

Use of polymer moulding compositions to bring about partial colour change by means of laser energy in order to produce very high-contrast optical information

5 The invention relates to the use of polymer moulding compositions to bring about partial colour change by means of laser energy, in particular in order to produce very high-contrast optical information, for example letters, numerals, patterns and/or pictures, etc.

10 The application of patterns, letters, numerals and/or pictures by means of laser markers to plastics mouldings for labelling and decorative purposes is becoming increasingly important. Laser marking affords a high degree of flexibility as to type, size and design of writing, irrespective of batch size, in addition to greater economy compared with conventional marking processes. The marking of electrical/electronic components, keytops, housings and identification documents is a classic laser marking application.

15 The following are the laser marking possibilities already known for plastics labelling.

1. Dark marks on a light background

20 A polymer matrix is coloured with light colorants - pigments or dyes. The energy delivered by the laser during laser marking is absorbed, thus causing partial carbonisation of the polymer matrix/the colorant. This results in a darkening of the light polymer matrix. This property is restricted to polymers which tend to carbonise.

25 The contrast ratios achievable in this way are inadequate for many fields of application. EP-A 0 190 997 describes the addition of colorants which change colour as a result of laser energy absorption. Thus polybutylene terephthalate is, for example, coloured red using iron oxide. Laser marking causes dark marks to appear on a red background. The contrast ratio has proved inadequate.

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2. Light markings on a dark background

35 Polymers, colorants or additives having a tendency to foam as a result of laser energy absorption have proved to be of value in this type of marking. The foaming causes light writing to appear on a dark background. The contrast ratios obtainable are inadequate for many fields of application.

The present invention relates to polymer moulding compositions which, on absorbing laser energy, give rise on a dark background to light marks which have a very high contrast ratio.

- 5 It has surprisingly been found that it is possible to obtain light marks on a dark background owing to laser energy absorption when very finely-divided carbon black is used in the polymer matrix. Different grey scales may be obtained by varying the laser energy.
- 10 The present invention provides the use of polymer moulding compositions comprising:
- A) from 99.97 to 50, preferably 99.97 to 70 parts by wt. of a polymer selected from the group of polyamides, polyolefins, graft polymers of the ABS type, polyacrylates, polymethacrylates or a mixture of polycarbonate, graft polymer of
 - 15 the ABS type and optionally copolymers,
 - B) from 0.03 to 0.5, preferably 0.03 to 0.3 parts by wt. of carbon black,
 - C) from 0 to 50 parts by wt. of reinforcements,
 - D) from 0 to 20 parts by wt. of elastomer modifying agent,
 - E) from 0 to 55 parts by wt. of flame retardants and
 - 20 F) from 0 to 2 parts by wt. of additives to aid processing

in order to produce light or grey marks on a dark background by means of a laser marker.

- 25 The present invention further provides the use of the coloured polymers to produce moulded objects which may be marked, labelled or provided with pictorial representations by means of a laser marker.

- 30 The polymer moulding compositions used according to the invention may be prepared on conventional commercial single and twin-screw extruders. The carbon black is dispensed in the form of pigment concentrate. Conventional commercial injection moulding machinery may be used to produce the mouldings.

- 35 Suitable thermoplastic polyamides according to the invention are generally aliphatic polyamides or polyamides with largely aliphatic segments. Polyamide 6 or polyamide 66 or copolyamides of polyamide 6 and diamines (preferably C₄-C₁₆, in particular C₄-C₈-alkylene diamines) and dicarboxylic acids (preferably C₄-C₁₂, in particular C₄-C₈-alkylene dicarboxylic acids) or polyamide 66 with a maximum comonomer proportion of 20 wt. %.

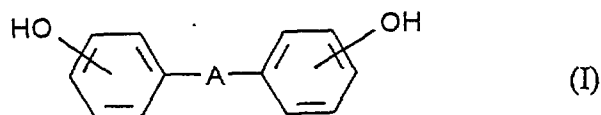
Polyolefins according to the invention are polymers of aliphatic unsaturated hydrocarbons such as, for example, ethylene, propylene, butylene or isobutylene, which are obtained by conventional processes, e.g. radical polymerisation, and have average molecular weights M_w (measured by gel chromatography) of between 5,000 and 3,000,000. Both high pressure polyolefins and low pressure polyolefins can be used. The unsaturated hydrocarbons may also be copolymerised with different vinyl monomers such as, for example, vinyl acetate, acrylic acid or acrylates in a known manner, wherein the maximum proportion of vinyl monomers is 30 wt.%, preferably up to 25 wt.%. Polyethylene and polypropylene are preferred.

