

is provided, it does not serve as a binding agent, but as an additive for viscosity adjustment. Such inks cannot be used for printing on polycarbonate films for the following reasons explained with regard to paper-based security and/or value documents.

A personalization of PC (polycarbonate) based security and/or value documents takes place in the practice by means of the so-called laser engraving method, wherein by optical/thermal interactions of a material of the security and/or value document with the laser radiation, locally highly resolved pyrolysis processes are produced and thus local blackenings due to carbon generation occur. The disadvantage of this method is the limitation to black & white or at best gray scale representations.

A colored personalization established for paper-based documents in the ink jet printing method is not widely used for PC based security and/or value documents up to now. One reason for this is the lacking compatibility of the used polymers/binders (in connection with the other ink components such as dyes, additives, solvents) with polycarbonate. This applies for instance to the binders known from the documents *Ullmann's Encyclopedia of Industrial Chemistry*, Electronic Release 2007, Wiley Verlag, chapter "Imaging Technology, Ink-Jet Inks, and *Ullmann's Encyclopedia of Industrial Chemistry*, Electronic Release 2007, Wiley Verlag, chapter "Paints and Coatings", such as nitrocellulose, cellulose ester (cellulose acetate butyrate, CAB), polyacrylates, polyesters, epoxides etc. Secondly, PC films imprinted with such inks cannot easily be

laminated. PC films imprinted over the full surface practically cannot be laminated at all, for the dye layer represents a barrier layer. In the event of an only partial printing process, there is the risk of a local delamination. Thirdly, polycarbonate is no sucking base. Common inks for ink jet printing are adjusted to good absorption times on paper and when imprinted on a non-sucking PC film they remain on the surface and can even after drying often completely be removed without residues, since the color does not penetrate into the material. Fourthly, ink jet printing layers made from insofar known inks lack temperature stability. Since in the field of security and/or value documents, imprinted PC films are typically laminated to each other under the action of pressure (> 2 bars) and temperature ($> 160^{\circ}\text{C}$), there is a risk of discoloration of the ink jet printing layer.

From the document EP 0 688 839 B1, silk-screen printing inks based on disubstituted dihydroxydiphenyl cycloalkanes are known. From this document can also be taken methods for making such polycarbonates. This document with its complete contents is hereby included in the scope of disclosure of the present application. Normally silk-screen printing inks can however not easily be used for ink jet printing, since ink jet printing poses special requirements for the used inks because of the nozzle technology of the printing heads.

Technical object of the invention.

It is therefore the technical object of the invention to provide means, which permit the application of ink jet printing for making a security and/or value document based on polycarbonate polymer layers and provide ink jet printing layers on such layers, which satisfy all optical requirements, may in particular also be colored, wherein during a lamination the optical properties are not impaired, and which do not act as an barrier layer during the lamination, but rather even contribute to the formation of a monolithic structure from the polymer layers.

Basics of the invention and preferred embodiments.

For achieving this technical object, the invention teaches the use of a preparation comprising: A) 0.1 to 20 wt % of a binding agent with a polycarbonate derivative based on a geminally disubstituted dihydroxydiphenyl cycloalkane, B) 30 to 99.9 wt % of a preferably organic solvent or of a mixture of solvents, C) 0 to 10 wt %, referred to dry mass, of a dye or of a mixture of dyes, D) 0 to 10 wt % of a functional material or of a mixture of functional materials, E) 0 to 30 wt % of additive and/or auxiliary substances, or of a mixture of such substances, the relative amounts of the components A) to E) always totaling 100 wt %, as an ink jet printing dye.

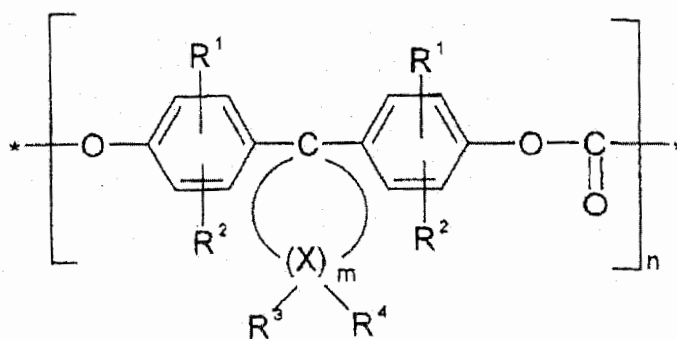
First of all, the invention is based on the finding that polycarbonate derivatives used according to the invention are highly compatible with polycarbonate materials for films, in par-

5 ticular with polycarbonates based on bisphenol
A, such as for instance Makrofol® films. The
high compatibility is shown by that the ink jet
printing layer provided according to the inven-
10 tion with a polycarbonate derivative combines
with the polycarbonate materials of the films to
form a monolithic structure. A layer boundary
between the materials cannot optically be de-
tected anymore after the lamination. Further,
15 the used polycarbonate derivative is stable at
high temperatures and does not show any discol-
orations at temperatures up to 200 °C and more
being typical for a lamination. Furthermore, it
is surprising that an ink composition known for
20 silk-screen printing (under adjustment of the
viscosity) is also suitable, with regard to the
used binder, for ink jet printing. Finally it
was found to be an advantageous property that
the dye of the composition penetrates into the
25 imprinted polymer layer, so that a printing
layer applied on the surface of the polymer
layer cannot be removed in a non-destructive
manner. Thus, compositions used according to the
invention are also suitable e.g. for the surface
30 personalization of security and/or value docu-
ments, since when printing on the polymer layer,
an integral structure is formed.

As a result, the invention achieves that a
security and/or value document based on polycar-
35 bonate films can be provided with a colored
overprint, for instance during the personaliza-
tion as a passport photograph, wherein the ink
jet printing layer does not only not act as a
barrier layer, but rather even more promotes the
formation of a monolithic structure during the

lamination. The structure fulfills with regard to integrity and durability all requirements.

