Opaquely colored, infrared-reflective plastics molding composition

Field of the invention

The invention relates to opaquely colored, infrared-reflective poly(meth)acrylate molding compositions which can be applied as IR-barrier layer to further plastics moldings.

Prior art

Because PMMA has very good properties, the corresponding molding compositions are, inter alia, processed to give coextruded layers, or processed as outer layers of in-mould-coated parts. These layers serve as outer layer inter alia of foils, of sheets, of profiles and of pipes, of which the main component or backing layer is composed to some extent of other plastics. These plastics, e.g. PVC, polystyrene, polycarbonate, ABS and ASA, have further important properties, such as impact resistance and/or low price.

Examples of applications for these coextrudates or in-mould-coated articles are construction applications, such as drainpipes and window frames; automobile applications, such as roof modules, external and internal protective coverings (panels), spoilers and mirror housings; household and sports applications, e.g. protective coverings on tools, external panels for boats and ski foils.

It is known that opaquely colored poly(meth)acrylate (PMMA) molding compositions can be used for weathering-protection of plastics moldings composed of, for example, polyvinyl chloride (PVC).

The coated plastics molding is then provided with a

colorant, such as TiO_2, which reflects the IR radiation at the boundary layer of the two plastics moldings and thus prevents excessive heating of the article.

DE 27 19 170 (Dynamit Nobel) describes a process for protection of PVC layers from the effects of sunlight via a layer which has been durably applied to the PVC layer and which has been equipped not only with UV stabilizers but also with IR reflectors. The IR reflectors used comprise bleaching chromate, molybdate red, molybdate orange, chromium oxide green, antimony sulfide, cadmium sulfoselenide, cadmium sulfide, anthraquinone black pigment, anthraquinone dark blue pigment, monoazo pigment or phthalocyanines. Some of these pigments are no longer approved. A PMMA not specified in any further detail is described as material for the outer layer. DE 26 05 325 (Dynamit Nobel) likewise describes a process for protection of PVC surfaces, and the protective layer applied is colored sufficiently opaquely to achieve maximum reflectance in the IR region and minimum permeability in the UV region. The objective is achieved via the use of at least one IR-reflective black pigment or IR-reflective color pigment. For the darker color pigments, no predominantly IR-absorptive pigments are used. The pigment used in the examples comprises titanium dioxide or anthraquinone black in combination with a UV absorber.

WO 00/24817 (Ferro) describes corundum-hematite structures into which oxides of aluminum, of antimony, of bismuth, of boron, of chromium, of cobalt, of gallium, of indium, of iron, of lanthanum, of lithium, of magnesium, of manganese, of molybdenum, of neodymium, of nickel, of niobium, of silicon, or of tin have been bound.

Object

The desire for dark-colored plastic moldings for outdoor applications requires solution of some problems:

- the plastics molding must be weather-resistant - irrespective of the coloring
- there must be good and durable adhesion between outer layer and plastics molding to be coated
- heating of the plastics moldings via direct sunlight may not exceed a permissible extent. The amount of heating may not become so great that the article expands unacceptably and temperatures above the glass transition temperature of the molding are reached. By way of example, this can cause irreversible warping of a window frame and prevent its subsequent opening
- the color pigments used must themselves likewise be weathering-resistant, and also toxicologically non-hazardous and inexpensive.

Further objects achieved by the inventive formulation are:

- the colored molding compositions are to have good processibility
- the formulation is to be stable at the processing temperatures.

Achievement of object

If various infrared-reflective, inorganic color pigments are used in a PMMA molding composition, these molding compositions can be used to produce dark-colored plastics moldings, and other plastics moldings can be coated with the abovementioned PMMA molding compositions, these having a markedly lower heating rate on insolation than moldings which are composed of

conventionally dark-colored PMMA or have been coated with the same.