The polymers of alkyl of (meth)acrylates used are preferably those of a C_1 - C_{18} -alkyl (meth)acrylate.

Acrylates which may be used are generally C_1 - C_{18} -alkyl esters such as methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec.-butyl, tert.-butyl, pentyl, hexyl, heptyl, octyl, 2-ethylhexyl, nonyl, decyl, lauryl or stearyl acrylate, preferably methyl acrylate, n-butyl acrylate and 2-ethylhexyl acrylate, and mixtures of these monomers.

Methacrylates which may be used are generally C_1 - C_{18} -alkyl esters such as methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec.-butyl, tert.-butyl, pentyl, hexyl, heptyl, octyl, 2-ethylhexyl, nonyl, decyl, lauryl or stearyl acrylate, preferably methyl methacrylate, and mixtures of these monomers.

Suitable thermoplastic aromatic polycarbonates according to the invention, mixed with graft polymers and optionally copolymers, are those based on diphenols of the formula I



in which A represents a single bond, a C_1 - C_5 -alkylene, C_2 - C_5 -alkylidene, or C_5 - C_6 -cycloalkylidene group, -S- or -SO₂-.

Suitable diphenols of the formula (I) are, for example, hydroquinone, resorcinol, 4,4'-dihydroxydiphenol, 2,2-bis-(4-hydroxyphenyl)-propane, 2,4-bis-(4-hydroxyphenyl)-2-methylbutane or 1,1-bis-(4-hydroxyphenyl)-cyclohexane.

Preferred diphenols of the formula (I) are 2,2-bis-(4-hydroxyphenyl)-propane and 1,1-bis-(4-hydroxyphenyl)-cyclohexane.

- 5 Diphenols of the formula (I) are either known from the literature or can be prepared using processes known from the literature.

Preparation of suitable polycarbonates according to the invention is known from the literature and may be performed, for example, with phosgene by the phase boundary
10 process or with phosgene by a process in a homogeneous phase (the so-called pyridine process), wherein the particular molecular weight required is produced in a known manner by using an appropriate amount of known chain terminators. Suitable chain terminators are, for example, monophenols such as phenol itself, p-cresol, p-tert.-butylphenol and p-isooctylphenol.

- 15 Suitable polycarbonates according to the invention have average molecular weights (M_w measured, for example, by ultracentrifuging or by measuring scattered light) of 10,000 to 200,000, preferably 20,000 to 80,000.

- 20 Suitable polycarbonates according to the invention are either homopolycarbonates or copolycarbonates.

Suitable polycarbonates according to the invention may be branched in a known manner, to be precise by incorporating 0.05 to 2.0 mol-%, with reference to the sum of the
25 diphenols used, of trifunctional or more than trifunctional compounds, for example those with three or more than three phenolic groups.

Graft polymers which may be used are those of the ABS type, either on their own or mixed with a polycarbonate:

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The graft polymers are a mixture of:

- 35 K.1.1 50 to 95, preferably 60 to 90, parts by wt. of styrene, α -methylstyrene, halogen or methyl ring-substituted styrene, C_1 - C_8 -alkyl methacrylate, in particular methyl methacrylate, C_1 - C_8 -alkyl acrylate, in particular methyl acrylate, or mixtures of these compounds and

- 5 K.1.2 5 to 50, preferably 10 to 40, parts by wt. of acrylonitrile, methacrylonitrile, C₁-C₈-alkyl methacrylates, in particular methyl methacrylate, C₁-C₈-alkyl acrylate, in particular methyl acrylate, maleic anhydride, C₁-C₄-alkyl or phenyl N-substituted maleic imides or mixtures of these compounds on
- K.2 5 to 95, preferably 20 to 70, parts by wt. of diene-based polymer with a glass transition temperature below -10°C.