In detail, the polycarbonate derivative may contain functional carbonate structure units of formula (I),



(I)

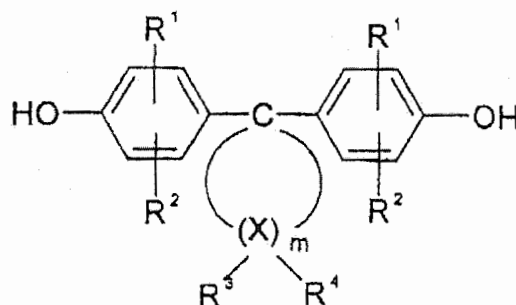
wherein R^1 and R^2 are independently from each other hydrogen, halogen, preferably chlorine or bromine, C_1 - C_8 alkyl, C_5 - C_6 cycloalkyl, C_6 - C_{10} aryl, preferred phenyl, and C_7 - C_{12} aralkyl, preferably phenyl- C_1 - C_4 alkyl, in particular benzyl; m is an integer from 4 to 7, preferably 4 or 5; R^3 and R^4 can be individually selected for each X , and independently represent hydrogen or C_1 - C_6 alkyl; X is carbon and n an integer greater than 20, with the proviso that at at least one atom X , R^3 and R^4 are both alkyl.

It is preferred, if at 1 to 2 atoms X , in particular at one atom X only, R^3 and R^4 both are alkyl. R^3 and R^4 may in particular be methyl. The X atoms in the alpha position to the diphenyl-substituted C atom (C_1) cannot be dialkyl-substituted. The X atoms in the beta position to C_1 can be disubstituted with alkyl.

Preferred is $m = 4$ or 5 . The polycarbonate derivative may for instance be formed on the basis of monomers, such as 4,4'-(3,3,5-trimethyl cyclohexane-1,1-diyl)diphenol, 4,4'-(3,3-dimethyl cyclohexane-1,1-diyl)diphenol, or 4,4'-(2,4,4-trimethyl cyclopentane-1,1-diyl)diphenol.

A polycarbonate derivative used according to the invention may for instance be made from diphenols of formula (Ia) according to the document DE 38 32 396.6, the scope of disclosure of which with its complete contents is hereby included in the scope of disclosure of this description.

A diphenol of formula (Ia) under formation of homopolycarbonates as well as several diphenols of formula (Ia) under formation of copolycarbonates can be used (the meaning of radicals, groups and parameters same as in formula I).



(Ia)

Furthermore, the diphenols of formula (Ia) can also be used in a mixture with other diphenols, for instance with those of formula (Ib)



for making high-molecular, thermoplastic, aromatic polycarbonate derivatives.

Suitable other diphenols of formula (Ib) are those, wherein Z is an aromatic radical with 6 to 30 C atoms, which may contain one or several aromatic nuclei, be substituted and contain aliphatic radicals or other cycloaliphatic radicals than those of formula (Ia) or heteroatoms as bridge members.

Examples for the diphenols of formula (Ib) are: hydroquinone, resorcin, dihydroxydiphenyls, bi-(hydroxyphenyl)-alkanes, bis-(hydroxyphenyl)-cycloalkanes, bis-(hydroxyphenyl)-sulfides, bis-(hydroxyphenyl)-ethers, bis-(hydroxyphenyl)-ketones, bis-(hydroxyphenyl)-sulfones, bis-(hydroxyphenyl)-sulfoxides, alpha, alpha'-bis-(hydroxyphenyl)-diisopropylbenzenes and their nuclear-alkylated and nuclear-halogenated compounds.

These and other suitable diphenols are e.g. described in the documents US-A 3 028 365, 2 999 835, 3 148 172, 3 275 601, 2 991 273, 3 271 367, 3 062 781, 2 970 131 and 2 999 846, in the documents DE-A 1 570 703, 2 063 050, 2 063 052, 2 211 956, the FR-A 1 561 518 and in the monograph "H. Schnell, *Chemistry and Physics of Polycarbonates*, Interscience Publishers, New York 1964", which with its complete contents is hereby included in the scope of disclosure of the present application.

Preferred other diphenols are for instance: 4,4'-dihydroxydiphenyl, 2,2-bis-(4-hydroxyphenyl)-propane, 2,4-bis-(4-hydroxyphenyl)-2-me-

thylbutane, 1,1-bis-(4-hydroxyphenyl)-cyclohexane, alpha,alpha-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)-cyclohexane, alpha,alpha-bis-(3,5-dimethyl-4-hydroxyphenyl)-p-diisopropylbenzene, 2,2-bis-(3,5-dichloro-4-hydroxyphenyl)-propane and 2,2-bis-(3,5-dibromo-4-hydroxyphenyl)-propane.

Particularly preferred diphenols of formula (Ib) are for instance: 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 and 1,1-bis-(4-hydroxyphenyl)-cyclohexane. In particular 2,2-bis-(4-hydroxyphenyl)-propane is preferred. The other diphenols may be used individually as well as in a mixture.

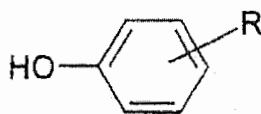
The molar ratio of diphenols of formula (Ia) to, if applicable, the also used other diphenols of formula (Ib) should be between 100 mol % (Ia) to 0 mol % (Ib) and 2 mol % (Ia) to 98 mol % (Ib), preferably between 100 mol % (Ia) to 0 mol % (Ib) and 10 mol % (Ia) to 90 mol % (Ib) and in particular between 100 mol % (Ia) to 0 mol % (Ib) and 30 mol % (Ia) to 70 mol % (Ib).

The high-molecular polycarbonate derivatives from the diphenols of formula (Ia), if applica-

ble, in combination with other diphenols, may be made according to the known polycarbonate production methods. The different diphenols may be linked in a statistical manner as well as also
5 block-wise.

The polycarbonate derivatives used according to the invention may be branched in a per se known manner. If the branching is desired, this can be achieved in a per se known manner by con-
10 densation of small amounts, preferably amounts between 0.05 and 2.0 mol % (referred to the used diphenols), at three or more than three-functional compounds, in particular such with three or more than three phenolic hydroxyl groups.
15 Some branching agents with three or more than three phenolic hydroxyl groups are: phloroglucin, 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-
20 (4-hydroxyphenyl)-phenylmethane, 2,2-bis-[4,4-bis-(4-hydroxyphenyl)-cyclohexyl]-propane, 2,4-bis-(4-hydroxyphenyl-isopropyl)-phenol, 2,6-is-(2-hydroxy-5-methyl-benzyl)-4-methylphenol, 2-
25 (4-hydroxyphenyl)-2-(2,4-dihydroxyphenyl)-propane, hexa-[4-(4-hydroxyphenyl-isopropyl)-phenyl]-orthoterephthalic acid ester, tetra-(4-hydroxyphenyl)-methane, tetra-[4-(4-hydroxyphenyl-isopropyl)phenoxy]-methane and 1,4-bis-[4',4''-
30 dihydroxytriphenyl)-methyl]-benzene. Some of the other three-functional compounds are 2,4-dihydroxy benzoic acid, trimesic acid, cyanuric chloride and 3,3-bis-(3-methyl-4-hydroxyphenyl)-2-oxo-2,3-dihydroindol.

