(54) Title: PRODUCTION AND USAGE OF PHOTOCROMIC RESIN MOLDED ARTICLES

(57) Abstract: Disclosed is a method of mixing a photochromic compound and a resin, by incorporating 1-2g of the photochromic compound into 500-1,000g of the resin at 60-80 °C for 4-8 hours with stirring in the presence of a mixed organic solvent without lower alcohols and lower acetates, to form an incorporated photochromic resin, and then drying the incorporated resin. Moreover, the mixed organic solvent not containing lower alcohols and lower acetates is used, and the photochromic compound is uniformly incorporated into the resin through stirring and heating processes, therefore resulting in uniform color distribution and high color intensity. Also, a photochromic resin molded article using the method is provided, and is advantageous in terms of excellent external appearance and low price, due to uniform incorporation of a high concentration of the photochromic compound into the resin.
Production and usage of photochromic resin molded articles

Technical Field

The present invention relates, in general, to methods of mixing a photochromic compound and a resin, and photochromic resin molded articles using the same. More specifically, the present invention is directed to a method of mixing a photochromic compound and a resin, which is advantageous in terms of exhibiting addition effect even though an expensive photochromic compound is used in a small amount, by uniformly mixing the photochromic compound with the resin to be stable to temperature variations; and a photochromic resin molded article prepared by the above method.

Background Art

In general, the term ‘photochromism’ means a reversible action of a compound which quickly changes its color when it is irradiated with light containing ultraviolet rays, such as sunlight, or light of a fluorescent lamp, and returns to its original color or a colorless state when it is no longer irradiated with light or is placed in a dark place. The compound having this property is called a photochromic compound.

Such a photochromic compound is present in double ground states respectively absorbing ultraviolet rays and visible light. Thus, the above compound exhibits a variety of colors when being irradiated with ultraviolet rays and returns to a colorless transparent state when not being irradiated with ultraviolet rays. That is, the photochromic compound develops various colors in the presence or absence of ultraviolet rays due to a reversible color change property thereof, and is exemplified by benzopyran based compounds (Korean Patent Application No. 98-018556), naphthopyran based compounds (Korean

Up to the present, photochromic compounds have been used for preparation of glasses for automobiles or buildings, or preparation of ophthalmic glasses such as sunglasses, glasses or plastic lenses. In this regard, Korean Patent Publication No. 94-07779 discloses an organic photochromic material for use in photochromic ophthalmic lenses and plastic matrices such as automotive roof skylight windows.

In recent years, photochromic compounds have been applied to cosmetic articles, such as cosmetics or nail polishes (Korean Patent Application No. 99-06813), and for coating agents (Korean Patent Application Nos. 99-06814 and 99-048421).

Meanwhile, various colors are conventionally provided by use of photochromic compounds as follows. That is, photochromic compounds are incorporated as raw materials upon preparation of a desired product, or are dissolved in a solvent together with a polymer and coated or filmed.

For example, in Korean Patent Application No. 2001-1402, there is disclosed a photochromic composition for coating/printing accessories comprising 20-30wt% of a resin, 1-3wt% of camphor, 4-6wt% of dibutylphthalate, 4-6wt% of ethylacetate, 12-18wt% of toluene, 12-18wt% of butylacetate, 4-6wt% of isopropyl alcohol, 10-12wt% of cellulose acetate butyrate, 0.1-0.3wt% of polyethylene wax, 8-12wt% of methyl isobutyl ketone, 10-15wt% of methyl isoethyl ketone, and 0.5-2wt% of a photochromic compound.

In addition, in Korean Patent Laid-open Publication No. 2001-84405, there is disclosed a method of preparing a photochromic resin molded article comprising the steps of dissolving a spiropyran based photochromic compound in a toluene/alcohol solvent, incorporating the solution to resin granules at 20-50°C for 0.05-48 hours, followed by heating the incorporated resin to 160-300°C and molding the heated resin.
Further, in Korean Patent Application No. 2001-29435, there is disclosed a method of preparing a master batch of a photochromic resin molded article, characterized in that 30-50 parts by weight of methylethylketone, 10-20 parts by weight of toluene, 10-20 parts by weight of xylene, 5-10 parts by weight of ethylacetate, 5-10 parts by weight of isopropyl alcohol, 0.001-5 parts by weight of a fragrance, and 0.1-20 parts by weight of a photochromic compound, are incorporated into 50-100 parts by weight of a resin for 1-24 hours with uniform stirring, dried to remove the solvent, primarily pulverized, heated and rapidly cooled.

However, thusly prepared film layer of the photochromic compound is easily peeled off, or the photochromic compound granules may be readily separated from the photochromic molded article. Despite excellent photochromism characteristics of the photochromic compound, limitations are imposed on use of the above compound in various fields requiring smooth and uniform film layers.

Further, the resin molded articles provided by the above method suffer from low durability and non-uniform incorporation of the photochromic compound into the resin.