- 10 Preferred graft substrates are polybutadiene, butadiene/styrene copolymers and acrylate rubbers. The graft substrate is particulate and generally has an average particle diameter (d_{50}) of 0.05 to 5 μm , preferably 0.1 to 0.8 μm .

15 The graft substrate may contain up to 50 wt.% of groups from other ethylenically unsaturated monomers such as styrene, acrylonitrile, esters of acrylic or methacrylic acid with 1 to 4 carbon atoms in the alcohol component (such as methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate), vinyl esters and/or vinyl ethers in addition to butadiene. The preferred graft substrate consists of pure polybutadiene.

- 20 Preferred graft polymers are, for instance, substrates K.2 such as polybutadienes, butadiene/styrene copolymers, i.e. copolymers of the type described in DE-OS 1 694 173 (= US-PS 3 564 077), grafted with styrene and/or acrylonitrile and/or alkyl (meth)acrylates; polybutadienes, butadiene/styrene or butadiene/acrylonitrile copolymers, polyisobutenes or polyisoprenes, grafted with ^{alkyl} acrylates or methacrylates, vinyl acetate, 25 acrylonitrile, styrene and/or alkylstyrenes, such as are described, for example in DE-OS 2 348 377 (= US-PS 3 919 353).

30 Since, during the grafting reaction, as is well known, the graft monomers are not absolutely completely grafted onto the graft substrate, graft polymers according to the invention are also understood to include those products which have been obtained by polymerising the graft monomers in the presence of the graft substrate.

35 The average particle size d_{50} is the diameter above and below which 50 wt.% of the particles respectively are present. It can be determined by means of ultracentrifuge measurements (W. Scholtan, H. Lange, Kolloid, Z. und Z. Polymere 250 (1972), 782-796).

A mixture of polycarbonate, graft polymer of the ABS type and optionally copolymer preferably consists of 50 to 96.5, in particular 60 to 96 parts by wt. of polycarbonate, up to 25 parts by wt., in particular 3 to 15 parts by wt. of graft polymer of the ABS type and optionally up to 40 parts by wt., in particular up to 20 parts by wt. of a copolymer of,

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50 to 95 wt.% of styrene, α -methylstyrene, ring-substituted styrene, methyl methacrylate or mixtures thereof, and

50 to 5 wt.% of (meth)acrylonitrile, methyl methacrylate or mixtures thereof.

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Very finely-divided carbon blacks are suitable as carbon black B) in the moulding compositions used according to the invention. The carbon black may be utilised as pure carbon black (particle size from 13 to 20 nm), in bead forms or as a concentrate, this being the case, for example, with Microlen Schwarz B[®] ex Ciba Geigy (Basle).

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Up to 50 wt-% of conventional commercial glass fibres and/or mineral fibres and/or mineral fillers such as kaolin, wollastonite, talcum or chalk are used as the reinforcement C) in the moulding compositions used according to the invention.

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Up to 20 wt-% conventional commercial EP(D)M (ethylene-propylene-diene) rubbers, grafted rubbers based on butadiene styrene acrylonitrile (see above), acrylate rubbers, polyurethanes or EVA copolymers having or not having functional coupling groups are used as the elastomer modifying agent D) according to the present invention.

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Up to 55 wt-% conventional commercial organic compounds or halogen compounds with synergists, or conventional commercial organic nitrogen compounds or organic/inorganic phosphorus compounds are used as the flame retardants E) (e.g. EP-A 345 522, DE-OS 43 28 656). Mineral flame retardants such as magnesium hydroxide or hydrated calcium magnesium carbonate may also be utilised.

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The additives E) to aid processing comprise up to 2 wt-% conventional commercial lubricants, stabilisers, mould release agents and nucleating agents.

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Conventional commercial laser systems, preferably Nd-YAG solid systems, may be used as energy sources. The wavelength may be between 193 nm and 10600 nm, preferably 1064 nm.

The moulding compositions used according to the invention may be utilised to apply optical information in the form of patterns, graphics, numerals, letters, written marks, pictures (for example passport pictures, portraits, photographs) etc. by means of laser energy, for example by means of laser markers.

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Photographic images may thus, for example, be transferred on to the moulding compositions used according to the invention.

