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(54) Title: HEAT-ABSORBING LAYER SYSTEM

(57) Abrégé/Abstract:
The invention relates to a heat-absorbing layer system, comprising at least one first layer (A), a second layer (B) and a third layer (C), wherein layer (A) contains an ultraviolet absorber, layer (B) contains an organic infrared absorber and an ultraviolet absorber and layer (C) is an interference layer which is reflecting in the infrared range.
ABSTRACT

The invention relates to a heat-absorbing layer system, comprising at least one first layer (A), a second layer (B) and a third layer (C), wherein layer (A) contains an ultraviolet absorber, layer (B) contains an organic infrared absorber and an ultraviolet absorber and layer (C) is an interference layer which is reflecting in the infrared range.
Heat-absorbing layer system

The invention relates to a heat-absorbing layer system which contains at least a first layer (A), a second layer (B) and a third layer (C), and to the preparation and use thereof and to products manufactured therefrom.

In automobile construction, thermoplastic glazing materials instead of glass are desired for safety reasons such as, for example, a high level of safety in the event of traffic accidents, but also for reasons of greater design freedom. A problem of using transparent thermoplastics for glazing elements in automobile construction is the excessive transmission in the near infrared (NIR) which, in summer, may lead to undesirably strong heating of the passenger compartment.

For applications in the automotive glazing sector, transmission in the visible range (LTA value) of at least 70% is specified for most cases. This value is defined in SAE J 1796 (May 1995 edition).

The TDS value (Solar Direct Transmittance) in accordance with SAE J 1796, May 1995 edition, is used for the efficiency of heat absorption. The value describes the percentage of solar energy that penetrates the sample and thus contributes to heating the vehicle interior. The higher the TDS value, the worse the heat-deflecting properties of the system.

Various heat-deflecting systems which have low transmission in the NIR have been described in the literature. On the one hand, surface coatings or lacquer systems are known, on the other hand, there are also infrared-absorbing additives for transparent thermoplastic polymers.

Infrared absorbers which are used as an additive to thermoplastics and restrict heating are described, for example, in J. Fabian, H. Nakazumi, H. Matsuoka, Chem. Rev. 92, 1197 (1992), US 5 712 332 and JP 06240146 A). A disadvantage of such
additives is the limited heat shielding and/or the low thermal and/or photochemical stability thereof.

Metallised films which are bonded with the transparent thermoplastic material of the glazing element are also known as NIR protection (see, for example, DE-A 195 37 263). Such films are available commercially, for example, under the name Scotchtint® from 3M. A disadvantage of such a system, however, is that the transmission in the visible range is too low. An LTA value of more than 70% with simultaneously good heat protection (TDS value <50%) cannot be achieved with this system.

Finally, films which have NIR-reflecting properties due to interference effects are known in the literature. Such films and the use thereof as heat-absorbing layer systems for transparent thermoplastic glazing elements are described, for example, in WO 97/01778 and WO 97/01440. Interference films of this kind are available commercially, for example, under the name "Solar Reflecting Film, N-NPE 1458LP" from 3M. Again, a disadvantage of such systems, however, is that too small a proportion of the solar thermal radiation is screened and the TDS values of the glazing elements provided with such films are too high.

Apart from the required spectral properties, it is also necessary for exterior applications for the heat-absorbing systems to have good long-term weathering resistance, i.e., good long-term light resistance to discolouration and fading.

Thin, film-like, heat-absorbing layer systems which simultaneously contain (A) a phthalocyanine infrared absorber and (B) an ultraviolet absorber are described in JP 10-077360 A. The weathering resistance of the thermal insulation layer is said to be thereby improved. According to one embodiment, a film-like coating layer with a thickness of 0.13 mm is proposed which contains both phthalocyanine infrared absorber and ultraviolet absorber. A coating layer of this kind exhibits acceptable weathering resistance in 48 hour accelerated weathering tests but a disadvantage is
the poor long-term weathering resistance in weathering tests of more than 500 hours. Moreover, the thin, film-like coating layers described in this publication exhibit inadequate optical properties and are therefore unsuitable for use in automotive glazing.

It is also generally known that certain thermoplastics may be protected by the use of UV-absorbing lacquers and/or coextruded layers with a high UV absorber content. It is known, for example, from EP 0 110 221 A, to improve the weathering resistance of polycarbonate plastic panels by coating with a layer containing 3 wt.% to 15 wt.% of a UV absorber. The multi-layer systems described in this printed matter do not contain an infrared absorber.

