

METHOD FOR PRINTING A LAYER ON A PORTABLE CARRIER BODY, NOTABLY A MEMORY CARD, AND A CARRIER BODY PRINTED ACCORDING TO SUCH A METHOD

The invention relates to the field of printing and concerns more particularly the printing of a visible thermoplastic or thermosetting polymerised layer of a portable information carrier body.

The term printing must be considered, in the present invention, in a broad sense, as being a technique in which an action is exerted on an object so as to leave a visible mark on the said object. The portable information carrier can be of any type. It is however a case notably of a standard information carrier in the chip card format to which reference will be made in the following description.

8-5453080

Chip cards and, more generally, memory cards, have a thermoplastic or thermosetting card body formed by one or more layers. Two faces of the said body are visible. These faces show a drawing, a logo, a photographic reproduction and, very often, written information printed in series according to various known methods.

Some printing methods use the simple deposition of a conventional ink. Other methods, generally more rapid and precise, use lasers.

Amongst the latter, methods are known in which a heat transfer of a coloured ink is effected by means of a laser and from a heat-resistance transfer film applied to one face of the polymerised card body. With different films or different segments of the same film containing inks of different colours, a card body is obtained showing a coloured pattern according to the travel of the laser radiation on the film or films. However, such methods, referred to as indirect, require an intermediary film from which the inks will be diffused, and are therefore slow. In addition, given that the diameter of the laser radiation applied to the film or films must be sufficient so that the inks can be transferred to the surface and/or into the card body and that, in addition, the coloured inks, which were not initially present in the card body, may diffuse in

the said body, the definition of the pattern obtained is mediocre.

In other known methods, a given area of a top layer of a multi-layer card body is removed, by virtue of a laser of the YAG type adjusted so as to emit an electromagnetic radiation in the infrared region, so that a sub-layer of the said body, whose colour is different from that of the top layer, appears. With several superimposed layers of different colours, it is possible to obtain a multi-colour card body where the pattern is defined by a directed scanning of the laser radiation. However, the removal of all the layers or sub-layers which cover a sub-layer in order to obtain a given colour in a predetermined area of the said sub-layer requires in theory several passages of the laser, which extends the duration of the processes. In addition, products are wasted and the surface of the printed card body does not remain intact since it shows differences in relief. Because of this, it is not always possible to correctly place, on the said card body, a perfectly flat transparent film.

Yet other methods propose either an evaporation of particular areas of the surface of the card body, or a foaming of the said areas. This evaporation or foaming are caused by the heat released from a laser radiation. The evaporation leaves a hole and can cause a coloured

sub-layer on the card body to appear. Foaming changes the nature of the surface of the card body, which for example shows differences in refractive index giving rise to the patterns. These methods are in general slow and the definition of the pattern, and its contrast, are mediocre. In addition, as before, the surface of the card body does not remain intact.

Finally, so-called bleaching methods propose a directed and selective destruction of pigments or other coloured molecules contained in a layer of the card body by means of laser whose radiation is emitted in the visible range. The colour appears negatively. Thus, in order to cause a given colour to appear, two laser irradiations are necessary. For example, in order to cause blue to appear on the surface of a black layer of a card body having blue, red and yellow pigments all together, two laser radiations locally destroy, one of them the red pigments and the other the yellow pigments. If it is wished to obtain white, the black layer of the card body is irradiated with three laser radiations of different wavelengths. These methods are slow since obtaining a colour at a given point requires several irradiations. In addition, the white obtained is imperfect since the destruction of the pigments or coloured molecules is never complete and, in practice, it is found that the colours obtained are pale.

Considering the aforementioned state of the art, a problem which the invention sets out to resolve is to propose a novel method of printing in series a visible thermoplastic or setting polymerised layer on a portable information carrier body, which is fast and which leaves the surface of the said layer intact.

The object of the claimed solution of the invention is a method of printing a visible thermoplastic or setting polymerised layer on a portable information carrier body, characterised in that it includes the following steps:

- mixing

- a thermoplastic or setting polymerisable binder, and

- at least one photochromic compound sensitive to laser radiation of a given wavelength so as to change from a first state to a second coloured state,

- with a view to forming a mixture;

- irradiating the mixture by means of a laser radiation of a given wavelength,

- fixing the second coloured state; and

- polymerising the mixture so as to form the polymerised layer of the carrier body.

