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(54) **Shaped article with a marking on a thermoplastic substrate and a process for the manufacture of the shaped article.**

(57) Shaped article with a marking on a thermoplastic substrate, which marking is made by foaming the thermoplastic synthetic material by means of high-energy irradiation, the thermoplastic synthetic material containing an agent which has caused crosslinking at the spot where the foaming of the thermoplastic synthetic material has occurred. The marking has good abrasion resistance.

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The invention relates to a shaped article with a marking on a thermoplastic substrate, which marking is made by foaming the thermoplastic by means of high-energy irradiation.

The invention also relates to a process for the manufacture of the shaped article with a marking on a thermoplastic substrate.

5 Such shaped articles are known from EP-A-469982. From this patent specification it is known to make a marking by subjecting a thermoplastic to high-energy irradiation, as a result of which moisture or air present expands and forms bubbles, causing local foaming of the material.

By the term 'marking' in the present application is understood a pattern containing information, such as an image, an emblem, a logo, a text consisting of letters and/or digits, a code, such as a bar code etc., or a
10 pattern with an aesthetic or decorative function.

Examples of shaped articles bearing a marking are housings of electronic or electrical equipment, keys, buttons, publicity signs, nameplates, company name signs, etc. Other examples are calibrated containers, such as measuring beakers, syringes and coffemaker reservoirs.

15 Increasingly, such markings are applied by subjecting the shaped article to high-energy irradiation in the pattern of the marking, for instance by means of a laser beam, causing the synthetic material to foam.

An advantage of such a marking is that it can be applied very accurately on the desired spot. A further advantage is that the shaped articles can be manufactured in series in the known manner without application of a marking, while subsequently any desired marking, different for each individual shaped article, can be applied. An additional advantage of such a marking is that it can be applied simply on
20 shaped articles with curved surfaces.

A drawback of the known shaped article with the marking is that the marking is not abrasion resistant. Fast abrasion of the marking on for instance keys or buttons may result in illegibility, which may be the cause of incorrect setting of equipments and, in consequence, unsafe situations.

The aim of the invention is to provide a shaped article which does not have this drawback.

25 This aim is achieved in that the thermoplastic synthetic material contains an agent which, due to the action of the high-energy irradiation, has caused crosslinking at the spot where the foaming of the thermoplastic synthetic material has occurred.

A further advantage of the shaped article according to the invention is that the marking possesses good resistance to solvents.

30 The shaped article may in principle contain any thermoplastic which can be foamed by means of high-energy irradiation in order to serve as substrate for the marking. Preferably, ABS (acrylonitrile-butadiene-styrene copolymer) is used. Acrylonitrile-butadiene-styrene copolymer is described for instance in EP-A-104695, in which it is described as a polymer composition consisting of:

- 35 A. 5-100 wt% of one or more graft copolymers obtained by polymerizing 10-90 parts by weight of a monomer mixture comprising
 - 20-40 wt% of an acrylic compound,
 - 60-80 wt% of a vinyl aromatic compound, and
 - 0-20 wt% of one or more unsaturated compounds, in the presence of 10-90 part by weight of rubber,
- B. 0-95 wt% of one or more copolymers obtained by polymerizing
 - 40 60-80 wt% of vinyl aromatic compounds,
 - 20-40 wt% of acrylic compounds,
 - 0-20 wt% of one or more unsaturated compounds.

Suitable acrylic compounds are acrylonitrile, methacrylonitrile alkyl acrylate, alkyl acrylate or mixtures thereof.

45 Suitable vinyl aromatic compounds are styrene and substituted styrene compounds like alpha-methylstyrene, p-vinyltoluene or mixtures thereof.

The rubber content of the graft copolymer is preferably between 15 and 50 wt% relative to the graft copolymer.

50 Suitable rubbers are butadiene rubbers like polybutadiene, butadiene-styrene, butadiene-acrylonitrile or butadiene-acrylate rubber.

Other examples of thermoplastic synthetic materials which foam when exposed to high-energy irradiation are polypropene, polyethene, polyamide, polyesters, polycarbonate, thermoplastic elastomers or mixtures of the above-mentioned polymers like acrylonitrile-butadiene-styrene copolymer with for example polyamide, polycarbonate or copolymers of styrene and maleic anhydride.