Finally, EP 0 774 551 A describes heat filters based on inorganic pigments which contain a UV-absorbing protective layer. Inorganic pigments have the disadvantage that they do not dissolve in thermoplastics so that no moulded articles which are transparent in the visible range and have little haze are obtained.

The object of the invention is to provide a heat-absorbing layer system which has outstanding long-term weathering resistance and excellent optical properties such as transparency and gloss with the simplest and most economical mode of production possible, and which may be used for thermal insulation of transparent plastic glazing elements. The heat-absorbing coating system should have a balanced ratio of LTA and TDS values, determined in accordance with SAE J 1796. More particularly, the heat-absorbing coating systems should have a TDS value of less than 50% and at the same time an LTA of more than 70%.

The object according to the invention is achieved by a transparent heat-absorbing layer system which contains a first layer (A), a second layer (B) and a third layer (C) and wherein layer (A) contains ultraviolet absorber, layer (B) contains organic infrared absorber and ultraviolet absorber, and layer (C) is an interference layer reflecting in the infrared range.
The heat-absorbing layer system according to the invention is characterised by a three-layer structure in which heat absorption takes place both by means of the interference layer (C) and by means of a layer (B) containing organic infrared absorber and ultraviolet absorber. Moreover, the layer system according to the invention contains a further layer (A) with additional ultraviolet absorber which protects the infrared absorber contained in layer (B) from decomposition due to solar radiation.

Surprisingly, it was found that the layer system according to the invention has excellent weathering resistance in addition to a particularly balanced ratio of LTA and TDS values. The layer systems according to the invention have good transparency with an LTA value of >70% and at the same time good heat absorption with TDS values of less than 50%. Moreover, the layer systems according to the invention are characterised by excellent long-term weathering resistance which makes them particularly suitable for use as glazing elements for exterior applications.

Layer (B) of the layer system according to the invention is characterised in that it contains both organic infrared absorber and ultraviolet absorber. Due to the joint presence of both additives in the same layer, a large proportion of the sensitive organic infrared absorber is protected from UV radiation. In addition, the organic infrared absorber is protected from decomposition by UV radiation by a further layer containing ultraviolet absorber (layer A, "UV layer"). As the UV layer (layer A) is designed, i.a. to protect NIR dye in layer (B) from UV rays, it is advantageous to arrange layer (A) in the direction of the incident light radiation above layer (B).

The interference layer (C) of the layer system according to the invention is an interference layer reflecting in the near infrared range. Interference layers (C) suitable according to the invention include, for example, selectively reflecting
alternating layer systems which contain at least two transparent layers (C1) and (C2) with different refractive indices.

Alternating layer systems that may be used as layer C are layer systems consisting of several layers ("quaterwave layers") with different refractive indices. According to the generally known rules of optics, selectively reflecting arrangements can be obtained in the near infra-red region. Preferably suitable are on the one hand thermoplastic alternating layer systems that are produced for example by co-extrusion, and on the other hand alternating layer systems consisting of layers of metals, metal oxides, metal nitrides and/or metal oxynitrides.

On account of their better processability and deformability, thermoplastic alternating layer systems are most particularly preferably used, such as for example the "Solar Reflecting Film, N-NPE 1458 LP" available from the 3M Company.

Starting with the side facing the incident light radiation, the following layer structure of the layer system according to the invention is advantageous:

layer (A) – layer (B) – layer (C) or
layer (A) – layer (C) – layer (B).

In this case, it is particularly advantageous if layer (A) is designed as a lacquer or as a polymer layer and layer (B) is designed as a polymer layer.

According to a preferred embodiment of the invention, the layer system according to the invention also comprises a substrate (S) based on glass or a transparent thermoplastic polymer. A substrate (S) based on polycarbonate or polyester carbonate is particularly preferred. In this case, the layer system according to the invention, starting with the side facing the incident light radiation, preferably has the following layer structure:
layer (A) – layer (B) – substrate (S) – layer (C) or
layer (A) – substrate (S) – layer (B) – layer (C) or
layer (A) – substrate (S) – layer (C) – layer (B) or
layer (A) – layer (C) – substrate (S) – layer (B) or
layer (A) – layer (B) – layer (C) – substrate (S) or
layer (A) – layer (C) – layer (B) – substrate (S).

Most particularly preferably, the layer system according to the invention, starting with the side facing the incident light radiation, has the following layer structure:

layer (A) – layer (B) – substrate (S) – layer (C) or
layer (A) – substrate (S) – layer (B) – layer (C).

If layer (B) is designed as substrate (S), layer (B) preferably has a thickness of 1 mm to 30 mm, particularly 2 mm to 8 mm, most preferably 3 mm to 5 mm.