It has now been found that use of pigments of the following classes

CAS Number	C.I. Name	C.I. Number	Chemical name
68186-85-6	C.I. Pigment Green 50	C.I. 77377	Cobalt titanite green spinel
1308-38-9	C.I. Pigment Green 17	C.I. 77288	Chromium oxide
109414-04-2	C.I. Pigment Brown 29		Chromium iron oxide
68187-09-7	C.I. Pigment Brown 35	C.I. 77501	Iron chromite brown spinel
71631-15-7	C.I. Pigment Black 30	C.I. 77504	Nickel iron chromite black spinel

C.I. nomenclature according to Colour Index, The Society of Dyers and Colourists (SDC)

in PMMA molding compositions permits preparation of opaquely dark-colored molding compositions without excessive heating in sunlight of the plastics moldings equipped therewith or of moldings produced with these materials. The property "dark" can be defined via the L* value according to DIN 6174 (01/1979): Farbmetrische Bestimmung von Farbabständen bei Körperfarben nach der CieLab-formel [Colourimetric determination of colour differences for mass tone colours by the CieLab formula]. The CieLab L* value for the opaquely dark-colored molding compositions is below 51, preferably below 41 and very particularly preferably below 31.

The amounts of the pigments or of their mixtures incorporated into the molding compositions are from 0.05 to 5.0% by weight, preferably from 0.075 to 3.0% by weight and very particularly preferably from 0.1 to 2% by weight.

Further colorants which are suitable for coloring of

PMMA molding compositions may be used additionally to vary the colour. These colorants may be either IR-reflective - e.g. titanium dioxide - or else non-IR-reflective. The proportion of these additional colorants may be from 0 to 3.0%, preferably from 0 to 2.5% by weight and particularly preferably from 0 to 2.0% by weight, based on the molding composition.

Dark colour shades are

- brown
- gray
- green and
- black

and mixed shades are also possible.

Examples

The molding composition Plexiglas® 7N is used as PMMA component. It is available commercially from Röhm GmbH & Co. KG.

The molding compositions of the present invention comprise poly(meth)acrylates. The expression (meth)acrylates encompasses methacrylates and acrylates and also mixtures of the two.

Poly(meth)acrylates are known to the person skilled in the art. These polymers are generally obtained via free-radical polymerization of mixtures which comprise (meth)acrylates.

These monomers are well known. Among these monomers are, inter alia, (meth)acrylates which derive from saturated alcohols, e.g. methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, n-butyl (meth)-acrylate, tert-butyl (meth)acrylate, pentyl (meth)acrylate and 2-ethylhexyl (meth)acrylate;

(meth)acrylates which derive from unsaturated alcohols, e.g. oleyl (meth)acrylate, 2-propynyl (meth)acrylate, allyl (meth)acrylate, vinyl (meth)acrylate;

aryl (meth)acrylates, such as benzyl (meth)acrylate or phenyl (meth)acrylate, where each of the aryl radicals may be unsubstituted or have up to four substituents;

cycloalkyl (meth)acrylates, such as 3-vinylcyclohexyl (meth)acrylate, bornyl (meth)acrylate;

hydroxyalkyl (meth)acrylates, such as
3-hydroxypropyl (meth)acrylate,
3,4-dihydroxybutyl (meth)acrylate,
2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)-acrylate;

glycol di(meth)acrylates, such as 1,4-butanediol di(meth)acrylate,

(meth)acrylates of ether alcohols, such as tetrahydrofurfuryl (meth)acrylate, vinyloxyethoxyethyl (meth)acrylate;

amides and nitriles of (meth)acrylic acid, such as
N-(3-dimethylaminopropyl)(meth)acrylamide,
N-(diethylphosphono)(meth)acrylamide,
1-methacryloylamido-2-methyl-2-propanol;

sulfur-containing methacrylates, such as
ethylsulfinylethyl (meth)acrylate,
4-thiocyanatobutyl (meth)acrylate,
ethylsulfonylethyl (meth)acrylate,
thiocyanatomethyl (meth)acrylate,
methylsulfinylmethyl (meth)acrylate,
bis((meth)acryloyloxyethyl) sulfide;

multifunctional (meth)acrylates, such as trimethyloylpropane tri(meth)acrylate.

The formulations to be polymerized may also comprise, alongside the (meth)acrylates set out above, further unsaturated monomers copolymerizable with the abovementioned (meth)acrylates. The amount generally used of these compounds is from 0 to 50% by weight, preferably from 0 to 40% by weight and particularly preferably from 0 to 20% by weight, based on the weight

of the monomers, and the comonomers here may be used individually or in the form of a mixture.