55 High-energy irradiation of a surface is preferably understood to be irradiation of a surface with a laser beam.

The agent which brings about the crosslinking does not produce or hardly produces this effect at the processing temperature of the thermoplastic synthetic material, but mainly does so under conditions at

which the shaped article is subjected to high-energy irradiation according to the invention, which is accompanied by foaming of the thermoplastic synthetic material. This means that the crosslinking by means of the agent can be brought about by the effect of the very high temperature which occurs during the irradiation or by the effect of UV light which can be present in the high-energy rays used.

5 A preferred embodiment of the invention relates to the shaped article with the marking on a thermoplastic substrate containing an agent which by the effect of high-energy irradiation brings about the crosslinking. An advantage of this embodiment is that only a minor quantity of the agent need be present in the thermoplastic synthetic material, so that the mechanical properties of the thermoplastic synthetic material are preserved better. The agent is preferably present in the thermoplastic synthetic material in an amount of 0.01 to 10 parts by weight per 100 parts by weight of the thermoplastic synthetic material. The agent preferably is a radical generator. Suitable radical generators are for instance compounds which form carbon radicals, such as 2,3-dimethyl-2,3-diphenylbutane.

10 Another preferred embodiment of the invention relates to the shaped article with the marking on a thermoplastic substrate containing an agent which by the effect of high-energy irradiation forms a network within itself. Preferably, such a network extends in the form of a co-continuous phase into the foamed thermoplastic synthetic material. The agent is preferably present in the thermoplastic synthetic material in an amount of 0.01 to 20 parts by weight per 100 parts by weight of the thermoplastic synthetic material. The agent is preferably composed of between 1 and 19 parts by weight of polypropylene glycol per 100 parts by weight of the thermoplastic synthetic material and between 1 and 19 parts by weight of caprolactone polymer per 100 parts by weight of the thermoplastic synthetic material, the sum of the parts by weight of polypropylene glycol and caprolactone polymer being 2-20. In this way it is ensured that the laser marking according to the invention possesses good abrasion resistance, while preserving the mechanical properties of the thermoplastic synthetic material. If the agent is melamine, the particles preferably have a diameter of $< 10 \mu$.

25 The shaped article according to the invention, without the marking applied onto it, can be manufactured in accordance with the known processes and irradiated with high-energy radiation in a pattern corresponding to the shape of the marking.

30 Thus it is possible for instance to mix a granulate or a powder of a thermoplastic polymer with the crosslinking agent in a tumbling barrel or a batch mixer provided with stirring gear and subsequently melt the mixture in a kneader, such as a single-screw extruder or a batch kneader. After the agent has been dispersed in the melt, the mixture thus obtained can be granulated and cooled. Using one of the known processes, the granulate can be melted down again and used for manufacture of the shaped articles according to the invention. For instance, by means of an extruder or an injection shaped article machine the granulate can be transformed into a shaped article fully consisting of thermoplastic synthetic material. Next, using one of the known processes, a marking can be made on the surface of the shaped article by means of a laser beam.

The shaped article according to the invention comes in many variants. For instance, the shaped article may be made entirely of the thermoplastic synthetic material. It is also possible to apply a coating of the thermoplastic synthetic material onto a shaped article made of metal or a ceramic material.

40 The invention will now be elucidated by means of the following non-restrictive examples.

EXAMPLES

Comparative experiment A

45 A mixture of 99.3 parts by weight of acrylonitrile-butadiene-styrene copolymer (Ronfalin®) SFA-34, from DSM, of the Netherlands), 0.6 part by weight of carbon black (Black Pearls® 880, from CABOT, of the Netherlands) and 0.1 part by weight of titanium dioxide (Tiofine® R41, from TIOFINE, of the Netherlands) was extruded at a temperature of 260 °C. The granulate obtained in this way was injection moulded to black sheets at a temperature of 240 °C with an ARBURG Allrounder® (320-90-750) injection shaped article machine.

