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(54) **Method for laser marking of polyolefin resins**

(57) A method for marking a polyolefin resin is disclosed which comprises irradiating with a YAG laser a polyolefin resin composition containing 0.1 to 1.0 part by weight of carbon black per 100 parts by weight of the polyolefin resin composition, wherein the carbon black has an average secondary particle size of not smaller than 150 nm.

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Description

[0001] This invention relates to a marking method for a polyolefin resin.

[0002] Molded articles made of a polyolefin resin, such as personal articles, domestic appliances, interior and exterior parts and engine parts of automobiles, are often marked with letters, patterns, symbols, etc.

[0003] Such marks can be put on the molded articles by applying thermosetting or UV-curing ink, but ink marking methods are of low productivity, take time for ink application and baking and involve many steps. Besides, ink marks lack durability, and tend to fall off due to insufficient ink adhesion and insufficient resistance to solvents or chemicals. Productivity could be improved by sticking an adhesive label having marks onto a resin molded article, but the durability of the adhesive label is similarly insufficient. In addition, the inks or adhesives must be removed from the molded articles to be recycled, which has reduced the applicability for recycling.

[0004] On the other hand, marking by laser beam processing, i.e., laser marking can be carried out easily and rapidly to achieve markedly improved productivity. In laser marking, a laser beam is applied to a resin molded article having incorporated therein a black pigment which synchronizes with the wavelength of the laser beam to cause the black pigment to burn and evaporate rapidly. As a result, only the black pigment of the laser beam-irradiated area is released to present a contrast between the irradiated area (marked area) and non-irradiated area (background). According to this technique, since the marking is to release only the pigment, the marks are very excellent in solvent resistance, chemical resistance and durability, and the thus marked articles are highly practical for recycling. For these reasons, various laser marking techniques have been studied recently.

[0005] For example, JP-A-1-254743 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") teaches that incorporation of titanium dioxide and carbon black into a resin makes laser marking possible. However, when this method is applied to a polyolefin resin composition, the laser marks formed have a brown or light brown color. The background being black, the marks lack a sufficient contrast to the background and have insufficient visibility.

[0006] Various proposals have been made in order to make laser marks white. For example, JP-A-4-246456 discloses a technique in which carbon black and/or graphite having high thermal conductivity is incorporated into a polyester resin so as to provide white laser marks. JP-A-7-238210 teaches that an epoxy resin composition containing carbon black, an antioxidant, and a blue colorant in specific ratios provides white laser marks. However, application of these techniques to a polyolefin resin composition fails to achieve sufficient whitening of laser marks.

[0007] A polyolefin resin composition for laser marking which comprises a polyolefin resin and a black pigment mainly comprising a metal oxide, which composition is capable of forming a white mark with improved visibility is also known (see JP-A-10-273537). However, since a black pigment comprising a metal oxide, which is more expensive than carbon black, has less coloring power than carbon black, it should be added in a larger amount, which leads to an increase of costs.

[0008] An object of the present invention is to provide a laser marking method for a molded article of a black-colored polyolefin resin composition by which a white mark having improved visibility in clear contrast against the black background can be formed.

[0009] This object has been achieved by the surprising finding that incorporation of carbon black having specific properties into a polyolefin resin makes the polyolefin resin capable of forming a white mark with improved visibility on its surface upon being irradiated with a laser beam.

[0010] The present invention provides a method for marking a polyolefin resin comprising irradiating a polyolefin resin composition containing 0.1 to 1.0 part by weight of carbon black having an average secondary particle size of not smaller than 150 nm per 100 parts by weight of the polyolefin resin composition with a YAG laser.

[0011] In the following, preferred embodiments the invention shall be illustrated.

[I] Polyolefin Resin Composition

[0012] The polyolefin resin composition which can be used in the present invention comprises a polyolefin resin and carbon black.

(1) Polyolefin Resin

[0013] The polyolefin resin used in the present invention is not particularly limited, and those generally used in polyolefin molded products can be used. Suitable polyolefin resins include ethylene resins, such as ethylene homopolymers and ethylene copolymers, e.g., ethylene- α -olefin (e.g., propylene) copolymers; propylene resins, such as propylene homopolymers and propylene- α -olefin random or block copolymers; and other α -olefin resins, such as polybutene-1, poly-4-methylbutene-1, poly-3-methylbutene-1, and poly-4-methylpentene-1. In addition, olefin copolymers comprising ethylene or propylene and copolymerizable monomers, such as unsaturated carboxylic acids or derivatives thereof

(e.g., acrylic acid, methyl methacrylate, ethyl acrylate, and maleic anhydride), aromatic unsaturated monomers (e.g., styrene and α -methylstyrene), vinyl esters (e.g., vinyl acetate and vinyl butyrate), vinylsilanes, etc.; and saponification products or metal-ionized products of these copolymers are also useful. These polyolefin resins can be used either individually or as a mixture thereof.