Among these are, inter alia, 1-alkenes, such as 1-hexene, 1-heptene; branched alkenes, such as vinylcyclohexane, 3,3-dimethyl-1-propene, 3-methyl-1-diisobutylene, 4-methyl-1-pentene;

acrylonitrile; vinyl esters, such as vinyl acetate; styrene, substituted styrenes having one alkyl substituent in the side chain, e.g. α-methylstyrene and α-ethylstyrene, substituted styrenes having one alkyl substituent on the ring, e.g. vinyltoluene and p-methylstyrene, halogenated styrenes, such as monochlorostyrenes, dichlorostyrenes, tribromostyrenes, and tetrabromostyrenes;
heterocyclic vinyl compounds, such as 2-vinylpyridine, 3-vinylpyridine, 2-methyl-5-vinylpyridine, 3-ethyl-4-vinylpyridine, 2,3-dimethyl-5-vinylpyridine, vinylpyrimidine, vinylpiperidine, 9-vinylcarbazole, 3-vinylcarbazole, 4-vinylcarbazole, 1-vinylimidazole, 2-methyl-1-vinylimidazole, N-vinylpyrrolidone, 2-vinylpyrrolidone, N-vinylpyrrolidine, 3-vinylpyrrolidine, N-vinylcaprolactam, N-vinylbutyrolactam, vinyloxolane, vinylfuran, vinylthiophene, vinylthiolane, vinylthiazoles, and hydrogenated vinylthiazoles, vinyloxazoles and hydrogenated vinyloxazoles;

vinyl and isoprenyl ethers;
maleic acid derivatives, such as maleic anhydride, methylmaleic anhydride, maleimide, methylmaleimide; and dienes, such as divinylbenzene.

The polymerization is generally initiated by known free-radical initiators. Examples of preferred initiators are the azo initiators well known to persons skilled in the art, e.g. AIBN and 1,1-azobis(cyclohexanecarbonitrile), and also peroxy compounds, such as methyl ethyl ketone peroxide, acetylacetone peroxide,

dilauryl peroxide, tert-butyl per-2-ethylhexanoate, ketone peroxide, methyl isobutyl ketone peroxide, cyclohexanone peroxide, dibenzoyl peroxide, tert-butyl peroxybenzoate, tert-butylperoxy isopropyl carbonate, 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane, tert-butylperoxy 2-ethylhexanoate, tert-butylperoxy 3,5,5-trimethylhexanoate, dicumyl peroxide, 1,1-bis(tert-butylperoxy)cyclohexane, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, cumyl hydroperoxide, tert-butyl hydroperoxide, bis(4-tert-butylcyclohexyl) peroxydicarbonate, mixtures of two or more of the abovementioned compounds with one another, and also mixtures of the abovementioned compounds with compounds not mentioned which can likewise form free radicals.

The amount often used of these compounds is from 0.1 to 10% by weight, preferably from 0.5 to 3% by weight, based on the total weight of the monomers.

Preferred poly(meth)acrylates are obtainable via polymerization of mixtures which comprise at least 20% by weight, in particular at least 60% by weight and particularly preferably at least 80% by weight, of methyl methacrylate, based in each case on the total weight of the monomers to be polymerized.

Use may be made here of various poly(meth)acrylates which differ, for example, in molecular weight or in monomer formulation.

The molding compositions may moreover comprise further polymers in order to modify properties. Among these are, inter alia, polyacrylonitriles, polystyrenes, polyethers, polyesters, polycarbonates and polyvinyl chlorides. These polymers may be used individually or in the form of a mixture, and it is also possible here to add, to the molding compositions, copolymers which are derivable from the abovementioned polymers. Among

these are, in particular, styrene-acrylonitrile polymers (SANs), the amount of which added to the molding compositions is preferably up to 45% by weight.

Particularly preferred styrene-acrylonitrile polymers may be obtained via polymerization of mixtures composed of
from 70 to 92% by weight of styrene
from 8 to 30% by weight of acrylonitrile
from 0 to 22% by weight of further comonomers, based in each case on the total weight of the monomers to be polymerized.