Thus, in order to obtain a given colour, a positive process is carried out: the suitable photochromic compound is irradiated with a single laser radiation with a chosen wavelength.

In addition, an object of the invention is a portable information carrier having a visible printed thermoplastic or setting polymerised layer on a carrier body, characterised in that the said polymerised layer contains:

- a thermoplastic or setting polymerised binder;

and

- at least one photochromic compound fixed in a second coloured state obtained from a first state by irradiation by means of a laser radiation of given wavelength.

The following description will give a better understanding of the way in which the invention can be put into practice. It is drafted with regard to a non-limitative example embodiment relating to a memory carrier in a card format of the chip card type.

However, it is to be understood that the invention applies to any information carrier, of any kind, in so far as the said carrier has a visible thermoplastic or setting polymerised layer.

Chip cards principally contain a micromodule included in a card body.

The micromodule is composed of an integrated circuit chip connected to metallic pads forming metallisations showing on the surface of the body of the card and/or an antenna embedded in the said body. Depending on whether the micromodule is connected to an antenna or to pads, the chip card is said respectively to be of contactless operation or operation with contacts. Where the card has two functioning modes, it is said to be hybrid.

The card body is a rectangular parallelepiped of small thickness whose dimensions, as defined notably by standard 7810, are around 85 mm in length, 54 mm in width and 0.76 mm in thickness. The card body shows thereby six faces, including two large parallel flat faces. It is composed of one or more superimposed layers, one layer of the said body appearing on each of the large faces. These visible layers are printed and show any pattern, coloured or otherwise. They are possibly covered with a transparent protective film.

The different layers of the card body and, in particular, the visible layers of the said body, are polymerised thermoplastic or thermo- or photosetting. They therefore comprise a polymer with one or more monomers. Monomers are for example: acrylonitrile butadiene styrene (ABS), polycarbonate (PC), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polymethyl methacrylate (PMMA) or any other polymeric derivative of the acrylic or methacrylic system.

The layer or layers of the card body are white or whitish in colour. This colour can be improved by adding, to the composition of the card body, a mineral filler, for example calcium carbonate or titanium dioxide. It should be noted that the white colour is not limitative and that certain card bodies are, before printing, coloured or even transparent in the case of a card body made of PMMA for example.

The printing method of the invention includes different steps.

A first step relates to a mixing, in the liquid phase, of at least one polymerisable binder, at least one photochromic compound and, advantageously, at least

one reagent. The mixture obtained is liquid, more or less viscous.

The polymerisable binder is a binder intended to form the polymerised structure or polymeric lattice of the visible layer or layers of the card body and the other layers of the said body. It contains one or more monomers or oligomers, one or more polymers, a reagent for the polymerisation of the said monomers or oligomers, a reagent intended for a polymerisation or even a post-polymerisation of the polymers, and various compounds or additives, for example a mineral filler intended for bleaching the card and a solvent.

The photochromic compounds are compounds able to undergo a reversible transformation caused by an electromagnetic radiation between two states having different absorption spectra. A first state is characterised by a first absorption spectrum which contains at least one absorption band and a second state is characterised by a second absorption spectrum which also contains at least one absorption band. In their first state, the photochromic compounds are normally colourless and their absorption spectrum does not belong to the visible range, i.e. to the range whose wavelengths are between 400 and 780 nm. However, an absorption band of the said spectrum is situated outside the visible range, in the ultraviolet range,

i.e. in the range where the wavelengths are between 20 and 400 nm. Preferentially, the said band is situated in a range from 200 to 400 nm. Thus an electromagnetic radiation whose wavelength is situated in the aforementioned absorption band is able to cause a transformation of the photochromic compound, from the first state to the second. This transformation can be unimolecular or bimolecular. The time taken for passing from the first state to the second state is very short, less than around 20 ns, in one example 40 to 50 ps, for spironaphthooxazines. In their second state, the photochromic compounds absorb some of the light which they receive, since their absorption spectrum contains, in this second state, bands situated in the visible range. The said photochromic compounds therefore appear coloured. The transformation is reversible and, given that the second state is metastable, a photochromic compound in its second state is able to transform itself into its first, more stable state. According to the way in which the transformation of the photochromic compounds takes place from the second state to the first state, the said compounds are either photoreversible, or thermoreversible, or photothermoreversible, or multiphotochromic or electrochemical.