Disclosure of the Invention

Leading to the present invention, the intensive and thorough research on methods of mixing a photochromic compound and a resin, carried out by the present inventors aiming to avoid the problems encountered in the prior art, resulted in the finding that lower alcohols and lower acetates, which have been usually used as an organic solvent of the photochromic compound, function to break a molecular structure of the photochromic compound and thus cause durability problems, and also mixing temperatures, which have been maintained at room temperature, lead to decreased production rates and low color intensity. As well, wave patterns are formed on injection molded articles. From this, it can
be confirmed that the photochromic compound is not uniformly incorporated into the resin.

Accordingly, an object of the present invention is to alleviate the problems encountered in the prior art and to provide a method of mixing a photochromic compound and a resin, capable of uniformly incorporating the photochromic compound into the resin, resulting in excellent durability of photochromic resin molded articles.

Another object of the present invention is to provide a photochromic resin molded article using the above method.

In accordance with an embodiment of the present invention, there is provided a method of mixing a photochromic compound and a resin, comprising the following steps of incorporating 1-2g of the photochromic compound to 500-1,000g of the resin at 60-80°C for 4-8 hours with stirring in the presence of a mixed organic solvent not containing lower alcohols and lower acetates, to form an incorporated photochromic resin, and drying the incorporated photochromic resin.

In accordance with another embodiment of the present invention, there is provided a photochromic resin molded article prepared by the above method, comprising lighters, ball-point pens, CD cases, file cases, sunglasses, goggles, cosmetic cases, cap visors, beverage cases, buttons, artificial fingernails, automotive parts or motorcycle parts.

Best Mode for Carrying Out the Invention

Based on the present invention, a photochromic compound is incorporated into a resin at a proper temperature for a suitable period of time in the presence of a mixed organic solvent not containing lower alcohols and lower acetates, and then dried.

As for the mixed organic solvent used as a solvent of the photochromic compound, lower alcohols, such as isopropylalcohol, and lower acetates, for
example, ethylacetate or butylacetate, function to break a molecular structure of the photochromic compound, thereby decreasing color durability of photochromic resin molded articles. Thus, in the present invention, use of the above mentioned solvents is excluded.

In order to dissolve 1-2g of the photochromic compound, the mixed organic solvent is preferably composed of at least two components selected from the group consisting of 100-600g of methylethylketone, 100-700g of toluene, 100-200g of xylene and 400-700g of methylene chloride.

In particular, of the above mentioned types of the organic solvent, the methylene chloride component has not been used as the solvent of the photochromic compound until now. However, in the present invention, this component may be used in the amount of 400-700g to dissolve the photochromic compound.

When the methylene chloride is used in an amount less than 400g, the surface of the resin molded article is colored due to oversaturation of color. On the other hand, if the amount of methylene chloride exceeds 700g, uniform incorporation into the resin becomes difficult and color intensity is low.

The photochromic compound useful in the present invention comprises preferably naphthopyrane based compounds. In addition, the resin is exemplified by polypropylene or polyethylene. However, limitations are not imposed on use of the above mentioned materials.

The photochromic compound is used in the amount of 1-2g, and the resin is used in the amount of 500-1,000g. As necessary, a light stabilizer, an antioxidant, a fragrance and/or a dye may be added in a small amount to the above components.

In the presence of the mixed organic solvent not containing lower alcohols and lower acetates, the photochromic compound is incorporated into the resin at 60-80°C for 4-8 hours and dried.

Conventionally, the photochromic compound and the resin are mixed at room temperatures, thereby decreasing a mixing rate and obtaining low color
intensity. As well, the surface of the molded article is disfigured by wave patterns. Thus, in the present invention, an incorporating process is performed at 60-80°C for 4-8 hours and then a drying process is carried out.

As such, if the temperature is lower than 60°C, solubility of the photochromic compound is decreased and color intensity becomes poor. Meanwhile, if the temperature exceeds 80°C, the compound is not easily incorporated into the resin due to melting of the resin. Further, if the period of time required for incorporation is shorter than 4 hours, color intensity is low and uniform color becomes difficult to achieve. On the other hand, if the time is longer than 8 hours, uniform color becomes difficult to achieve due to melting of the resin.

Therefore, the photochromic compound is dissolved in the mixed organic solvent and uniformly mixed with the resin, and heated at 60-80°C, whereby the photochromic compound is uniformly incorporated into the resin. Therefore, color resistance and color durability of the resin can be maintained, and the molded article having excellent properties of such resin can be obtained.

Then, thusly obtained photochromic resin is molded at 160-220°C to afford the molded article.

The molded article is exemplified by lighters, ball-point pens, CD cases, file cases, sunglasses, goggles, cosmetic cases, cap visors, beverage cases, buttons, artificial fingernails, automotive parts or motorcycle parts. However, the molded article is not limited to the above exemplification.

A better understanding of the present invention may be obtained through the following example which is set forth to illustrate, but is not to be construed as the limit of the present invention.