Examples

The following products were used in the Examples:

- 5 Polyamide 6 = Durethan B 31SK[®] ex Bayer AG
Polyamide 6, glass-fibre reinforced (30%) = Durethan BKV 30 H[®] ex Bayer AG
Polyamide 6, glass-fibre reinforced (30%), with modified impact strength = Durethan BKV 130[®] ex Bayer AG
Polyamide 6, glass-fibre reinforced (30%) with reduced water absorption = Durethan RM
- 10 KU 2-2501[®] ex Bayer AG
Polyamide 6, glass-fibre and glass bead-reinforced = Durethan BG 30 X[®] ex Bayer AG
Partially aromatic polyamide = Durethan T 40[®] ex Bayer AG
ABS = Novodur P2H[®] ex Bayer AG
ABS + polycarbonate, with flame retardant = Bayblend FR 90[®]
- 15 PMMA = Plexiglas 7N[®] ex Röhm GmbH Darmstadt
Microlen Schwarz B[®] carbon black/Ciba Geigy

- The dyes were premixed with the granules and extruded and granulated in a twin-screw compounder. The granules obtained were injection-moulded to form slabs on an Arburg injection moulding machine and marked using a FOBALLAS ND-YAG laser.
- 20

White or grey marks, depending on laser beam energy intensity, are produced on a black background. All the written marks and symbols are distinguished by very high degrees of contrast and different grey scales.

Table 1

Example		1	2	3	4	5	6
Durethan B 31 SK		99.8					
Durethan T 40	%		99.8				
Novodur P 2H	%			99.8			
Bayblend FR 90	%				98.8		
Plexiglas 7N	%					99.8	
Hostalen PP	%						99.8
Microten Schwarz B	%	0.2	0.2	0.2	0.2	0.2	0.2
Contrast		v.g.	v.g.	v.g.	v.g.	v.g.	v.g.

v.g. = very good

Table 2

Example		7	8	9	10
Durethan BKV 30 H		99.7			
Durethan BKV 130	%		99.6		
Durethan RM 2501	%			99.8	
Durethan BG 30 X	%				99.7
Microten Schwarz B*	%	0.3	0.4	0.2	0.3
Contrast		v.g.	v.g.	v.g.	v.g.

* 50%-concentrate

v.g. = very good

Claims

THIS SHEET HAS BEEN REPLACED

1. Use of polymer moulding compositions comprising
 - 5 A) from 99.97 to 50 parts by wt. of a polymer selected from the group of polyamides, polyolefins, graft polymers of the ABS type; polyacrylates, polymethacrylates or a mixture of polycarbonate, graft polymer of the ABS type and optionally copolymers,
 - B) from 0.03 to 0.5 parts by wt. of carbon black,
 - 10 C) from 0 to 50 parts by wt. of reinforcements,
 - D) from 0 to 20 parts by wt. of elastomer modifying agent,
 - E) from 0 to 55 parts by wt. of flame retardants and
 - F) from 0 to 2 parts by wt. of additives to aid processing
- 15 in order to produce light or grey marks on a dark background by means of laser marking.
2. Use according to Claim 1, characterised in that they contain polyamides as polymers.
- 20 3. Use according to Claim 1, wherein 0.03 to 3 parts by wt. of carbon black are used.
4. Use according to Claim 1, characterised in that they contain as reinforcements from 0 to 50 parts by wt. of glass fibres, mineral fibres or mineral fillers.
- 25 5. Use according to Claim 1, characterised in that they contain as the elastomer modifying agent from 0 to 40 parts by wt. of EPM, EPDM, acrylate rubbers or EVA copolymers.
- 30 6. Use according to Claim 1, characterised in that they contain as flame retardants from 0 to 55 parts by wt. of conventional commercial flame retardants based on organic compounds of halogen, nitrogen or phosphorus or magnesium hydroxide or hydrated calcium magnesium carbonate.
- 35 7. Use according to Claim 1, characterised in that they contain as additives to aid processing from 0 to 2% lubricants, stabilisers, mould release agents and nucleating agents.





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8. Use according to Claim 1 in order to apply optical information by means of laser energy.
9. Pictures according to Claims 1 and 8.
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10. Passport picture, portrait, photograph transferred according to Claim 9.