It is also advantageous if layer (A) or layer (B) is designed as substrate (S). It is most particularly preferred if layer (B) is designed as substrate (S).

Moreover, it was found that it is advantageous if the individual layers of the layer system according to the invention are designed in certain thicknesses.

Layers (A) and (B) preferably have a thickness of 1 μm to 100 μm in each case. They may be designed in each case as a lacquer or as a coextruded layer. In the former case, the layer preferably has a thickness of 3 μm to 5 μm, in the latter case a thickness of 30 μm to 80 μm. If layer (A) or (B) is designed as a substrate (S), this preferably has a thickness of 1 mm to 30 mm, particularly 3 mm to 5 mm.

Layer (C) preferably has a thickness of 0.1 μm to 200 μm. It is designed preferably as a film.
The substrate (S) preferably has a thickness of 1 mm to 30 mm, particularly 3 mm to 5 mm.

The layer system according to the invention has excellent transparency and haze behaviour and at the same time outstanding long-term weathering resistance. More particularly, it is characterised in that it has, in addition to a TDS value of less than 50%, an LTA value of more than 70%. Both from a production angle and in terms of specific properties for use in automotive glazing, it has proved to be particularly advantageous if NIR/UV layer (layer B) and UV layer (layer A) are designed as coextruded polymer layers in the appropriate thicknesses.

According to a preferred embodiment of the invention layer (B), as the only layer in the layer system to do so, contains organic IR absorbers.

According to a further preferred embodiment of the invention, the layer system according to the invention contains, in addition to layers (A), (B) and (C), at least one further transparent layer (D) which preferably contains neither an organic infrared nor an ultraviolet absorber. Layer (D) is also called a "clear layer" and its purpose is to improve the mar resistance or to increase the mechanical stiffness. One or more clear layers may be present in the layer system according to the invention. The use of 1 to 3 clear layers, particularly preferably 1 clear layer, is preferred. The clear layers may be arranged in any place in the layer system, i.e. above, below and/or between the layers (A), (B) and (C). A layer system in which the clear layer (D) is arranged as the uppermost layer, relative to solar irradiation is, however, particularly advantageous. There are no particular restrictions with regard to the material of clear layer (D); as a rule, however, it is advantageous for the clear layer to be designed as a polymer or glass layer. Suitable polymer layers include, in particular, layers of transparent thermoplastics. Particularly suitable transparent thermoplastics are polycarbonates or copolycarbonates. It is advantageous for the optical properties of the layer system if the same polymer is used in layer (D) as in the other layers. In the case of a layer system according to the invention in which
layers (A) and/or (B) are, for example, layers based on polycarbonate, it is advantageous if layer (D) is also a layer based on polycarbonate.

Layer (D) may be designed as a lacquer or as a coextruded layer. In the former case, layer (D) preferably has a thickness of 0.1 μm to 30 μm, particularly 0.3 μm to 10 μm. In the latter case, layer (D) preferably has a thickness of 0.01 mm to 30 mm, particularly 3 mm to 5 mm.

Organic infra-red absorbers that are suitable for use in the layer systems according to the invention are compounds that have their absorption maximum in the near infra-red between 700 nm and 1500 nm. Infrared absorbers known from the literature are suitable, of the kind described by substance classes in, e.g., M. Matsuoka, Infrared Absorbing Dyes, Plenum Press, New York, 1990. Particularly suitable infrared absorbers are those from the substance classes comprising phthalocyanines, naphthalocyanines, metal complexes, azo dyes, anthraquinones, squaric acid derivatives, immonium dyes, perylenes and polymethines. Of these, phthalocyanines and naphthalocyanines are most particularly suitable. In view of the improved solubility in thermoplastics, phthalocyanines and naphthalocyanines with barrier side groups are preferred.

There are no particular restrictions as regards the amount of organic infrared absorber contained in layer (B), provided that the desired absorption of thermal radiation and a sufficient transparency of the layer system is guaranteed. It has proved to be particularly advantageous if layer (B) contains organic infrared absorber in an amount of 0.001 to 10 g/m², particularly 0.1 to 1 g/m². Depending on the extinction coefficient and layer thickness of the NIR/UV layer (layer B), the infrared absorbers are used preferably in concentrations from 1 ppm to 10,000 ppm, preferably from 10 ppm to 1,000 ppm and most particularly preferably from 20 ppm to 400 ppm. Mixtures of infrared absorbers are also particularly suitable. The skilled person may achieve optimum absorption in the near infrared range with dyes of different wave lengths of the absorption maxima.
Suitable ultraviolet absorbers for use in the layer system according to the invention are compounds that have an absorption maximum between 280 nm and 370 nm, preferably between 320 and 350 nm. Such compounds and the preparation thereof are known from the literature and described, for example, in EP 0 839 623 A, WO 96/15102 and EP 0 500 496 A. Ultraviolet absorbers which are particularly suitable for use in the layer system according to the invention are benzotriazoles, triazines, benzophenones and/or arylated cyanoacrylates.