In particular embodiments, the proportion of the poly(meth)acrylates is at least 20% by weight, preferably at least 60% by weight and particularly preferably at least 80% by weight.

Particularly preferred molding compositions of this type are available commercially with the trade mark PLEXIGLAS® from Röhm GmbH & Co. KG.

The weight-average molecular weight $\overline{M_w}$ of the homo- and/or copolymers to be used according to the invention as matrix polymers can vary widely, the molecular weight usually being matched to the intended use and the method of processing of the molding composition. However, it is generally in the range from 20 000 to 1 000 000 g/mol, preferably from 50 000 to 500 000 g/mol and particularly preferably from 80 000 to 300 000 g/mol, with no intended resultant restriction.

The following substances were used as colorants:

- Cromophtal Brown 5R, Ciba Specialty Chemicals
- Sandoplast Red Violet R, Clariant
- Thermoplast Blue 684, BASF
- Ultramarine Blue 31, Nubiola

- Bayferrox 180 M, Bayer
- Bayferrox 645 T, Bayer
- Microlith Green GA, Ciba speciality Chemicals
- Pigment black FW1, Degussa
- PK 24-10204, Ferro
- PK 10456, Ferro
- Titanium dioxide CL 2220, Kronos

Coloring of molding compositions:

Colorants and molding compositions were homogenized by roll-milling. The formulations for the individual examples have been documented in Annex 1. A Plexiglas® GS White 003 sheet (40 mm * 21 mm) of thickness 3 mm was also used (see testing of molding compositions). 1.5% of titanium dioxide Cl 2220 is present as colorant, IR-reflective pigment in the cast sheet composed of PMMA.

PLEXIGLAS® 7N provides the residual amounts to give 100% by weight.

Annex 1: Formulations for examples

Formulation	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Inv. Ex. 1	Inv. Ex. 2	Inv. Ex. 3	Inv. Ex. 4
Chromophtal Brown 5R	0.90%							
Sandoplast Red Violet R	0.17%							
Thermoplast Blue 684	0.10%							
Ultramarine Blue 31		0.65%						
Bayferrox 180 M		0.33%						
Bayferrox 645 T		0.18%						
Microlith Green GA		0.10%						
Pigment black FW1			1.00%					
Thermoplast Black X70				0.60%				
Printex 140 V				0.09%				
PK 24-10204					1%	0.80%	0.60%	
PK 10456								1%