5 **[0014]** Preferred of them are ethylene resins, such as ethylene homopolymers and ethylene-propylene copolymers; and propylene resins, such as propylene homopolymers, propylene-ethylene random copolymers, propylene-ethylene block copolymers, and propylene-ethylene-butene copolymers. The ethylene content of the ethylene-propylene copolymer mainly comprising ethylene is about 60 to 95% by weight, and that of the propylene-ethylene random or block copolymer mainly comprising propylene is about 0.5 to 20% by weight.

10 **[0015]** Specific examples of suitable polyolefin resins are high-density polyethylene, medium-density polyethylene, low-density polyethylene, linear low-density polyethylene, branched low-density polyethylene, ethylene-propylene copolymers, propylene homopolymers, propylene-ethylene random copolymers, propylene-ethylene block copolymers, propylene-ethylene-butene copolymers, polybutene-1, poly-4-methylbutene-1, poly-3-methylbutene-1, and poly-4-methylpentene-1.

15 **[0016]** Particularly suitable polyolefin resins are propylene resins, such as propylene homopolymers and propylene-ethylene block or random copolymers. Propylene-ethylene block copolymers are especially preferred.

[0017] The polyolefin resin usually used in the present invention should preferably have a melt flow rate (MFR) of about 0.1 to 300 g/10min, more preferably about 1 to 150 g/10 min.

20 (2) Carbon Black

(a) Types

25 **[0018]** Carbon black is classified according to the process of its production into furnace black, channel black, thermal black, etc. and by raw material into acetylene black, ketjen black, oil black, gas black, etc. Any of these carbon black species can be used in the present invention. Acetylene black and ketjen black that have high electrical conductivity are particularly preferred.

(b) Particle Size (average primary particle size)

30 **[0019]** It is usually preferred for the carbon black used in the present invention to have an average primary particle size of not smaller than 30 nm, preferably from 40 to 150 nm, still preferably from 60 to 120 nm.

(c) Aggregate (average secondary particle size)

35 **[0020]** It is important for the fine carbon black particles having the above particle size to agglomerate to form secondary particles (aggregate) having a diameter of not smaller than 150 nm, preferably from 150 to 1,000 nm, still preferably from 200 to 500 nm. If carbon black having an average secondary particle size (average aggregate size) of smaller than 150 nm is used, the mark assumes a pale brown color having reduced visibility.

40 Measurement Method:

[0021] The primary and secondary particle sizes of carbon black can be measured as follows.

45 Measurement of Average Primary Particle Size:

[0022] The maximum diameters of selected particles are measured under an electron microscope to obtain a number average.

50 Measurement of Average Secondary Particle Size:

[0023] A frequency distribution curve of Stoke's equivalent diameter of secondary particles is prepared according to a centrifugal sedimentation method by means of a disc centrifuge manufactured by Joyes Loebel Co., G.B. and the 50% diameter of the curve is read.

55 (3) Compounding Amount

[0024] The carbon black is used in an amount of 0.1 to 1.0 part by weight, preferably 0.1 to 0.7 part by weight, partic-

ularly preferably 0.2 to 0.5 part by weight, per 100 parts by weight of the polyolefin resin composition. If the amount of the carbon black is less than 0.1 part, absorption of laser energy is insufficient for making marks. On the other hand, more than 1 part of carbon black absorbs excessive laser energy to generate excessive heat while being released, which will cause the resin to change its color. It follows that the marked area turns light brown due to scorching and is poorly visible.

(4) Additional ingredients

[0025] If desired, the polyolefin resin composition used in the present invention can contain inorganic fillers, such as talc and glass fiber.