Particularly suitable ultraviolet absorbers are hydroxy benzotriazoles such as 2-(3',5'-bis-(1,1-dimethylbenzyl)-2'-hydroxyphenyl)-benzotriazole (Tinuvin® 234, Ciba Spezialitätenchemie, Basel), 2-(2'-hydroxy-5'-(tert.-octyl)-phenyl)-benzotriazole (Tinuvin® 329, Ciba Spezialitätenchemie, Basel), 2-(2'-hydroxy-3'- (2-butyl)-5'-(tert.-butyl)-phenyl)-benzotriazole (Tinuvin® 350, Ciba Spezialitätenchemie, Basel), bis-(3-(2H-benztriazolyl)-2-hydroxy-5-tert.-octyl)methane, (Tinuvin® 360, Ciba Spezialitätenchemie, Basel), 2-(hydroxy-2-hydroxyphenyl)-4,6-diphenyl-1,3,5-triazine (Tinuvin® 1577, Ciba Spezialitätenchemie, Basel) and benzophenone 2,4-dihydroxybenzophenone (Chimasorb22®, Ciba Spezialitätenchemie, Basel), 2-propenoic acid, 2-cyano-3,3-diphenyl-2,2-bis[[2-cyano-1-oxo-3,3-diphenyl-2-propenyl]oxy]methyl]-1,3-propanediylester (9CI) (Uvinul® 3030, BASF AG Ludwigshafen). Mixtures of these ultraviolet absorbers may also be used.

Nanoscale inorganic UV absorbers with or without organic UV absorbers may also be used. TiO₂, ZnO and CeO₂ are preferred. The size of these particles is less than 100 nm: the preparation is known.

There are no particular restrictions with regard to the amount of ultraviolet absorber contained in the layer system. According to a preferred embodiment of the invention, layer (A) contains ultraviolet absorber in an amount of 0.1 wt.% to 40 wt.%, particularly 1 wt.% to 10 wt.%. Moreover, it has proved to be
advantageous if layer (B) contains ultraviolet absorber in an amount of 0.1 wt.% to 10 wt.%, particularly 0.2 wt.% to 1 wt.%.

There are no particular restrictions with regard to the base material for layers (A), (B) and (C), (D) and (S), provided that the material has good transparency and weathering resistance and is thus suitable for use in automotive glazing. It has proved to be particularly advantageous, however, if the individual layers of the layer system are layers based on polymers or lacquers. This means that the organic infrared absorbers and/or ultraviolet absorbers, if contained in the individual layers, are introduced into a polymer or lacquer layer.

The use of transparent thermoplastic polymers is preferred.

Transparent thermoplastic polymers within the meaning of the invention include, e.g., polymers of ethylenically unsaturated monomers and/or polycondensates of bifunctional reactive compounds. Examples of transparent thermoplastic polymers include polycarbonates or copolycarbonates based on diphenols, poly- or copolyacrylates and poly- or copolymethacrylate such as, e.g., poly- or copolymethylmethacrylates and copolymers with styrene such as, e.g., transparent polystyrene acrylonitrile (PSAN) or polymers based on ethylene and/or propylene, and aromatic polyesters such as PET, PEN or PETG and transparent thermoplastic polyurethanes. Moreover, polymers based on cyclic olefins (e.g. TOPAS®, a commercial product from Ticona), poly- or copolycondensates of terephthalic acid such as, e.g., poly- or copolyethylene terephthalate (PET or CoPET) or PETG may also be incorporated.

Mixtures of several transparent thermoplastic polymers are also possible.

Polycarbonates or copolycarbonates are preferred.
Particularly preferred polycarbonates are the homopoly carbonate based on bisphenol A, the homopoly carbonate based on 1,3-bis-(4-hydroxyphenyl)-3,3,5-trimethylecyclohexane and the copoly carbonates based on both monomers bisphenol A and 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylecyclohexane.

Polycarbonates within the meaning of the present invention are both homopolycarbonates and copolycarbonates; the polycarbonates may be linear or branched, in the known way.

The polycarbonates are prepared in the known manner from diphenols, carbonic acid derivatives, optionally chain terminators and branching agents.