PLEXIGLAS® 7N

to 100% by weight

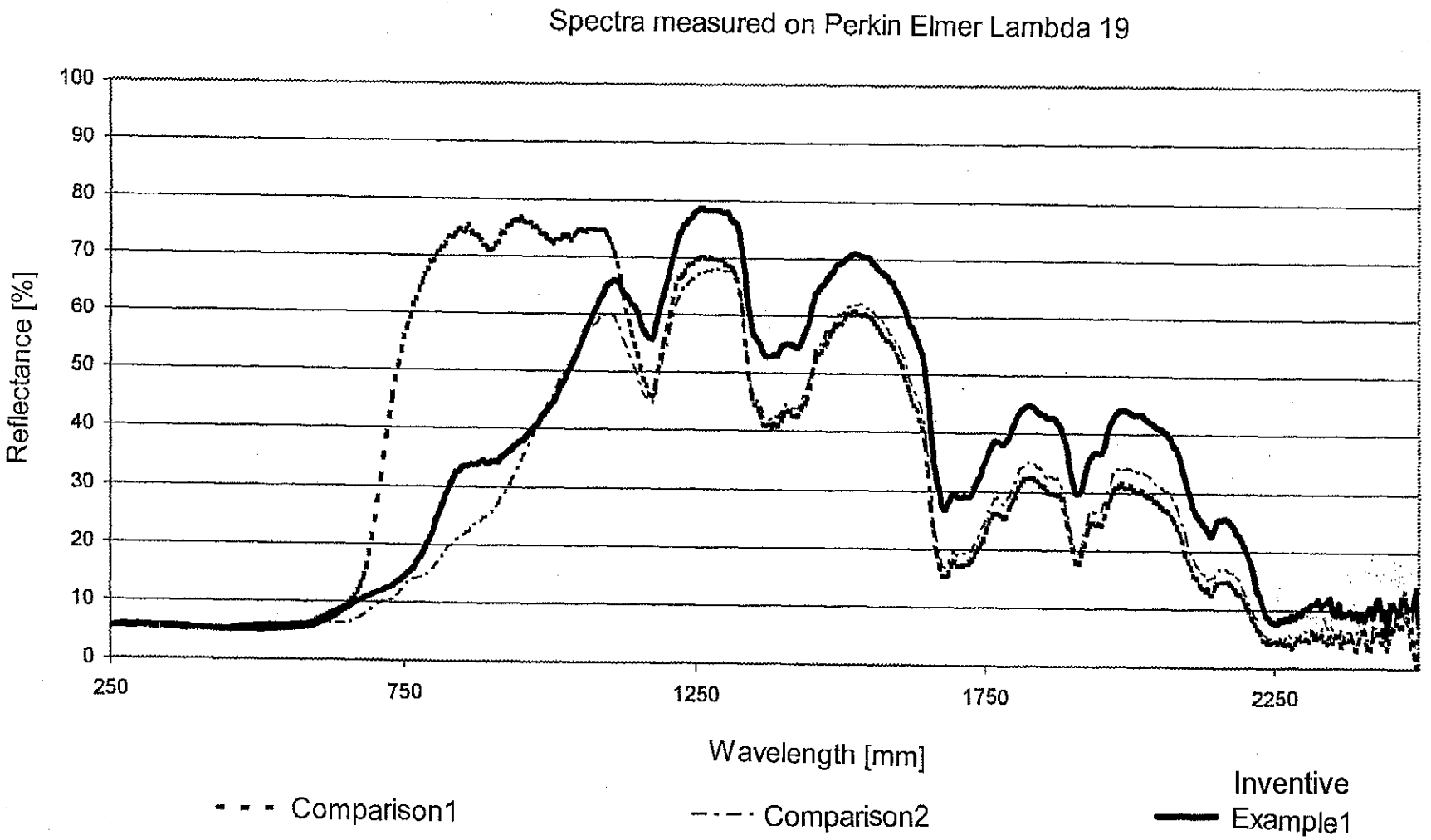
Testing of molding compositions:
A press was used to produce pressed plaques of thickness 0.5 mm from the colored molding compositions. The corresponding test specimens were tested by the following methods:

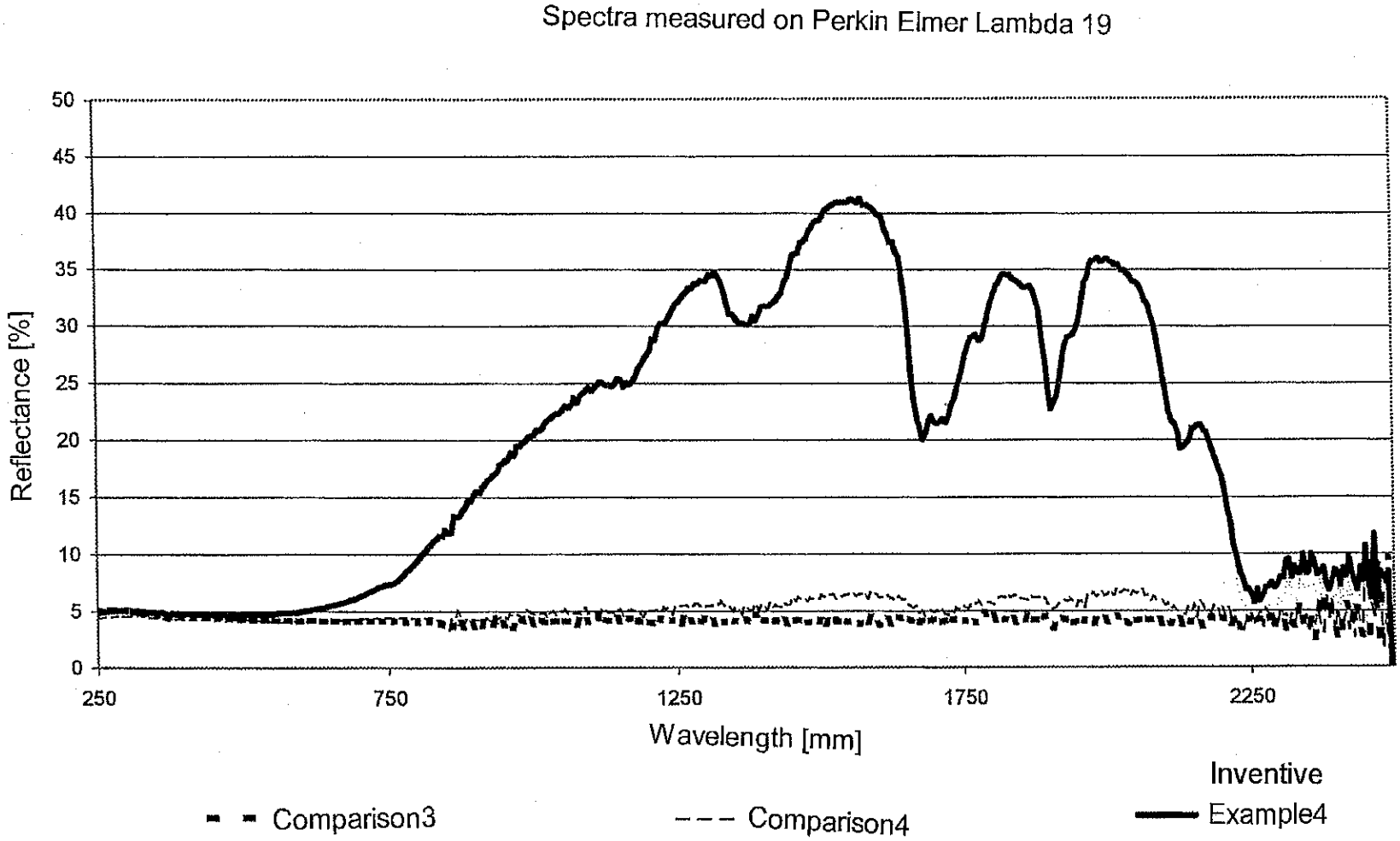
Heating behavior: The specimen of diameter 50 mm and thickness 0.5 mm was placed on a Rohacell® cube of edge length 50 mm. A thermocouple of diameter of 0.5 mm was fixed under the centre of the specimen with Tesa® film. A Plexiglas® GS White 003 sheet (40 mm*21 mm) had been impressed into the Rohacell®. The specimen with thermocouple was secured onto this using double-sided-adhesive Tesa® Fotostrip. The specimen was irradiated using a 60 W incandescent lamp regulated with 220 V (AC voltage stabilizer). Vertical distance between lower edge of glass bulb and specimen 50 mm. The temperature was read off after 20 minutes of irradiation. Heating was measured by a method based on the standard ASTM D4803-97.