As chain stoppers for the per se known control of the molecular weight of the polycarbonate derivatives are used monofunctional compounds in usual concentrations. Suitable compounds are e.g. phenol, tert-butylphenols or other alkyl-substituted phenols. For controlling the molecular weight, in particular small amounts of phenols of formula (Ic) are suitable



(Ic)

wherein R is a branched C8 and/or C9-alkyl radical.

Preferably the share of CH₃ protons in the alkyl radical R is between 47 and 89 % and the share of the CH and CH₂ protons is between 53 and 11 %; also preferably R is in an o and/or p position to the OH group, and particularly preferably the upper limit of the ortho share is 20 %. The chain stoppers are used in general in amounts from 0.5 to 10, preferably 1.5 to 8 mol %, referred to the used diphenols.

The polycarbonate derivatives may preferably be made according to the phase boundary method (cf. H. Schnell *Chemistry and Physics of Polycarbonates*, Polymer Reviews, Vol. IX, page 33ff., Interscience Publ. 1964) in a per se known manner.

Herein, the diphenols of formula (Ia) are dissolved in an aqueous alkaline phase. For mak-

ing copolycarbonates with other diphenols, mix-
tures of diphenols of formula (Ia) and the other
diphenols, for instance those of formula (Ib),
are used. For controlling the molecular weight,
5 chain stoppers e.g. of formula (Ic) may be
added. Then a reaction is performed in presence
of an inert, preferably polycarbonate-dissolv-
ing, organic phase with phosgene according to
the method of the phase boundary condensation.
10 The reaction temperature is between 0 °C and 40
°C.

The, if applicable, also used branching
agents (preferably 0.05 to 2.0 mol %) may either
be presented with the diphenols in the aqueous
15 alkaline phase or be added dissolved in the or-
ganic solvent before the phosgenation. Beside
the diphenols of formula (Ia) and, if applica-
ble, other diphenols (Ib), thus their mono
and/or bis-chlorocarbonic acid esters can also
20 be used, the latter being added dissolved in or-
ganic solvents. The amount of chain stoppers and
of branching agents then depends on the molar
amount of diphenolate radicals corresponding to
formula (Ia) and, if applicable, formula (Ib);
25 when chlorocarbonic acid esters are also used,
the amount of phosgene can correspondingly be
reduced in a known manner.

Suitable organic solvents for the chain
stoppers and, if applicable, for the branching
30 agents and the chlorocarbonic acid esters are
for instance methylene chloride, chlorobenzene
and in particular mixtures of methylene chloride
and chlorobenzene. If applicable, the used chain
stoppers and branching agents can be dissolved
35 in the same solvent.

As an organic phase for the phase boundary polycondensation serve for instance methylene chloride, chlorobenzene and mixtures of methylene chloride and chlorobenzene.

5 As an aqueous alkaline phase serves for instance a NaOH solution. Making the polycarbonate derivatives according to the phase boundary method can be catalyzed in a usual manner by catalyzers such as tertiary amines, in particular
10 tertiary aliphatic amines such as tributylamine or triethylamine; the catalyzers can be used in amounts from 0.05 to 10 mol %, referred to the moles of used diphenols. The catalyzers can be added before the phosgenation or during
15 or also after the phosgenation.

The polycarbonate derivatives can be made according to the known method in a homogeneous phase, the so-called "pyridine method" and according to the known method for the transesterification of molten mass by using for instance
20 diphenyl carbonate instead of phosgene.

The polycarbonate derivatives may be linear or branched, they are homopolycarbonates or copolycarbonates based on the diphenols of formula
25 (Ia).

By the arbitrary composition with other diphenols, in particular with those of formula (Ib), the polycarbonate properties can be varied in a favorable manner. In such copolycarbonates,
30 the diphenols of formula (Ia) are contained in polycarbonate derivatives in amounts from 100 mol % to 2 mol %, preferably in amounts from 100 mol % to 10 mol % and in particular in amounts

from 100 mol % to 30 mol %, referred to the total amount of 100 mol % of diphenol units.

A particularly advantageous embodiment of the invention is characterized by that the polycarbonate derivative comprises a copolymer in particular consisting of monomer units M1 based on formula (Ib), preferably bisphenol A, and monomer units M2 based on the geminally disubstituted dihydroxydiphenyl cycloalkane, preferably of the 4,4'-(3,3,5-trimethyl cyclohexane-1,1-diyl)diphenol, wherein the molar ratio M2/M1 is preferably greater than 0.3, in particular greater than 0.4, for instance greater than 0.5. For such copolymers it has namely been found that surprisingly the glass temperature T_g below 150 °C after a first heating cycle may be increased in a second heating cycle, which can substantially improve the stability of the obtained structure.

It is preferred, if the polycarbonate derivative has an average molecular weight (mean weight) of at least 10,000, preferably of 20,000 to 300,000.

The component B may in principle be substantially organic or aqueous. Substantially aqueous means that up to 20 wt % of the component B can be organic solvents. Substantially organic means that up to 5 wt % water may be present in the component B. Preferably the component B comprises or consists of a liquid aliphatic, cycloaliphatic, and/or aromatic hydrocarbon, a liquid organic ester, and/or of a mixture of such substances. The used organic solvents are preferably halogen-free organic solvents. These

may in particular be aliphatic, cycloaliphatic, aromatic hydrocarbons, such as mesitylene, 1,2,4-trimethylbenzene, cumene and solvent naphtha, toluene, xylene; (organic) esters, such as methylacetate, ethylacetate, butylacetate, methoxypropylacetate, ethyl-3-ethoxypropionate. Preferred are mesitylene, 1,2,4-trimethylbenzene, cumene and solvent naphtha, toluene, xylene, acetic acid methyl ester, acetic acid ethyl ester, methoxypropylacetate, ethyl-3-ethoxypropionate. Particularly preferred are: mesitylene (1,3,5-trimethylbenzene), 1,2,4-trimethylbenzene, cumene (2-phenylpropane), solvent naphtha and ethyl-3-ethoxypropionate.