Diphenols suitable for the preparation of polycarbonates include, for example, hydroquinone, resorcinol, dihydroxydiphenyls, bis-(hydroxyphenyl)-alkanes, bis(hydroxyphenyl)-cycloalkanes, bis-(hydroxyphenyl)-sulfides, bis-(hydroxyphenyl)-ethers, bis-(hydroxyphenyl)-ketones, bis-(hydroxyphenyl)-sulfones, bis-(hydroxyphenyl)- sulfoxides, α-α'-bis-(hydroxyphenyl)-diisopropylbenzenes, and the compounds thereof alkylated and halogenated on the nucleus.
Preferred diphenols are 4,4'-dihydroxydiphenyl, 2,2-bis-(4-hydroxyphenyl)-propane, 2,4-bis-(4-hydroxyphenyl)-2-methylbutane, 1,1-bis-(4-hydroxyphenyl)-p-diisopropylbenzene, 2,2-bis-(3-methyl-4-hydroxyphenyl)-propane, 2,2-bis-(3-chloro-4-hydroxyphenyl)-propane, bis-(3,5-dimethyl-4-hydroxyphenyl)-methane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane, bis-(3,5-dimethyl-4-hydroxyphenyl)-sulfone, 2,4-bis-(3,5-dimethyl-4-hydroxyphenyl)-2-methylbutane, 1,1-bis-(3,5-dimethyl-4-hydroxyphenyl)-p-diisopropylbenzene, 2,2-bis-(3,5-dichloro-4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dibromo-4-hydroxyphenyl)-propane and 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane.

Particularly preferred diphenols are 2,2-bis-(4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dichloro-4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dibromo-4-hydroxyphenyl)-propane, 1,1-bis-(4-hydroxyphenyl)-cyclohexane and 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane.


In the case of homopolycarbonates, only one diphenol is used, and in the case of copolycarbonates several diphenols are used.

Examples of suitable carbonic acid derivatives include phosgene or diphenylcarbonate.

Suitable chain terminators which may be used in the preparation of polycarbonates include both monophenols and monocarboxylic acids. Suitable monophenols are
phenol itself, alkyl phenols such as cresols, p-tert.-butylphenol, p-n-octylphenol, p-
iso-octylphenol, p-n-nonylphenol and p-iso-nonylphenol, halogenated phenols such
as p-chlorophenol, 2,4-dichlorophenol, p-bromophenol and 2,4,6-tribromophenol,
2,4,6-triiodophenol, p-iodophenol, and mixtures thereof.

A preferred chain terminator is p-tert.-butylphenol and phenol.

Suitable monocarboxylic acids are also benzoic acid, alkylbenzoic acids and
halogenated benzoic acids.

Preferred chain terminators also include phenols corresponding to formula (I)

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    R
O(1)
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wherein

R is hydrogen or a C₁ to C₃₀ alkyl radical, is linear or branched, is preferably
tert.-butyl or a branched or unbranched C₈ and/or C₉ alkyl radical.

The amount of chain terminator to be used is preferably 0.1 mole% to 5 mole%,
based on moles of diphenols used in each case. The addition of chain terminators
may take place before, during or after phosgenation.

Suitable branching agents are the tri- or more than trifunctional compounds known
in polycarbonate chemistry, particularly those with three or more than three phenolic
OH groups.
Suitable branching agents include, for example, phloroglucinol, 4,6-dimethyl-2,4,6-
tri-(4-hydroxyphenyl)-heptene-2, 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)-heptane,
1,3,5-tri-(4-hydroxyphenyl)-benzene, 1,1,1-tri-(4-hydroxyphenyl)-ethane, tri-(4-
hydroxyphenyl)-phenylmethane, 2,2-bis-[4,4-bis-(4-hydroxyphenyl)cyclohexyl]-
propane, 2,4-bis-(4-hydroxyphenylisopropyl)-phenol, 2,6-bis-(2-hydroxy-5’-
methylbenzyl)-4-methylphenol, 2-(4-hydroxyphenyl)-2-(2,4-dihydroxyphenyl)
propane, hexa-(4(4-hydroxyphenylisopropyl)-phenyl)-orthoterephthalic acid ester,
tetra-(4-hydroxyphenyl)-methane, tetra-(4-(4-hydroxyphenylisopropyl)-phenoxyl)-
methane and 1,4-bis-((4’,4”-dihydroxytriphenyl)-methyl)-benzene, and 2,4-
dihydroxybenzoic acid, trimesic acid, cyanuric chloride and 3,3-bis-(3-methyl-4-
hydroxyphenyl)-2-oxo-2,3-dihydroindole.