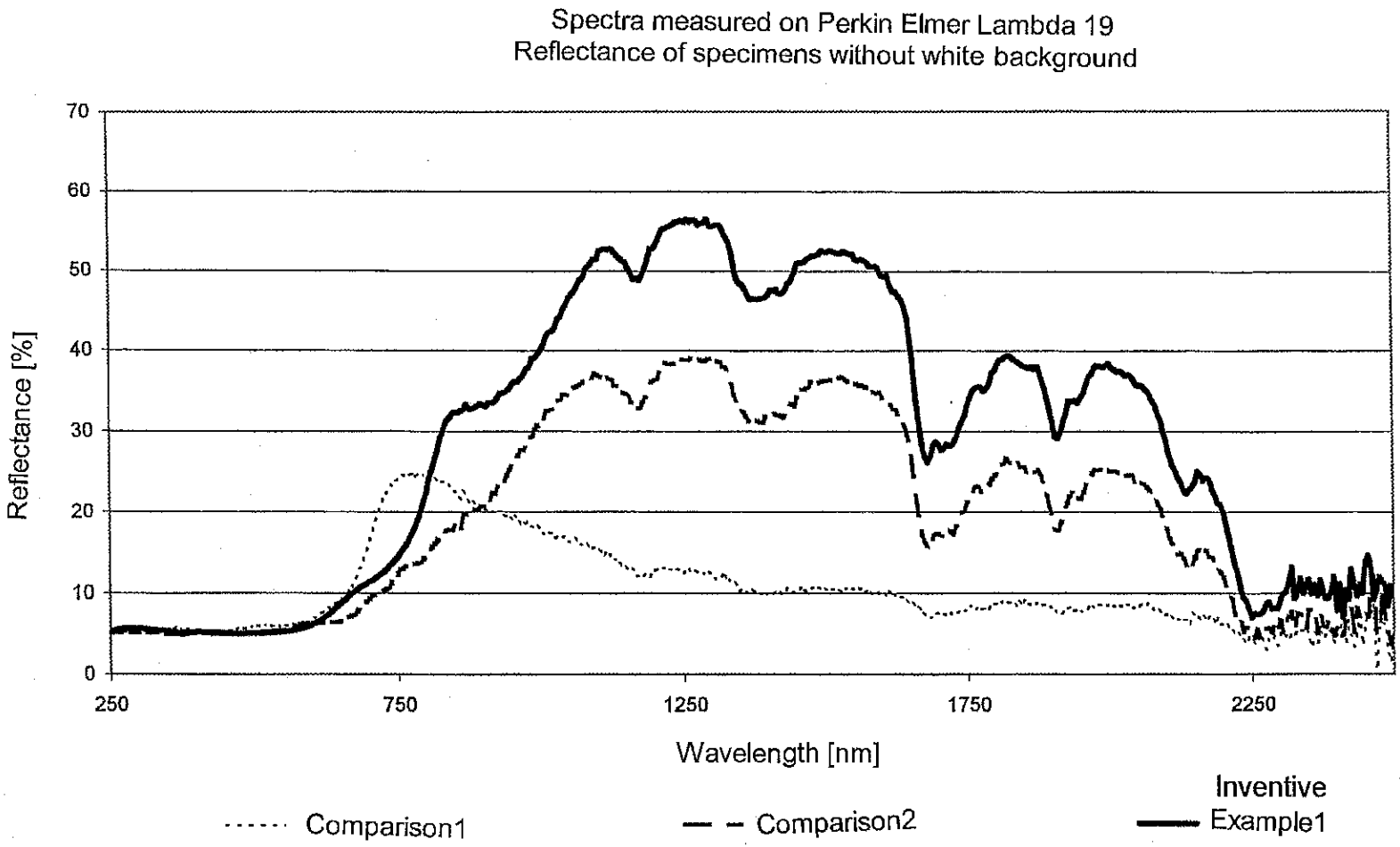
Light reflectance: Spectra measured on Perkin Elmer Lambda 19. For this, the specimens were measured with and sometimes without the Plexiglas GS White 003 sheet of thickness 3 mm.

The results for heating behavior of the test specimens can be seen in Table 2.

	L* value	a* value	b* value	Temperature after irradiation. Measurement using NiCr-Ni thermocouple of diameter 0.5 mm with Testo 950 indicator		
SPECIMEN	D65/10; reflection; heating; CieLab	D65/10; reflection; heating; CieLab	D65/10; reflection; heating; CieLab	D65/10; reflection; heating; CieLab	D65/10; reflection; heating; CieLab	D65/10; reflection; heating; CieLab
				[°C/20 min]	[°C]	[°C]
Comparison 1 (brown, organic, IR-transparent)	30.1	3.3	4.1	31.0	55.0	24.0
Comparison 2 (brown, inorganic, IR-absorbent)	28.2	3.4	1.9	35.1	57.3	22.2
Inventive example 1 (brown)	28.3	4.5	2.2	29.4	53.3	23.9
Inventive example 2 (brown)	27.2	3.9	1.8	32.3	56.0	23.7
Inventive example 3 (brown)	27.7	4.0	1.9	31.7	55.6	23.9
Comparison 3 (black, inorganic, IR-absorbent)	24.3	0.0	-0.8	43.8	67.7	23.9
Comparison 4 (black, inorganic, IR-absorbent)	24.0	-0.1	-0.9	42.8	66.8	24.0
Example 4 (black)	26.1	1.3	0.6	37.4	61.4	24.0