A suitable mixture of solvents comprises for instance L1) 0 to 10 wt %, preferably 1 to 5 wt %, in particular 2 to 3 wt %, of mesitylene, L2) 10 to 50 wt %, preferably 25 to 50 wt %, in particular 30 to 40 wt %, of 1-methoxy-2-propanolacetate, L3) 0 to 20 wt %, preferably 1 to 20 wt %, in particular 7 to 15 wt %, of 1,2,4-trimethylbenzene, L4) 10 to 50 wt %, preferably 25 to 50 wt %, in particular 30 to 40 wt %, of ethyl-3-ethoxypropionate, L5) 0 to 10 wt %, preferably 0.01 to 2 wt %, in particular 0.05 to 0.5 wt %, of cumene, and L6) 0 to 80 wt %, preferably 1 to 40 wt %, in particular 15 to 25 wt %, of solvent naphtha, the relative amounts of the components L1 to L6 always totaling 100 wt %.

Typically the first polycarbonate layer and the second polycarbonate layer have a glass temperature T_g of more than 145 °C, in particular more than 147 °C.

The polycarbonate derivative typically has an average molecular weight (mean weight) of at least 10,000, preferably from 20,000 to 300,000.

The preparation may comprise in detail: A) 0.1 to 10 wt %, in particular 0.5 to 5 wt %, of a binding agent with a polycarbonate derivative based on a geminally disubstituted dihydroxydiphenyl cycloalkane, B) 40 to 99.9 wt %, in particular 45 to 99.5 wt %, of an organic solvent or of a mixture of solvents, C) 0.1 to 6 wt %, in particular 0.5 to 4 wt %, of a dye or of a mixture of dyes, D) 0.001 to 6 wt %, in particular 0.1 to 4 wt %, of a functional material or of a mixture of functional materials, E) 0.1 to 30 wt %, in particular 1 to 20 wt %, of additive and/or auxiliary substances, or of a mixture of such substances.

If a dye should be provided, in principle any dye or mixture of dyes can be used as a component C. Dyes are all coloring substances. This means, they may be dyes (a survey of dyes is given in *Ullmann's Encyclopedia of Industrial Chemistry*, Electronic Release 2007, Wiley Verlag, chapter "Dyes, General Survey"), as well as pigments (a survey of organic and inorganic pigments is given in *Ullmann's Encyclopedia of Industrial Chemistry*, Electronic Release 2007, Wiley Verlag, chapter "Pigments, Organic" and "Pigments, Inorganic"). Dyes should be soluble or (stably) dispersible or suspensible in the solvents of the component B. Furthermore, it is advantageous, if the dye is stable, in particular color-stable at temperatures of 160 °C and more for a period of more than 5 min. It is also possible that the dye is subjected to a given

and reproducible color change under the processing conditions and is selected correspondingly. Pigments must be present, in addition to the temperature stability, in particular in a finest particle size distribution. In the practice of ink jet printing this means that the particle size should not exceed 1.0 μm , since otherwise occlusions in the printing head will result. Normally, nano-scale solid pigments have proven themselves.

The dyes may be kationic, anionic or also neutral. Examples for dyes used in ink jet printing are: Brillantschwarz C.I. Nr. 28440, Chromogenschwarz C.I. Nr. 14645, Direkttiefschwarz E C.I. Nr. 30235, Echtschwarzsatz B C.I. Nr. 37245, Echtschwarzsatz K C.I. Nr. 37190, Sundanschwarz HB C.I. 26150, Naphtolschwarz C.I. Nr. 20470, Bayscript® Schwarz Flüssig, C.I. Basic Black 11, C.I. Basic Blue 154, Cartasol® Türkis K-ZL Flüssig, Cartasol® Türkis K-RL Flüssig (C.I. Basic Blue 140), Cartasol Blau K5R Flüssig. Suitable are further e.g. the commercially obtainable dyes Hostafine® Schwarz TS Flüssig (sold by Clariant GmbH Germany), Bayscript® Schwarz Flüssig (C.I. mixture, sold by Bayer AG Germany), Cartasol® Schwarz MG Flüssig (C.I. Basic Black 11, registered trademark of Clariant GmbH Germany), Flexonylschwarz® PR 100 (E C.I. Nr. 30235, sold by Hoechst AG), Rhodamin B, Cartasol® Orange K3 GL, Cartasol® Gelb K4 GL, Cartasol® K GL, or Cartasol® Rot K-3B. Further, as soluble dyes can be used anthraquinone, azo, quinophthalone, cumarin, methin, perinone, and/or pyrazole dyes, e.g. obtainable under the trade name Macrolex®. Further suitable dyes are described in the document *Ullmann's Encyclopedia*

of Industrial Chemistry, Electronic Release
2007, Wiley Verlag, chapter "Colorants Used in
Ink Jet Inks". Well soluble dyes will lead to an
optimum integration in the matrix or the binder
5 of the printing layer. The dyes can be added ei-
ther directly as a dye or pigment or as a paste,
a mixture of dye and pigment together with an
additional binder. This additional binder may be
different from a binder according to the inven-
10 tion (e.g. may be a polyester), should however
be chemically compatible with the additional
components of the preparation used according to
the invention. If such a paste is used as a dye,
the amount of the component B refers to the dye
15 without the other components of the paste. These
other components of the paste must then be sub-
sumed under the component E. When using so-
called colored pigments in the scale colors
cyan-magenta-yellow and preferably also (soot-)
20 black, full-tone color images are possible.

The component D comprises substances, which
by using technical means can immediately be seen
by the human eye or by using suitable detectors.
These are materials familiar to the man skilled
25 in the art (cf. also van Renesse, *Optical Docu-
ment Security*, 3rd ed., Artech House, 2005),
which are used for the protection of value and
security documents. Thereto belong luminescent
substances (dyes or pigments, organic or inor-
30 ganic) such as e.g. photoluminophores, elec-
troluminophores, anti-Stokes luminophores,
fluorophores, but also magnetizable, photo-
acoustically addressable or piezoelectric mate-
rials. Furthermore, Raman-active or Raman-ampli-
35 fying materials can be used, same as so-called
barcode materials. Here, too, the preferred cri-

teria are either the solubility in the component B or for pigmented systems particle sizes $< 1 \mu\text{m}$ and temperature stability for temperatures $> 160^\circ\text{C}$ in the meaning of the explanations with regard to the component C. Functional materials can directly be added or via a paste, i.e. mixture with an additional binder, which is then a constituent of the component E, or the binder of the component A used according to the invention.

