively, two or more laser beams may be used.

**[00046]** As reported by Sakoske et al., during the irradiation step, the surface of the substrate may be exposed to any desired type of atmosphere. For example, the atmosphere may comprise air at atmospheric, sub-atmospheric or super-atmospheric pressures. Furthermore, the atmosphere may comprise an inert gas such as nitrogen, argon or carbon dioxide, an oxidizing atmosphere such as air or oxygen, a reducing atmosphere such as hydrogen or carbon monoxide, or a vacuum. Oxidizing or reducing gases can be used in a combination with inert gases.

**[00047]** Additional embodiments are explained in the Examples.

EXAMPLES

**[00048]** Table 2 shows the ingredients and sources for the ingredients used to exemplify the invention.

| Table 2 -- Recipes | | | |
|---|---|---|---|
| **Ingredient Name** | **Commercial Source** | **Example 1** | **Example 2** |
| Pearlthane™ D15N95UV TPU | Merquinsa | 96% | 91% |
| $Bi_2O_3$ | Pharmacie Centrale de France | 4% | 4% |
| Yellow Colorant Concentrate | PolyOne Corporation | 0% | 5% |

**[00049]** Examples 1-2 were made via an extruder, with the TPU being fed into the input hopper and bismuth oxide (Example 1) and the bismuth oxide and colorant concentrate were fed into a side hopper of a Werner & Pfleiderer_ZSK twin screw extruder having a 25mm diameter and a Length:Distance ratio of 30. The extruder was operated at a temperature of between 200 and 220°C in the mixing zones and at a rotation of about 500 revolutions per minute. The fully mixed compound was extruded after cooling of strands in a water bath through a pelletizer and made into pellets of approximately 2 mm diameter.

**[00050]** Pellets from each of the Examples were molded into plaques of 120 mm length, 120 mm width, and 3 mm thickness in an injection molding machine operating at about 220°C.

**[00051]** A plaque from each of the Examples was exposed to a Nd:YAG laser at 1064 nm wavelength (made by TRUMPF located in Roissy en France (95) FRANCE) using the following parameters: 2000 to 32,000 pulses/second; 10 to 120 cm per second; 1.7kW power; 60μm dot size; and 0-10% percent seam overlap.

**[00052]** Both Examples 1 and 2 showed laser markings with high intensity and dark contrast, either in blank or yellow, respectively.

**[00053]** The invention is not limited to the above embodiments. The claims follow.

What is claimed is:

1. A thermoplastic compound, comprising: (a) thermoplastic polyurethane; (b) a laser radiation opacifier substance; and (c) optionally visible-spectrum colorant, wherein the laser radiation opacifier substance is comprises bismuth oxide.

2. The thermoplastic compound of Claim 1, further comprising polymers of ethylenically unsaturated monomers or copolymers of ethylenically unsaturated monomers or combinations thereof as a blend with the thermoplastic polyurethane.

3. The thermoplastic compound of Claim 1 or Claim 2, wherein the bismuth oxide is bismuth trioxide.

4. The thermoplastic compound of Claim 1 or Claim 2, wherein the compound further comprises a thermosetting material.

5. The thermoplastic compound of Claim 1 or Claim 2, wherein the compound further comprises additives to improve properties selected from the group consisting of handling, processing, stability, durability, color, and combinations thereof.

6. The thermoplastic compound of Claim 1 or Claim 2, wherein the laser radiation opacifying substance also comprises BiOCl.

7. The thermoplastic compound of Claim 1, wherein the thermoplastic polyurethane comprises from about 85 to about 99.5 weight percent of the compound and wherein the bismuth oxide comprises from about 0.5 to about 15 weight percent of the compound.

8. The thermoplastic compound of Claim 7, wherein the colorant comprises from 0 to about 5 weight percent of the compound.

9. A thermoplastic article molded from the thermoplastic compound of any of Claims 1-8.

10. The thermoplastic article of Claim 9, wherein the thermoplastic article is an identification tag for domestic livestock.

11. The thermoplastic article of Claim 9, wherein the thermoplastic article has laser-marked symbols, numbers, images, or a combination thereof.

12. A method of using the thermoplastic article of Claim 9, comprising the step of marking with a laser beam the thermoplastic article to create a symbol, a number, an image, or a combination thereof on the thermoplastic article.

# INTERNATIONAL SEARCH REPORT

Int ional application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. B41M5/26 C08K3/22 A01K11/00

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)
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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, PAJ, WPI Data, CHEM ABS Data, PAPERCHEM, PIRA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | US 6 214 917 B1 (R.LINZMEIER ET AL.)<br>10 April 2001 (2001-04-10)<br>cited in the application<br>claims 1,6,12,13,16-18<br>column 1, line 7 - line 46 | 1-12 |
| X | US 6 503 316 B1 (G.E.SAKOSKE ET AL.)<br>7 January 2003 (2003-01-07)<br>cited in the application<br>column 1, line 7 - column 2, line 5<br>column 10, line 20 - line 28<br>claims 1,6,11,19,20 | 1-12 |

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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 |
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| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31–70) 340–2040, Tx. 31 651 epo nl,<br>Fax: (+31–70) 340–3016 | Bacon, A |

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Int ional application No
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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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