50 A part of the surface of the sheets was then irradiated with a laser beam from an SHG Nd:YAG Q-switch laser, type Haas Laser® 6411 Engraving System (from Haas Laser, Germany). The pulse time was 110 nanoseconds, the wavelength was 532 nanometres, at a high radiation energy density (about 20 Joule/cm²). The marking obtained in this way had a white/grey colour.

55 The abrasion resistance of this marking was tested by means of the device used in the Taber abraser test (ASTM D4060: 'Standard Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser'). The abrasion resistance was qualified as 'good', 'reasonable' or 'poor'.

The impact resistance of the marked material was measured in kJ/m² according to DIN 51320 (Izod impact test, notched).

The abrasion resistance and impact resistance values found are given in table 1.

5 Example I

Comparative experiment A was repeated, but now using 94.3 parts by weight of acrylonitrile-butadiene-styrene copolymer (Ronfalin® SFA-34, from DSM, of the Netherlands), 0.6 part by weight of carbon black (Black Pearls® 880, from CABOT, of the Netherlands) and 0.1 part by weight of titanium dioxide (Tiofine® R41, from TIOFINE, of the Netherlands), 2.5 parts by weight of PPG 2000 (polypropylene glycol 2000, from Hofag Chemical Corporation, of the USA) and 2.5 parts by weight of CAPA® 656 (from Interlox Chemicals Ltd., of the UK).

The abrasion resistance and impact resistance values found are given in table 1.

15 Example II

Example I was repeated, but now PPG 2000 and CAPA® 656 were replaced by 5 parts by weight of Perkadox® 30 (from AKZO Chemicals Division, of the Netherlands).

The results are given in table 1.

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Example III

Example II was repeated, but now Perkadox® 30 was replaced by 5 parts by weight of CP-FLAM® (from Nordmann Rassmann GmbH & Co., of Germany).

25

The results are given in table 1.

Example IV

Example II was repeated, but now Perkadox® 30 was replaced by 5 parts by weight of Spinflam® MF83 (from Himont, of Italy).

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The results are given in table 1.

Example V

Example II was repeated, but now Perkadox® 30 was replaced by 5 parts by weight of Ceepree® C-200 (from ICI Chemicals & Polymers Ltd., of the UK).

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The results are given in table 1.

Example VI

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Example II was repeated, but now Perkadox® 30 was replaced by 5 parts by weight of Ceepree® Microfine (from ICI Chemicals & Polymers Ltd., of the UK).

The results are given in table 1.

45 Example VII

Example II was repeated, but now Perkadox® 30 was replaced by 2 parts by weight of pentaerythritol (Qual. R., pulverized, from Degussa, of Germany) and 3 parts by weight of Exolyt® 422 (ammonium polyphosphate, from Hoechst Holland n.v., of the Netherlands).

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The results are given in table 1.

Example VIII

Example II was repeated, but now Perkadox® 30 was replaced by 2 parts by weight of Dures 22091 (novolac, from Occidental Chemical, of Belgium) and 3 parts by weight of Exolyt® 422 (ammonium polyphosphate, from Hoechst Holland n.v., of the Netherlands).

55

The results are given in table 1.

Example IX

Example II was repeated, but now Perkadox® 30 was replaced by 1 part by weight of Madurit® MW909 (cured melamine-formaldehyde resin, from Hoechst Holland n.v., of the Netherlands) and 94.3 parts by weight of ABS were replaced by 98.3 parts by weight of ABS.

The results are given in table 1.

Example X

Example II was repeated, but now Perkadox® 30 was replaced by 3 parts by weight of Melamine Superfine®, D90 < 5 µm (from DSM, of the Netherlands) and 94.3 parts by weight of ABS were replaced by 96.3 parts by weight of ABS.

The results are given in table 1.

Example XI

Example II was repeated, but now Perkadox® 30 was replaced by 2 parts by weight of trishydroxyethyl isocyanurate (from BASF AG, of Germany) and 3 parts by weight of Exolyt® 422 (ammonium polyphosphate, from Hoechst Holland n.v., of the Netherlands).

The results are given in table 1.