The component E comprises the substances normally used for inks in ink jet printing, such as anti-foam agents, set-up agents, wetting agents, tensides, floating agents, drying agents, catalyzers, (light) stabilizers, preservation agents, biocides, tensides, organic polymers for viscosity adjustment, buffer systems, etc. Set-up agents are for instance conventional set-up salts. An example is sodium lactate. As biocides may be used all commercially available preservation agents, which are used for inks. Examples are Proxel®GXL and Parmetol® A26. Tensides may be all commercially available tensides, which are used for inks. Preferred are amphoteric or non-ionic tensides. Of course, however, the use of special anionic or cationic tensides, which do not alter the properties of the dye, is also possible. Examples for suitable tensides are betaines, ethoxilated diols etc. Examples are the product series Surfynol® and Tergitol®. The amount of tensides is for instance selected such that the surface tension of the ink is in the range from 10 to 60 mN/m, preferably from 25 to 45 mN/m, measured at 25°C . A buffer system may be provided, which stabilizes the pH value in the range from 2.5 to 8.5, in particular in the range from 5 to 8. Suitable buffer systems are

lithium acetate, borate buffer, triethanolamine or acetic acid/sodium acetate. A buffer system will in particular be applied in the case of a substantially aqueous component B. For adjusting the viscosity of the ink, (if applicable) water-soluble polymers may be provided. These may be all polymers being suitable for conventional ink formulations. Examples are water-soluble starch, in particular with an average molecular weight from 3,000 to 7,000, polyvinylpyrrolidone, in particular with an average molecular weight from 25,000 to 250,000, polyvinyl alcohol, in particular with an average molecular weight from 10,000 to 20,000, xanthan gum, carboxymethyl cellulose, ethylene oxide/propylene oxide block copolymer, in particular with an average molecular weight from 1,000 to 8,000. An example for the above block copolymer is the product series Pluronic®. The share of biocide, referred to the total amount of ink, may be in the range from 0 to 0.5 wt %, preferably from 0.1 to 0.3 wt %. The share of tenside, referred to the total amount of ink, may be in the range from 0 to 0.2 wt %. The share of set-up agents, referred to the total amount of ink, may be from 0 to 1 wt %, preferably from 0.1 to 0.5 wt %.

To the auxiliary agents also belong all other components, such as for instance acetic acid, formic acid or n-methyl pyrrolidone or other polymers from the used dye solution or paste.

With regard to substances, which are suitable as component E, reference is made for instance to *Ullmann's Encyclopedia of Chemical Industry*, Electronic Release 2007, Wiley Verlag,

chapter "Paints and Coatings", section "Paint Additives".

5 The invention further relates to a method for making a structure with at least one first polymer layer and, optionally, a second polymer layer, each made from a polycarbonate polymer based on bisphenol A, wherein on the first polymer layer an ink jet printing layer is arranged, comprising the following steps: a) on at least
10 one partial region of the first polymer layer, the ink jet printing layer from a preparation used according to the invention is applied, b) optionally, the ink jet printing layer is dried, c) optionally after step a) or step b), the second polymer layer is placed on the first polymer layer, covering the ink jet printing layer, and
15 the first polymer layer and the second polymer layer are laminated with each other under pressure, at a temperature from 120 °C to 230 °C and
20 for a defined time.

In other words, a structure according to the invention may only consist of a polymer layer and of a printing layer applied by means of the preparation used according to the invention, may
25 however also comprise another polymer layer, if applicable, in another structure with additional layers. It is for instance possible that the printing layer is provided as the uppermost layer within a structure (if applicable, with
30 additional layers). Further, the printing layer can be imprinted directly and without another cover on a polymer layer adapted as an overlay film.

The ink jet printing layer may be provided over the full surface on the first polymer layer. In most cases, however, the ink jet printing layer will be provided in a partial region only of the surface of the first polymer layer.

The specific pressure (pressure directly at the workpiece) in step d) is typically in the range from 1 bar to 10 bars, in particular in the range from 3 bars to 7 bars. The temperature in step d) is preferably in the range from 140 °C to 200 °C, in particular in the range from 150 °C to 180 °C. The time of the step d) may be in the range from 0.5 s to 120 s, in particular from 5 s to 60 s.

In step b), drying can be performed at a temperature in the range from 20 °C to 120 °C, in particular from 20 °C to 80 °C, preferably from 20 °C to 60 °C, for a time of at least 1 s, preferably from 5 s to 6,000 s.

The first polycarbonate layer and the second polycarbonate layer may, independently from each other, have a glass temperature T_g of more than 145 °C.

The thickness of the first polycarbonate layer and of the second polycarbonate layer may be, identical or different, in the range from 10 to 1,000 μm , in particular from 20 to 200 μm .

The thickness, measured in directions orthogonal to a main face of a polycarbonate layer, of the ink jet printing layer may be, before or after drying, in the range from 0.01 to

10 μm , in particular from 0.05 to 5 μm , preferably from 0.02 to 1 μm .

5 Subject matter of the invention is also a structure obtainable with a method according to the invention. Such a structure typically contains at least one first polycarbonate layer and a second polycarbonate layer and an ink jet printing layer from a preparation used according to the invention and arranged between the first
10 polycarbonate layer and the second polycarbonate layer.

15 A method according to the invention for making a structure may be used for making a security and/or value document, wherein optionally simultaneously with, before or after the production of the structure, the first polycarbonate layer and/or the second polycarbonate layer are directly or indirectly connected in a stack with at least one additional layer, for instance a
20 carrier layer.

25 Examples for security and/or value documents are: identity cards, passports, ID cards, access control cards, visas, tax symbols, tickets, driver's licenses, vehicle documents, banknotes, checks, postage stamps, credit cards, any chip cards and adhesive labels (e.g. for product protection). Such security and/or value documents typically comprise at least one substrate, a printing layer and optionally a transparent
30 cover layer. Substrate and cover layer themselves may be composed of a multitude of layers. A substrate is a carrier structure, onto which the printing layer with information, images, patterns and the like is applied. As materials

for a substrate, all conventional materials on a paper and/or (organic) polymer basis can be used. Such a security and/or value document comprises within the total multi-layer structure a structure according to the invention. Beside the structure according to the invention, at least one (additional) printing layer may be provided, which may be applied on an external surface of the structure or on an additional layer connected with the structure.

Finally, the invention relates to a security and/or value document to be thus made or comprising a structure according to the invention.