The amount of branching agents optionally to be used is preferably 0.05 mole% to
2 mole%, again based on moles of diphenols used in each case.

The branching agents may be charged either with the diphenols and the chain
terminators in the aqueous alkaline phase, or dissolved in an organic solvent and
added before phosgenation. In the case of the transesterification process, the
branching agents are used together with the diphenols.

The compositions according to the invention may also contain conventional polymer
additives, such as, e.g., the antioxidants and mould release agents described in EP-A
0 839 623, WO 96/15102 and EP-A 0 500 496, but also flame retardants, glass
fibres, fillers, foaming agents, pigments, optical brighteners or dyes known from the
literature and in the amounts conventionally used for the thermoplastics in each
case. Amounts of up to 5 wt.% in each case are preferred, preferably 0.01 wt.% to
5 wt.%, based on the amount of the compositions, particularly preferably 0.01 wt.%
to 1 wt.%, based on the amount of the compositions. Mixtures of several additives
are also suitable.
The ions present as an impurity are contained in the thermoplastic polycarbonates preferably in amounts of less than 10 ppm, particularly preferably less than 5 ppm.

The expert is familiar with the measures for the preparation of the thermoplastic polycarbonates.

In the case of several thermoplastic layers, the thermoplastics may be of different types or of the same type.

Suitable moulded articles/protective layer combinations are given, for example, in EP 0 320 632 A. The same types of plastics are preferred.

Lacquer systems suitable for use in the layer system according to the invention are those of which the crosslinking components contain acrylate, allyl, epoxy, siloxane, isocyanate, anhydride and/or melamine formaldehyde functions. Comprehensive descriptions of such lacquer systems may be found in: "Lehrbuch der Lacke und Beschichtungen", editor: Dr. Hans Kittel, Verlag Hirzel, Stuttgart, 1998; in "Lackkunstharze" by Hans Wagner, Hans Friedrich Sarx, Carl Hanser Verlag Munich, 1971; particularly for epoxy resins in "Epoxy Resins, Chemistry and Technology", edited by Clayton A. May and Yoshio Tanaka, Marcel Dekker, Inc., New York, 1973, chapter 7, pages 451 ff.

Siloxane lacquers of the kind described, e.g., in DE 4020316 A are particularly preferred.

The thickness of the lacquer layers is 1 µm to 200 µm, preferably 2 µm to 50 µm and most particularly preferably 2 µm to 10 µm. The viscosity of the lacquer is preferably 5 mPa.s to 10,000 mPa.s.

Optionally, the polymers or lacquers used in the layers (A), (B), (C), (D) and/or (S) may contain further additives such as, e.g., the antioxidants, flame retardants, fillers,
foaming agents, conventional dyes and pigments, optical brighteners and nucleating agents or the like described in EP 0 839 623 A1 and EP 0 500 496 A1, preferably in amounts of up to 5 wt.% in each case, preferably 0.01 wt.% to 5 wt.%, based on the total mixture, particularly preferably 0.01 wt.% to 1 wt.% based on the amount of plastic. Mixtures of said additives are also suitable.

Moreover, the thermoplastics may also contain conventional heat stabilisers. Particularly suitable heat stabilisers according to the invention include hindered phenols, for example, octadecyl-3-(3',5'-di-tert.-butyl-4'-hydroxyphenyl)-propionate (Irganox® 1076, Ciba Specialty Chemicals, Basel, Switzerland). Moreover, particularly suitable heat stabilisers according to the invention include phosphites, particularly tris(2,4-di-tert.-butyl-phenyl)-phosphite (Irgafos® 168, Ciba Specialty Chemicals, Basel, Switzerland) or phosphines such as, e.g., triphenylphosphine.

The thermoplastics of the layer system according to the invention may also contain conventional mould release agents. Particularly suitable mould release agents are pentaerythritol tetrastearate (PETS) or glycerol monostearate (GMS).

The organic infrared absorbers, ultraviolet absorber and other additives may be introduced into the individual layers of the layer system according to the invention by known methods such as compounding, incorporation in solution, coextrusion, kneading, incorporation during injection moulding or as a masterbatch.

The layer system according to the invention may be prepared by known methods such as coating, coextrusion, hot pressing, dipping, bonding, pressing, UV or thermal curing, laminating, multi-component injection moulding, application from solution, back injection or the like in one or more and optionally different steps.

The moulded articles thus obtained may be brought to the desired shape before or after coating by likewise known methods such as thermoforming.
The skilled person is familiar with the measures for the preparation of the transparent thermoplastics.