Example XII

Example II was repeated, but now Perkadox® 30 was replaced by 3 parts by weight of Melamine Superfine®, D90 < 100 µm (from DSM, of the Netherlands) and 94.3 parts by weight of ABS were replaced by 96.3 parts by weight of ABS.

The results are given in table 1.

TABLE 1

Results of abrasion resistance and impact resistance tests of comparative experiment A and examples I-XII			
Abrasion resistance		Impact resistance	Izod (kJ/m ²)
Comparative experiment A		poor	21
Example	I	good	21
	II	good	20
	III	good	10
	IV	good	2
	V	good	8
	VI	good	10
	VII	good	10
	VIII	good	8
	IX	reasonable	10
	X	good	15
	XI	good	9
	XII	good	5

Claims

1. Shaped article with a marking on a thermoplastic substrate, which marking is made by foaming the thermoplastic by means of high-energy irradiation, characterized in that the thermoplastic synthetic material contains an agent which, due to the action of the high-energy irradiation, has caused crosslinking at the spot where the foaming of the thermoplastic synthetic material has occurred.
2. Shaped article according to claim 1, characterized in that ABS (acrylonitrile-butadiene-styrene copolymer) is used as thermoplastic synthetic material.

3. Shaped article according to claim 1, characterized in that the agent has brought about the crosslinking by crosslinking of the thermoplastic synthetic material.
- 5 4. Shaped article according to claim 3, characterized in that the agent is present in the thermoplastic synthetic material in a quantity of 0.01 to 10 parts by weight per 100 parts by weight of the thermoplastic synthetic material.
5. Shaped article according to claims 3 and 4, characterized in that the agent is a radical generator.
- 10 6. Shaped article according to claim 5, characterized in that the agent is 2,3-dimethyl-2,3-diphenylbutane.
7. Shaped article according to claim 1, characterized in that the agent has brought about the crosslinking by forming a network within itself.
- 15 8. Shaped article according to claim 7, characterized in that the agent is present in the thermoplastic synthetic material in a quantity of 0.1 to 20 parts by weight per 100 parts by weight of the thermoplastic synthetic material.
- 20 9. Shaped article according to claim 7, characterized in that between 1 and 19 parts by weight of polypropylene glycol per 100 parts by weight of the thermoplastic synthetic material and between 1 and 19 parts by weight of caprolactone polymer per 100 parts by weight of the thermoplastic synthetic material are present in the thermoplastic synthetic material, the sum of the parts by weight of polypropylene glycol and caprolactone polymer being 2-20.
- 25 10. Shaped article according to claims 7 and 8, characterized in that the agent is melamine and the melamine particles have a diameter of $< 10 \mu$.
- 30 11. Process for the manufacture of a shaped article with a marking on a thermoplastic substrate, involving the addition of an agent which, due to the action of high-energy irradiation, causes crosslinking at the spot where the foaming of the thermoplastic synthetic material occurs.

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EUROPEAN SEARCH REPORT

Application Number
EP 95 20 1142

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)
D,A	EP-A-0 469 982 (SONY) 5 February 1992 * the whole document * ---	1,2,11	B41M1/30
P,A	WO-A-94 12352 (DSM) 9 June 1994 * page 2, line 26 - page 2, line 31; claims 1,4,5,14,17,30,33 * ---	1,2,11	
A	& NL-A-9 202 096 (DSM) 1 April 1994 ---		
A	EP-A-0 566 312 (GE PLASTICS JAPAN) 20 October 1993 * page 3, line 5 - page 3, line 17 * * page 3, line 37 - page 3, line 51; claim 1 * ---	1,2,11	
A	PATENT ABSTRACTS OF JAPAN vol. 10 no. 67 (C-333) ,15 March 1986 & JP-A-60 206845 (KANEKAFUCHI KAGAKU) 18 October 1985, * abstract * ---	2-6	
A	EP-A-0 430 092 (NIPPON OIL) 5 June 1991 * claims 1,6,9,10 * -----	1-6,11	TECHNICAL FIELDS SEARCHED (Int.Cl.6) B29C B41M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 August 1995	Examiner Labeeuw, R
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			