The invention can however also be used in other technical fields. Abrasion-resistant decorations of injection-molded parts can be made by in-mold lamination of films. According to prior art, PC films are imprinted by silk-screen printing, plastically deformed (e.g. deep-drawing), placed in an injection mold and in-mold laminated with a thermoplastic material. In this way, e.g. casings for mobile phones or decorative housings are made. Multi-colored decorations require the production of several printing forms/printing screens and are therefore only economical for high quantities. With an ink used according to the invention, however, also piece productions or unique motives are possible, and thus e.g. individualized, highly abrasion-resistant casings for mobile phones (for example with a photograph) or personalized tachometer discs (e.g. initials of the owner) can be produced.

Therefore, the invention also relates to a method for making a structure with at least one

polymer layer and an injection-molded part from a polymer material, wherein between the polymer layer and the injection-molded part an ink jet printing layer is arranged, comprising the following steps: a) on at least one partial region of the polymer layer, the ink jet printing layer from a preparation used according to the invention is applied, b) optionally, the ink jet printing layer is dried, c) after step a) or step b), the polymer layer is placed in an injection mold (if necessary after plastic deformation of the imprinted polymer layer for fitting to the walls of the injection mold), the ink jet printing layer showing toward inside, d) into the injection mold, the polymer material is injected at a temperature of at least 60 °C, and e) after cooling-off to a temperature of at least 20 °C below the temperature of the step d), the structure is taken from the injection mold.

The polymer layer may preferably be a polycarbonate layer based on bisphenol A. As polymer materials, in principle all thermoplastic polymers usual in the field of plastic injection can be used.

The temperature in step d) may be in the range from 80 °C to 200 °C, in particular in the range from 100 °C to 180 °C. The temperature in step e) may be at least 40 °C below the temperature in step d).

In principle, otherwise all explanations given in the context with a structure for a security and/or value document will apply in an analogous manner.

Therefore, the invention also comprises a structure comprising at least one polycarbonate layer and an injection-molded part and an ink jet printing layer from a preparation used according to the invention and arranged between the polycarbonate layer and the injection-molded part.

In the following, the invention is described in more detail with reference to non-limiting embodiments. There are:

Figure 1: a representation of a test print area, and

Figure 2: details of a portrait of a person made by a method according to the invention.

Example 1: making polycarbonate derivatives to be used according to the invention.

Example 1.1: making a first polycarbonate derivative.

205.7 g (0.90 mole) bisphenol A (2,2-bis-(4-hydroxyphenyl)-propane, 30.7 g (0.10 mole) 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethyl cyclohexane, 336.6 g (6 mole) KOH and 2,700 g water are dissolved in an inert gas atmosphere under stirring. Then a solution of 1.88 g phenol in 2,500 ml methylene chloride is added. Into the well stirred solution, 198 g (2 mole) phosgene are introduced at pH 13 to 14 and 21 to 25 °C. Then 1 ml ethylpiperidine is added and stirred for another 45 min. The bisphenolate-free aqueous phase is separated, after acidification with

phosphoric acid, the organic phase is washed neutrally with water and freed from solvent.

5 The polycarbonate derivative had a relative solution viscosity of 1.255. The glass temperature was determined to be 157 °C (DSC).

Example 1.2: making a second polycarbonate derivative.

10 In an analogous manner to Example 1, a mixture of 181.4 g (0.79 mole) bisphenol A and 63.7 g (0.21 mole) 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethyl cyclohexane was reacted to the polycarbonate derivative.

15 The polycarbonate derivative has a relative solution viscosity of 1.263. The glass temperature was determined to be 167 °C (DSC).

Example 1.3: making a third polycarbonate derivative.

20 In an analogous manner to Example 1, a mixture of 149.0 g (0.65 mole) bisphenol A (2,2-bis-(4-hydroxyphenyl)-propane and 107.9 g (0.35 mole) 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethyl cyclohexane was reacted to the polycarbonate derivative.

25 The polycarbonate derivative had a relative solution viscosity of 1.263. The glass temperature was determined to be 183 °C (DSC).

Example 1.4: making a fourth polycarbonate derivative.

5 In an analogous manner to Example 1, a mixture of 91.6 g (0.40 mole) bisphenol A and 185.9 g (0.60 mole) 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethyl cyclohexane was reacted to the polycarbonate derivative.

The polycarbonate derivative had a relative solution viscosity of 1.251. The glass temperature was determined to be 204 °C (DSC).

10 Example 1.5: making a fifth polycarbonate derivative.

As in Example 1, a mixture of 44.2 g (0.19 mole) bisphenol A and 250.4 g (0.81 mole) 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethyl cyclohexane was reacted to the polycarbonate.

15 The polycarbonate derivative had a relative solution viscosity of 1.248. The glass temperature was determined to be 216 °C (DSC).

Example 2: making a liquid preparation being suitable for making an ink jet printing dye.

20 A liquid preparation was made from 17.5 weight parts of the polycarbonate derivative from Example 1.3 and 82.5 weight parts of a solvent mixture according to Table I.

Table I

25	Mesitylene	2.4
	1-methoxy-2-propanolacetate	34.95
	1,2,4-trimethylbenzene	10.75

Ethyl-3-ethoxypropionate	33.35
Cumol	0.105
Solvent naphtha	18.45

5 A colorless, highly viscous solution with a solution viscosity of 800 mPa·s at ambient temperature was obtained.

Example 3: making a first ink jet printing dye used according to the invention.

10 In a 50 mL wide-neck thread glass, 4 g polycarbonate solution of Example 2 and 30 g of the mixture of solvents of Example 2 were homogenized with a magnetic stirrer. A colorless, low-viscous solution with a solution viscosity of 1.67 mPa·s at ambient temperature was obtained.

15 The surface tension of this basic ink was determined with an OEG Surftens measuring system according to the pendant drop method to be $21.4 \pm 1,9$ mN/m.

20 An addition of a pigment or of a dye was not made, since this ink only served for use in the test print of Example 6.

Example 4: making a second ink jet printing dye used according to the invention.

25 In an analogous manner to Example 3, 10 g polycarbonate solution of Example 2 and 32.5 g mixture of solvents of Example 2 were homogenized with a magnetic stirrer (4 % PC solution).

A colorless, low-viscous solution with a solution viscosity of 5.02 mPa·s at 20 °C was obtained. Here, too, no addition of a pigment or dye was made, since this ink only served for use
5 in the test print of Example 7.