The individual layers may be applied to one another at the same time as or immediately after forming of the basic article, e.g. by coextrusion or multi-component injection moulding. Application may also, however, take place onto the finished formed basic article, e.g., by lamination with a film or by coating with a solution.

Layer (A) is prepared preferably by coating, layer (B) by injection moulding and layer (C) by hot laminating or back injection with layer (B). According to a further preferred embodiment of the invention, layers (A) and (B) are prepared by coextrusion.

Alternatively, layer (C) may also be bonded on. Adhesives used for layer (C) may be any adhesives known to the skilled person for bonding plastics, for example, those based on polyurethane and/or acrylate. The use of solvent-free and completely transparent adhesives is preferred.

The layer systems according to the invention may find general application wherever heat transmission is undesirable. The use for automotive components is particularly suitable, e.g., glazing elements, car sunroofs, plastic headlamp diffusors and architectural applications such as building glazing, greenhouse components, conservatories, bus shelters or similar applications. Twin-wall sheets or multi-wall sheets may also be used. Moreover, the use for injection moulded parts such as food containers, components of electrical devices and in spectacle lenses, e.g. for goggles such as welding goggles, is possible.

The layer system according to the invention is suitable for the manufacture of moulded articles, particularly for the manufacture of transparent plastic glazing elements such as, e.g., plastic glazing elements based on polycarbonate and/or
copolycarbonate. The invention also provides, therefore, moulded articles manufactured with the layer system according to the invention.
Examples

The invention is described in more detail below on the basis of embodiments.

Preparation of test specimens

In order to prepare test specimens, an additive-free, unstabilised polycarbonate (Makrolon®  2808 and Makrolon®  3108 from Bayer AG, Leverkusen) with an average molecular weight of about 28,000 and 30,000 respectively (M<sub>n</sub> by GPC) was compounded at 300 °C in a twin-shaft extruder with the amount of additive given in Table 1 and then granulated. Coloured test sheets were then injection moulded from these granules (76 mm x 50 mm x 2.5 mm (layer B)).

The following compounds were used as IR absorbers:

IR absorber (A): Vanadyl-5,14,23,32-tetraphenyl-2,3-naphthalocyanine (Aldrich, Steinheim, Germany), and

IR absorber (B): Copper (II)-1,4,8,11,15,18,22,25-octabutoxy-29H,31H-phthalocyanine (Aldrich, Steinheim, Germany).

The UV absorber used was 2-(2'-hydroxy-3'-(2-butyl)-5'(tert.-butyl)-phenyl)benzotriazole (Tinuvin® 350) and bis-(3-(2H-benzotriazolyl)-2-hydroxy-5-tert.-octyl)methane (Tinuvin® 360) from Ciba Spezialitätenchemie Basel, Switzerland.
Table 1

Composition of the specimens

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Layer (A): 7% UV absorber in Makrolon® 3108</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Layer (B): 70 ppm IR absorber (A) + 0.3% UV absorber in Makrolon® 2808</td>
</tr>
<tr>
<td></td>
<td>Layer (C): 3M® Solar Reflecting Film N-NPE 1458LP</td>
</tr>
<tr>
<td>2</td>
<td>Layer (A): 7% UV absorber in Makrolon® 3108</td>
</tr>
<tr>
<td></td>
<td>Layer (B): 70 ppm IR absorber (B) + 0.3% UV absorber in Makrolon® 2808</td>
</tr>
<tr>
<td></td>
<td>Layer (C): 3M® Solar Reflecting Film N-NPE 1458LP</td>
</tr>
</tbody>
</table>

The coloured test sheets were then bonded with a 50 μm to 70 μm thick polycarbonate film composed of 7% bis-(3-(2H-benzazolyl)-2-hydroxy-5-tert.-octyl)methane, (Tinuvin® 360, Ciba Spezialitätenchemie, Basel) in Makrolon® 3108 (thermoplastic).

The coloured test sheets thus coated were then bonded on the side of layer (B) with a reflecting film of the "Solar Reflecting Film, N-NPE 1458LP" type (3M®, St. Paul, USA), such that a layer system with the following layer structure was obtained:

layer (A) – layer (B) – layer (C)

The adhesive used was an adhesive of the Helmitin 35050 type (Forbo Helmitin, Pirmasens, DE).

Transmission properties

The transmission spectra of specimens 1 and 2 were measured with a "lamda 9" UV-VIS-NIR spectrometer from Perkin Elmer in the range from 300 nm to 2,500 nm.
From this the LTA and TDS values were determined in accordance with SAE J 1796 (May 1995 edition).