(a) Inorganic Filler

Talc

[0026] Talc which can be used in the present invention preferably has an average particle size of not greater than 5 μm , more preferably from 0.5 to 3 μm , and a specific surface area of preferably not less than 3.5 m^2/g , more preferably from 3.5 to 6 m^2/g . The average particle size is obtained as a 50% diameter of a cumulative distribution curve determined according to a liquid phase sedimentation photo-extinction method by use of, e.g., Model CP manufactured by Shimadzu Corp. The specific surface area is measured by an air permeation method by use of, e.g., Model SS-100 (constant pressure type) manufactured by Shimadzu Corp. Talc to be used is prepared by, for example, dry grinding followed by dry classification.

[0027] For the purpose of improving dispersibility in the polyolefin resin, talc can be treated with various surface treating agents, such as organic titanate coupling agents, organic silane coupling agents, fatty acids, fatty acid metal salts, and fatty acid esters.

[0028] Talc is preferably added in an amount of 1 to 60 % by weight based on the polyolefin resin composition.

Glass Fiber

[0029] Glass fiber which can be used in the present invention includes glass fiber having been treated with silane coupling agents, such as aminosilanes (e.g., γ -aminopropyltriethoxysilane), epoxysilanes (e.g., γ -glycidoxypolytrimethoxysilane) and vinylsilanes (e.g., vinyltrichlorosilane).

[0030] Glass fiber having an average fiber diameter of 5 to 25 μm , particularly 8 to 15 μm , is preferred. If the fiber diameter is less than 5 μm , the productivity of strands as well as glass fiber-reinforced resin is considerably reduced and the production costs are increased. Glass fiber thicker than 25 μm tends to have a too broad distribution of residual fiber length, which deteriorates the appearance of the molded article, and the aspect ratio of glass fibers is diminished so that the degree of improvement in mechanical properties such as flexural modulus is reduced.

[0031] Glass fiber strands usually consist of 100 to 5,000 filaments, preferably 300 to 3,000 filaments, still preferably 500 to 2,000 filaments. As to the glass composition, alkali-free glass, such as E glass, is preferred. The glass fiber length is usually 2 to 20 mm, preferably 3 to 10 mm, still preferably 4 to 9 mm, particularly preferably 5 to 8 mm. Glass fiber is preferably used in an amount of 1 to 70% by weight, particularly 10 to 40% by weight, based on the polyolefin resin composition.

(b) Other additional ingredients

[0032] If desired, the polyolefin resin composition can further contain other additives as far as the effects of the present invention are not impaired. Useful additives include phenol type, sulfur type or phosphorus type antioxidants; benzophenone type or benzotriazole type weathering agents; nucleating agents, such as organoaluminum compounds, ultraviolet absorbers, organophosphorus compounds, and sorbitol compounds; and dispersants.

[II] Marking

(1) YAG laser

[0033] In the present invention it is essential to use a YAG laser for laser marking. A YAG laser is a solid state laser using an yttrium-aluminum-garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$) generally doped with about 1% Nd^{3+} and has near infrared output at a wavelength of 1.06 μm . It is capable of pulse oscillation on excitement with light of a xenon flash lamp and continuous oscillation on excitement with continuous light from a tungsten iodine lamp, a krypton arc lamp, etc.

[0034] If a carbon dioxide gas laser is used in place of a YAG laser, the surface of the molded article is only etched with little release of the irradiated pigment so that the resulting mark lacks clear contrast against the background and is not clearly visible.

5 (2) Irradiation

[0035] Laser marking on a molded article with a YAG laser can be carried out by imagewise scanning the molded article with a laser beam or irradiating the molded article with a laser beam through a mask. The output of the laser may be continuous or pulsating (normal or Q switch pulses).

10

[III] Use

[0036] The mark thus formed on the polyolefin resin, being white in color, is distinctly visible in clear contrast against the background. Therefore, the present invention is suitably applied to marking on various polyolefin molded articles, such as personal articles, domestic appliances, interior and exterior parts and engine parts of automobiles, with letters, patterns, and symbols.

15

[0037] The present invention will now be illustrated in greater detail with reference to Examples.

EXAMPLES 1 TO 4 AND COMPARATIVE EXAMPLES 1 TO 6

20

[0038] A molded article of the polyolefin resin composition shown in Table 1 below was marked with a YAG laser or a carbon dioxide gas laser under the following conditions, and the contrast between the mark and the background and the visibility of the mark were evaluated in accordance with the following methods. The results obtained are shown in Table 1.