Spectra measured on Perkin Elmer Lambda 19
Reflectance [%]
100
90
80
70
60
50
40
30
20
10
0
250
750
1250
1750
2250
Wavelength [mm]
Comparison1
Comparison2
Inventive Example1


Spectra measured on Perkin Elmer Lambda 19
Reflectance [%]
50
45
40
35
30
25
20
15
10
5
0
250
750
1250
1750
2250
Wavelength [mm]
Comparison3
Comparison4
Inventive
Example4


Spectra measured on Perkin Elmer Lambda 19
Reflectance of specimens without white background
Reflectance [%]
70
60
50
40
30
20
10
0
250
750
1250
1750
2250
Wavelength [nm]
Comparison1
Comparison2
Inventive Example1

The reflectance spectra can be seen in Table 3 (brown colours with Plexiglas GS White 003 sheet of thickness 3 mm), Table 4 (black colours with Plexiglas GS White 003 sheet of thickness 3 mm), and Table 5 (brown colours without Plexiglas GS White 003 sheet of thickness 3 mm).

The examples clearly reveal the improvements achieved via the invention described here:

- Table 2 shows that the heating rate for the inventive brown pressed plaques (inventive Examples 1, 2, 3) is better than comparison 2 (brown pressed plaques produced using an inorganically IR-absorbent colorant) and comparable with comparison 1 (colorant used here being IR-transparent - IR reflection taking place at the white Plexiglas GS sheet). From the inventive black pressed plaques (inventive Example 4), it can also be seen that the heating rate here is clearly better (lower) than for comparisons 3 and 4.
- Table 3 and 4 clearly show that, based on the respective shade, the inventive pressed plaques clearly reflect IR light (wavelength > 700 mm) better than the comparisons. Comparison 1 is an exception here - however, the reflection here takes place at the white Plexiglas® GS sheet.
- Table 5 clearly shows that even without the underlying Plexiglas® GS sheet, the inventive brown pressed plaques clearly reflect the IR light better than the comparisons.

Patent Claims

1. Use of inorganic pigments for preparation of dark-colored molding compositions mainly composed of polymethyl (meth)acrylate, characterized in that the inorganic pigments are IR-reflective, and that the molding produced therefrom has a heating rate of less than 50°C/20 min.

2. Use of inorganic pigments for preparation of dark-colored molding compositions according to Claim 1, characterized in that the molding produced therefrom has a heating rate of less than 45°C/20 min.

3. Use of inorganic pigments for preparation of dark-colored molding compositions according to Claim 1, characterized in that the molding produced therefrom has a heating rate of less than 40°C/20 min.

4. Use of inorganic pigments for preparation of dark-colored molding compositions according to Claim 1, characterized in that the molding composition is composed of a mixture composed of polymethyl (meth)acrylate and of up to 45% by weight of a further matrix composed of

- from 70 to 92% by weight of styrene
- from 8 to 30% by weight of acrylonitrile
- from 0 to 22% by weight of further comonomers

and of inorganic pigments.

5. Use of the dark-colored molding compositions according to Claims 1-4 for production of plastics moldings.

6. Use of the plastics molding according to Claim 5 for coating of plastics moldings, characterized in that the plastics molding is applied with the aid of conventional methods to the second plastics molding.

7. Use of the plastics molding according to Claim 6, characterized in that at least one further plastics layer is applied with the aid of conventional methods to the plastics molding.

8. Molding compositions which have been rendered IR-reflective and are composed of polymethyl (meth)acrylate,

characterized in that

the amount of PMMA molding composition is from 95 to 99.5% by weight and the amount of IR-reflective pigment is from 5 to 0.5% by weight.

9. Molding composition which has been rendered IR-reflective and is composed of PMMA and of further polymers

characterized in that

the molding composition is composed of from 90 to 40% by weight of PMMA and of from 0 to 45% by weight of a matrix composed of

- from 70 to 72% by weight of polystyrene
- from 8 to 30% by weight of polyacrylonitrile
- from 0 to 22% by weight of further copolymers and
- from 0.5 to 5% by weight of IR-reflective pigment.