Example 1

300g of methylethylketone, 400g of toluene, 2g of a photochromic compound (Photochromic, sold by Prism Co. Ltd., Japan) and 300g of a dye (Blue Sky) were mixed by use of Henchel mixer. The mixture was further
added with 1,000g of polypropylene, 0.05g of a light stabilizer (Seikaplen 100, Japan) and 0.03g of an antioxidant (Sanol LS 76, Japan) and mixed at 500 rpm for 1 min. Then, an incorporating process was performed at about 70°C for about 5 hours, to form an incorporated photochromic resin.

The incorporated resin was dried for 3 hours in a drying zone to remove the solvent, pulverized, and injection-molded at 200°C by use of an injector, to prepare a molded article.

When the molded article was exposed to ultraviolet rays, color intensity could be discerned with the naked eye. Intensity and durability of color were determined. The results are shown in Table 1, below.

Example 2

The present example was performed in the same manner as in the above example 1, except that the dye was replaced with another dye (Red), and the solvent comprising 150g of xylene and 550g of methylene chloride was used, and polyethylene was used as the resin. Intensity and durability of color of the molded article were determined. The results are shown in Table 1, below.

Comparative Example 1

The present example was performed in the same manner as in the above example 1, except that the mixed organic solvent comprising 40g of methylethylketone, 15g of toluene, 15g of xylene, 10g of ethylacetate and 5g of isopropylalcohol was used, and an incorporating process was carried out at a room temperature (25°C).

When the molded article was exposed to ultraviolet rays, color intensity could be discerned with the naked eye. Intensity and durability of color were determined. The results are shown in Table 1, below.

Comparative Example 2

The present example was performed in the same manner as in the above
comparative example 1, except that polyethylene was used as a copolymerization resin. Intensity and durability of color were determined. The results are shown in Table 1, below, in which color durability was determined by visually observing color change after the molded article was exposed 300 times to ultraviolet rays at 1 hr intervals.

**TABLE 1**

<table>
<thead>
<tr>
<th>Physical Properties</th>
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<th>Ex. 2</th>
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<tr>
<td>Yield Tensile Strength (kg/cm²)</td>
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**Industrial Applicability**

As described above, the present invention provides a method of mixing a photochromic compound and a resin and a photochromic resin molded article using the same. In the presence of a mixed organic solvent not containing lower alcohols and lower acetates, the photochromic compound is uniformly incorporated into the resin through stirring and heating processes, thereby representing high color intensity as well as uniform color distribution.

In addition, the photochromic resin molded article is advantageous in terms of excellent external appearance and low price, by uniformly incorporating a high concentration of the photochromic compound into the resin.

Although the preferred embodiments of the present invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.
Claims

1. A method of mixing a photochromic compound and a resin, comprising the following steps of:
   incorporating 1-2g of the photochromic compound into 500-1,000g of the resin at 60-80°C for 4-8 hours with stirring in the presence of a mixed organic solvent not containing lower alcohols and lower acetates, to form an incorporated photochromic resin; and
   drying the incorporated photochromic resin.

2. The method as defined in claim 1, wherein the mixed organic solvent comprises two or more components selected from the group consisting of 100-600g of methylethylketone, 100-700g of toluene, 100-200g of xylene and 400-700g of methylene chloride.

3. The method as defined in claim 1, wherein the photochromic compound comprises naphthopyrane based compounds.

4. The method as defined in claim 1, wherein the resin comprises polypropylene or polyethylene.

5. A photochromic resin molded article prepared according to any one of claims 1 to 4.

6. The photochromic resin molded article as defined in claim 5, comprising lighters, ball-point pens, CD cases, file cases, sunglasses, goggles, cosmetic cases, cap visors, beverage cases, buttons, artificial fingernails, automotive parts or motorcycle parts.
INTERNATIONAL SEARCH REPORT

CLASSIFICATION OF SUBJECT MATTER

IPC7: C08J 3/215

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)

IPC7: C08J 3/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, EPDOC, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>X</td>
<td>WO 00/26018 A1 (SKYRAD LTD) 11 May 2000 (11.05.00) page 1, lines 3-22; page 5, lines 12-18; page 7, lines 20-22; claims 1-5.</td>
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<td>DE 4304488 C1 (JAKOB H.) 1 June 1994 (01.06.94) page 3, lines 46-51; page 4, lines 38-63; page 6, lines 34-48.</td>
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<td>X</td>
<td>EP 0629620 A1 (GREAT LAKES CHEMICAL ITALIA S.r.l.) 21 December 1994 (21.12.94) page 10, lines 29-56; claims 1-5,8.</td>
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<td>X</td>
<td>US 3505353 A (GAUTRON R.L.) 7 April 1970 (07.04.70) column 2, line 40 - column 3, line 20; claims.</td>
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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
  - B" earlier application or patent but published on or after the international filing date
  - L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  - O" document referring to an oral disclosure, use, exhibition or other means
  - P" document published prior to the international filing date but later than the priority date claimed
  - T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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  - S" document member of the same patent family

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Date of mailing of the international search report 20 November 2003 (20.11.2003)

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Facsimile No. 1/53424/535
Form PCT/ISA/210 (second sheet) (July 1998)

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Telephone No. 1/53424/459
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