Example 5: making a third ink jet printing dye used according to the invention.

A polycarbonate solution according to Example 4 was prepared and additionally reacted with
10 approx. 2 % pigment Black 28. An ink results, by means of which black & white images can be printed on polycarbonate films, and reference is made to Example 8.

Example 6: drop size when printing with an
15 ink according to Example 3.

The solution of Example 3 was transferred by filtration into a printer cartridge and printed with an ink jet printer FUJIFILM-Dimatix DMP 2800 under variation of various printing parameters. The used printer is a so-called drop-on-demand system, wherein the drop generation is
20 made by a piezoelectric printing head. The DMP 2800 has a stroboscopic image recording system, by means of which the drop formation and the drop path can be investigated. The prints were
25 dried at 100 °C for 30 min. Depending on the base, different drop sizes can be achieved, as is shown in Table 1.

Table 1

	Substrate	Glass	Polycarbonate (smooth)	Velin paper
5	Ø individual drops	~ 74µm	~ 85µm	~ 100µm

As expected, on sucking bases, the drops will be absorbed more than on non-sucking bases such as glass or plastic.

10 Example 7: determination of the layer thickness of an ink jet printing layer.

An ink according to Example 4 was printed on glass substrates. The so-called drop distance (pitch, see also Figure 1) varied from 10 to 45
15 µm. The prints were again dried at 100 °C for 30 min. Then layer thickness measurements were made (Arithmetic Step Height = ASH) with a profilometer (Dektak 6M; 12.5 µm Stylus), and the results are listed in Table 2.

20 Table 2

	Pitch	ASH [nm]
	10 µm	685
25	30 µm	100
	45 µm	27

By the drop distance alone, the layer thickness can be adjusted in a wide range.

Example 8: making an image and verifying the optical quality after the lamination.

Using the ink of Example 5, a portrait of a person was printed on Makrofol® 4-4. The thus produced portrait was laminated together with transparent Makrofol® 6-2-films at temperatures > 180 °C, pressures > 5 bar and times > 10 min to form a structure of approx. 800 µm thickness. Light-microscopic investigations before and after the lamination were made, in order to evaluate the edge definition of individual pixels. The results are shown in Figure 2. There are shown on top in Figure 2 colored printing images (top) and thereunder the same printing images, however after conversion into black & white. On the left side, there is shown a detailed representation of the ink jet printing layer made according to the invention before the lamination. On the right side, the same detailed representation is shown after the lamination. It can be seen that the pixel patterns are maintained also after the lamination in nearly the same resolution. The horizontal lines result from the overlapping sections of the individual ink jet nozzles of the printing head and have therefore nothing to do with the ink according to the invention.

Apart from that, an optical investigation of the structure did not show any recognizable phase limit. The structure is a monolithic block excellently resisting to delamination.

Patent claims:

1. The use of a preparation comprising

A) 0.1 to 20 wt % of a binding agent with a polycarbonate derivative based on a geminally
5 disubstituted dihydroxydiphenyl cycloalkane,

B) 30 to 99.9 wt % of a solvent or of a mixture of solvents,

C) 0 to 10 wt %, referred to dry mass, of a dye or of a mixture of dyes,

10 D) 0 to 10 wt % of a functional material or of a mixture of functional materials,

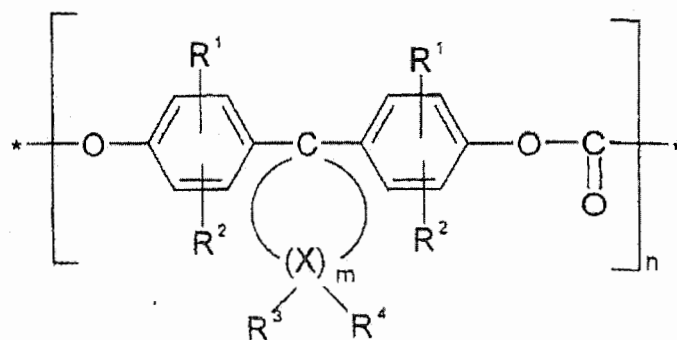
E) 0 to 30 wt % of additive and/or auxiliary substances, or of a mixture of such substances,

15 the relative amounts of the components A) to E) always totaling 100 wt %,

as an ink jet printing dye.

2. The use according to claim 1, wherein the polycarbonate derivative has an average molecular weight (mean weight) of at least 10,000,
20 preferably from 20,000 to 300,000.

3. The use according to one of claims 1 or 2, wherein the polycarbonate derivative comprises functional carbonate structure units of formula (I),



(I)

wherein

R¹ and R² are independently from each other hydrogen, halogen, preferably chlorine or bromine, C₁-C₈ alkyl, C₅-C₆ cycloalkyl, C₆-C₁₀ aryl, preferably phenyl, and C₇-C₁₂ aralkyl, preferably phenyl-C₁-C₄ alkyl, in particular benzyl,

m is an integer from 4 to 7, preferably 4 or 5,

R³ and R⁴ can be individually selected for each X, and independently represent hydrogen or C₁-C₆ alkyl

X is carbon and

n is an integer greater than 20,

with the proviso that at at least one atom X, R³ and R⁴ are both alkyl.

4. The use according to claim 3, wherein at 1 to 2 atoms X, in particular at only one atom X, R³ and R⁴ are both alkyl.

5. A method according to claim 3 or 4, wherein R³ and R⁴ are methyl.

6. The use according to one of claims 3 to 5, wherein the X atoms in the alpha position to the diphenyl-substituted C atom (C1) are not dialkyl-substituted.

5 7. The use according to one of claims 3 to 6, wherein the X atoms in the beta position to C1 are disubstituted with alkyl.

8. The use according to one of claims 3 to 7, wherein m is 4 or 5.

10 9. The use according to one of claims 3 to 8, wherein the polycarbonate derivative is based on

4,4'-(3,3,5-trimethyl cyclohexane-1,1-diyl) diphenol,

15 4,4'-(3,3-dimethyl cyclohexane-1,1-diyl) diphenol, or

4,4'-(2,4,4-trimethyl cyclopentane-1,1-diyl) diphenol.

20 10. The use according to one of claims 1 to 9, wherein the polycarbonate derivative comprises a copolymer in particular consisting of monomer units M1 based on formula (Ib), for instance based on bisphenol A, and monomer units M2 based on the geminally disubstituted dihydroxydiphenyl cycloalkane, preferably of the
25 4,4'-(3,3,5-trimethyl cyclohexane-1,1-diyl) diphenol, wherein the molar ratio M2/M1 preferably

is greater than 0.3, in particular greater than 0.4, preferably greater than 0.5.