Table 2

<table>
<thead>
<tr>
<th>Specimen</th>
<th>LTA [%]</th>
<th>TDS [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>75.8</td>
<td>44.1</td>
</tr>
<tr>
<td>2</td>
<td>70.7</td>
<td>40.0</td>
</tr>
</tbody>
</table>

The test results show that the layer systems according to the invention, in a simple structure, have good transparency (LTA value >70) and at the same time efficient thermal insulation (TDS value <50). A particularly balanced ratio of LTA to TDS value is obtained by the use of the IR absorber vanadyl-5,14,23,32-tetraphenyl-2,3-naphthalocyanine in the layer structure according to the invention (specimen 1). In addition, the layer systems according to the invention have excellent long-term weathering stability. Even after Xe-WOM weathering of 3,000 hours, the layer systems according to the invention are characterised by excellent transparency and outstanding gloss values.
Patent claims

1. Heat-absorbing layer system containing at least a first layer (A), a second layer (B) and a third layer (C), wherein

- layer (A) contains ultraviolet absorber
- layer (B) contains organic infrared absorber and ultraviolet absorber and
- layer (C) is an interference layer reflecting in the infrared range.

2. A layer system according to claim 1, characterised in that the interference layer (C) is a selectively reflecting alternating layer system which contains at least two transparent layers (C1) and (C2) with different refractive indices.

3. A layer system according to claim 2, characterised in that layer (C) comprises a multiplicity, particularly 20 to 2,000, of layers (C1) and (C2) arranged alternately one above the other.

4. A layer system according to claim 2 or 3, characterised in that layers (C1) and (C2) contain different thermoplastic materials.

5. A layer system according to claim 1, characterised in that layer (C) is a selectively reflecting alternating layer system of metal, oxide, nitride and/or oxynitride layers.

6. A layer system according to one of the preceding claims, characterised in that layers (A) and (B) have a thickness of 1 μm to 100 μm in each case.

7. A layer system according to claim 1, characterised in that layer (C) has a thickness of 0.1 μm to 200 μm.
8. A layer system according to claim 1, characterised in that the substrate (S) has a thickness of 1 mm to 30 mm, particularly 3 mm to 5 mm.

9. A layer system according to one of the preceding claims, characterised in that the infrared absorber is selected from the group comprising phthalocyanines, naphthalocyanines and perylenes.

10. A layer system according to one of the preceding claims, characterised in that the ultraviolet absorber is selected from the group comprising hydroxybenzotriazoles, hydroxytriazines, hydroxybenzophenones and arylated cyanoacrylates.

11. A layer system according to one of the preceding claims, characterised in that layers (A) and (B) are layers based on polymer and/or lacquer.

12. A layer system according to claim 11, characterised in that the polymer used is a transparent thermoplastic, particularly a polycarbonate or a copolycarbonate.

13. A layer system according to one of the preceding claims, characterised in that the individual layers, starting with the side facing the incident light radiation, are arranged in the following order: layer (A) – layer (B) – layer (C) or layer (A) – layer (C) – layer (B).

14. A layer system according to claim 13, characterised in that layer (A) is designed as a lacquer or as a polymer layer and layer (B) is designed as a polymer layer.

15. A layer system according to one of the preceding claims, characterised in that the layer system comprises a substrate (S) based on glass or a
transparent thermoplastic polymer, particularly polycarbonate or polyester carbonate.

16. A layer system according to claim 15, characterised by the following layer structure, starting with the side facing the incident light radiation:

layer (A) – layer (B) – substrate (S) – layer (C) or
layer (A) – substrate (S) – layer (B) – layer (C) or
layer (A) – substrate (S) – layer (C) – layer (B).

17. A layer system according to claim 15 or 16, characterised in that layer (B) is designed as substrate (S).

18. A process for the preparation of a layer system according to one of claims 1 to 17, characterised in that the layer system is prepared by coextrusion, multi-component injection moulding, injection moulding, back injection, spraying, bonding and/or laminating of the individual layers (A), (B) and (C), and optionally of further layers such as the substrate (S).

19. A process according to claim 18, characterised in that layer (A) is prepared by coating, layer (B) by injection moulding and layer (C) by hot laminating or back injection with layer (B).

20. A process according to claim 18 to 19, characterised in that layers (A) and (B) are prepared by coextrusion.

21. Moulded articles containing a layer system according to one of claims 1 to 17.
22. Moulded articles according to claim 21, characterised in that the moulded article is a transparent plastic glazing element, particularly a transparent plastic glazing element based on polycarbonate and/or copolycarbonate.

23. The use of a layer system according to one of claims 1 to 17 for shielding plastic glazing elements from heat radiation.