25

YAG Laser Marking Conditions:

[0039]

30 Apparatus: Laser Marker Engine SL475H, manufactured by NEC Corporation
Wavelength: 1.06 μm (Nd:YAG laser)
Frequency: 10 Hz
Output: 6 W
Aperture: 2.0 mm
35 Scanning speed: 700 mm/sec

Carbon Dioxide Gas Laser Marking Conditions:

[0040]

40

Apparatus: Xymark™, manufactured by Lumonix • Pacific Co.
Wavelength: 10.6 μm
Output: 100 W
Scanning speed: 20 m/min (330 mm/sec)

45

Method of Evaluation of Laser Marking Properties:

1) Contrast

50 **[0041]** The lightness of the mark and the background was measured with MMP-300A manufactured by Nihon Den-shoku Kogyo K.K. to obtain a lightness difference (ΔL). The greater the difference, the clearer the contrast.

2) Visibility

55 **[0042]** The visibility of the mark was organoleptically evaluated with the naked eye and rated A (good), B (poor) or C (very poor).

TABLE 1

	Example				Comparative Example					
	1	2	3	4	1	2	3	4	5	6
Composition (part by wt.)										
Polypropylene resin	100	100	60	80	100	100	60	80	100	100
Carbon black A ¹⁾	0.3									
Carbon black B ²⁾		0.3	0.3	0.3					1.2	0.3
Carbon black C ³⁾					0.3					
Carbon black D ⁴⁾						0.3	0.3	0.3		
Talc			40				40			
Glass fiber				20				20		
Irradiation Laser	YAG	YAG	YAG	YAG	YAG	YAG	YAG	YAG	YAG	CO ₂
Results of Evaluation										
L value on background	14	16	24	17	13	11	19	13	8	16
L value on mark	50	56	48	52	43	38	32	37	30	20
Contrast (ΔL)	36	40	24	35	30	27	13	24	22	4
Visibility	A	A	A	A	B	B	C	B	B	C

Note:

- 1) Average secondary particle size: 181 nm; average particle size: 45 nm
- 2) Average secondary particle size: 245 nm; average particle size: 80 nm
- 3) Average secondary particle size: 100 nm; average particle size: 56 nm
- 4) Average secondary particle size: 50 nm; average particle size: 18 nm

[0043] The marking method of the present invention provides a polyolefin resin molded article having highly visible marks such as letters, patterns, and signals in clear contrast against the background.

Claims

1. A method for marking a polyolefin resin, which comprises irradiating with a YAG laser a polyolefin resin composition containing 0.1 to 1.0 part by weight of carbon black per 100 parts by weight of the polyolefin resin composition, wherein the carbon black has an average secondary particle size of not smaller than 150 nm.
2. The method for marking a polyolefin resin according to claim 1, wherein the carbon black has an average primary particle size of not smaller than 30 nm.
3. The method for marking a polyolefin resin according to claim 1 or 2, wherein the polyolefin resin is a propylene resin.



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EUROPEAN SEARCH REPORT

Application Number
EP 98 12 4418

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 710 570 A (QUANTUM CHEM CORP) 8 May 1996 * page 4, line 16 - line 17 * * page 6, line 29 - line 32 * * claims * ---	1-3	B41M5/26
X	EP 0 330 869 A (BAYER AG) 6 September 1989 * page 2, line 15 * * page 2, line 40 * * claim 2 * ---	1-3	
A,P	EP 0 827 980 A (DAICEL CHEM) 11 March 1998 * page 6, line 18 - line 20 * * page 8, line 38 - line 39 * * claim 1 * ---	1-3	
A	EP 0 413 664 A (CIBA GEIGY AG) 20 February 1991 * page 3, line 15 - line 18 * * page 3, line 45 - line 51 * * page 4, line 58 * -----	1-3	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.6) B41M
Place of search THE HAGUE		Date of completion of the search 19 March 1999	Examiner Martins Lopes, L
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 12 4418

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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19-03-1999

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 0710570	A	08-05-1996	NONE		
EP 0330869	A	06-09-1989	DE	3805056 A	31-08-1989
			JP	1254743 A	11-10-1989
			US	4959406 A	25-09-1990
EP 0827980	A	11-03-1998	CN	1176972 A	25-03-1998
			JP	11001596 A	06-01-1999
EP 0413664	A	20-02-1991	DE	59008746 D	27-04-1995
			JP	3106944 A	07-05-1991
			US	5075195 A	24-12-1991