11. The use according to one of claims 1 to 10, wherein the component B) is halogen-free.

5 12. The use according to one of claims 1 to 11, wherein the component B) consists of a liquid aliphatic, cycloaliphatic, and/or aromatic hydrocarbon, a liquid organic ester, and/or of a mixture of such substances.

10 13. The use according to claim 12, wherein the hydrocarbon and/or the organic ester is selected from the group consisting of "mesitylene, 1,2,4-trimethylbenzene, cumene, solvent naphtha, toluene, xylene, methylacetate, ethylacetate, 15 butylacetate, methoxypropylacetate, ethyl-3-ethoxypropionate".

14. The use according to claim 13, wherein the component B) consists of:

20 L1) 0 to 10 wt %, preferably 1 to 5 wt %, in particular 2 to 3 wt %, of mesitylene,

 L2) 10 to 50 wt %, preferably 25 to 50 wt %, in particular 30 to 40 wt %, of 1-methoxy-2-propanolacetate,

25 L3) 0 to 20 wt %, preferably 1 to 20 wt %, in particular 7 to 15 wt %, of 1,2,4-trimethylbenzene,

L4) 10 to 50 wt %, preferably 25 to 50 wt %, in particular 30 to 40 wt %, of ethyl-3-ethoxypropionate,

5 L5) 0 to 10 wt %, preferably 0.01 to 2 wt %, in particular 0.05 to 0.5 wt %, of cumene, and

L6) 0 to 80 wt %, preferably 1 to 40 wt %, in particular 15 to 25 wt %, of solvent naphtha,

10 the relative amounts of the components L1 to L6 always totaling 100 %.

15. The use according to one of claims 1 to 14, wherein the preparation comprises:

15 A) 0.1 to 10 wt %, in particular 0.5 to 5 wt %, of a binding agent with a polycarbonate derivative based on a geminally disubstituted dihydroxydiphenyl cycloalkane,

B) 40 to 99.9 wt %, in particular 45 to 99.5 wt %, of an organic solvent or of a mixture of solvents,

20 C) 0.1 to 6 wt %, in particular 0.5 to 4 wt %, of a dye or of a mixture of dyes,

D) 0.001 to 6 wt %, in particular 0.1 to 4 wt %, of a functional material or of a mixture of functional materials,

25 E) 0.1 to 30 wt %, in particular 1 to 20 wt %, of additive and/or auxiliary substances, or of a mixture of such substances.

16. A method for making a structure with at least one first polymer layer and, optionally, a

second polymer layer, each made from a polycarbonate polymer based on bisphenol A, wherein on the first polymer layer an ink jet printing layer is arranged, comprising the following steps:

a) on at least one partial region of the first polymer layer, the ink jet printing layer from a preparation according to one of claims 1 to 15 is applied,

b) optionally, the ink jet printing layer is dried,

c) optionally after step a) or step b), the second polymer layer is placed on the first polymer layer, covering the ink jet printing layer, and the first polymer layer and the second polymer layer are laminated with each other under pressure, at a temperature from 120 °C to 230 °C and for a defined time.

17. The method according to claim 16, wherein the temperature in step d) is in the range from 140 °C to 200 °C, in particular in the range from 150 °C to 180 °C.

18. The method according to one of claims 16 or 17, wherein the first polycarbonate layer and the second polycarbonate layer have a glass temperature T_g of more than 145 °C.

19. The method according to one of claims 16 to 18, wherein the thickness of the first polycarbonate layer and of the second polycarbonate

layer is up to 1,000 μm , in particular from 20 to 200 μm .

5 20. The method according to one of claims 16 to 19, wherein the thickness, measured in directions orthogonal to a main face of a polycarbonate layer, of the ink jet printing layer is in the range from 0.01 to 10 μm , in particular from 0.05 to 5 μm .

10 21. A structure obtainable with a method according to one of claims 16 to 20.

15 22. The structure comprising at least one first polycarbonate layer and an ink jet printing layer from of a preparation according to one of claims 1 to 15 and arranged on the first polycarbonate layer, wherein optionally on the side of the printing layer opposite to the first polycarbonate layer, a second polycarbonate layer may be arranged.

20 23. The use of a method according to one of claims 16 to 20 for making a security and/or value document, wherein optionally simultaneously with, before or after the production of the structure, the first polycarbonate layer and/or the second polycarbonate layer are directly or indirectly connected in a stack with
25 at least one additional layer, for instance a carrier layer.

24. The security and/or value document obtainable according to claim 23.

25. The security and/or value document comprising a structure according to claim 21 or 22.

5 26. A method for making a structure with at least one polymer layer and an injection-molded part from a polymer material, wherein between the polymer layer and the injection-molded part an ink jet printing layer is arranged, comprising the following steps:

10 a) on at least one partial region of the polymer layer, the ink jet printing layer from a preparation according to one of claims 1 to 15 is applied,

15 b) optionally, the ink jet printing layer is dried,

 c) after step a) or step b), the polymer layer is placed in an injection mold, the ink jet printing layer showing toward inside,

20 d) into the injection mold, the polymer material is injected at a temperature of at least 60 °C, and

 e) after cooling-off to a temperature of at least 20 °C below the temperature of step d),
25 the structure is taken from the injection mold.

27. The method according to claim 26, wherein the temperature in step d) is in the range from 80 °C to 200 °C, in particular in the

range from 100 °C to 180 °C, and/or wherein the temperature in step e) is at least 40 °C below the temperature in step d).

5 28. The method according to one of claims 26 or 27, wherein the polycarbonate layer has a glass temperature T_g of more than 145 °C.

10 29. The method according to one of claims 26 to 28, wherein the thickness of the polycarbonate layer is in the range from 10 to 1,000 µm, in particular from 20 to 200 µm.

15 30. The method according to one of claims 26 to 29, wherein the thickness, measured in directions orthogonal to a main face of the polycarbonate layer, of the ink jet printing layer is in the range from 0.01 to 10 µm, in particular from 0.05 to 5 µm.

31. The structure obtainable with a method according to one of claims 26 to 30.

20 32. The structure comprising at least one polycarbonate layer and an injection-molded part and an ink jet printing layer from a preparation according to one of claims 1 to 15 and arranged between the polycarbonate layer and the injection-molded part.