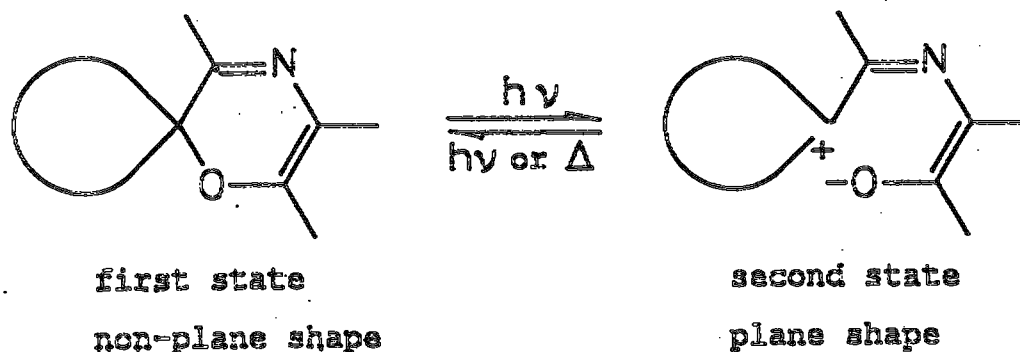
The photochromic compounds of the invention can simply be dissolved in the solvent of the mixture or

advantageously contained in microparticles or microcapsules which dissolve in the said solvent, thus releasing the said compounds into the mixture. They are soluble in the polymerisable binder. To this end, chains, for example hydrophilic chains, can advantageously be grafted onto the said compounds.

In practice, the mixture of the invention contains three different colourless photochromic compounds: a first, a second and a third compound. The first compound appears, in its second state, yellow or green, the second compound appears, in its second state, magenta red, and a third compound appears, in its second state, cyan blue. These compounds are chosen so that, in the mixture, the absorption band of the first compound in its first state is distinguished sufficiently from the absorption band of the second compound in its first state, the said bands also being distinguished sufficiently from the absorption band of the third compound in its first state. Thus, in the mixture, it is possible to selectively irradiate one of the compounds in its absorption band in order to cause its transformation, without the transformation of the other compound occurring.

Photochromic compounds which can advantageously be used in the method of the invention are bi- or polycyclic spirannic compounds having one carbon atom

common to two rings: the spirannic atom. Amongst these compounds, the spirooxazines and the spiropyranes and derived compounds react, under the effect of an electromagnetic radiation H , according to the following reaction:



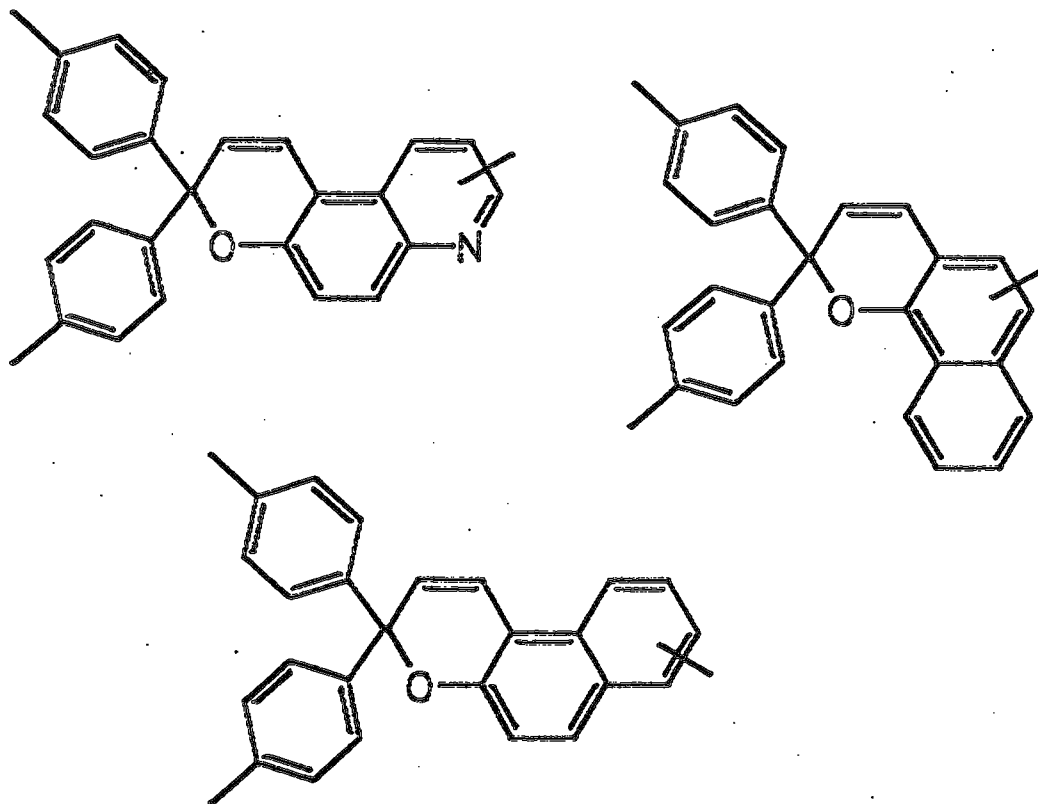
In their first state, the rings of the spirannic atom of the spirooxazines and spiropyranes are distributed in space at right-angles and appear colourless. However, in their second state, these rings form a plane and appear coloured. In addition, these compounds have the property of being able to be mixed in a polymeric medium whilst preserving, in such a medium, their photochromic properties. Naturally, according to the nature, for example the polarity or viscosity of the mixture, the said properties can be modified and, notably, it is possible to observe, on the coloured form of the second state, hypsochromic or bathochromic effects which may range up to 80 nm.

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

Naturally, other photochromic compounds can be used. These may for example be chromenes whose general formulae are of the type:



The reagent or reagents are intended to fix the second coloured state and the coloured state solely of the photochromic compound or compounds present in the mixture and solely this second coloured state. It is a case, in one example, of divalent metal salts such as Mn^{2+} , Ni^{2+} , Zn^{2+} , Ca^{2+} , Pb^{2+} , Cd^{2+} , Mg^{2+} or Co^{2+} or Cu^{2+} generally associated with a mineral counter-ion of the type NO_3^- , Cl^- , Br^- or ClO_4^- , but also with an organic counter-ion such as 1-hydroxy-2-naphthoate, 2-

hydroxybenzoate, 2-hydroxycarbazole-1-carboxylate, or organo-metallic complexes such as [Ni, acetylacetonate, N,N,N',N'-tetramethylethylenediamine] ClO₄, [Ni.acetylacetonate-N,N,N',N'-tetramethylethylenediamine] BPh₄, [Ni.benzoylacetonate-N,N,N',N'-tetramethylethylenediamine]ClO₄.

The mixture will however advantageously include other compounds.

It is a case notably of additives, for example solvents, for separating the spectra, the absorption bands of the photochromic compounds present in the mixture so that a laser radiation acts on a given photochromic compound and solely on this photochromic compound without the possibility of interference.

It is also a case of different additives, such as anti-UV stabilisers intended to protect the carrier from ageing.

The mixture obtained, containing the photochromic compounds, is then, according to the invention, spread on a support for manufacturing the layer to be printed of the card body. This support consists, in one example, of a base and lateral sides forming a frame. This cavity can contain one or more polymerised or pre-polymerised layers or sub-layers of the card body as

well as, optionally, a micromodule inserted in the said layers or sub-layers.

Next the mixture spread on the manufacturing support for the layer to be printed is irradiated with a laser electromagnetic radiation whose wavelength belongs to the UV range and, preferably, to the range extending from 200 to 400 nm, and corresponding to an absorption band of one and only one photochromic compound present in the mixture, so that the said compound is transformed into the coloured form of its second state. It should be noted that the power of the laser irradiations can be modulated, notably according to the wavelength, so that, for example, the photochromic response is itself modulated, the colours obtained being thereby shaded.

Thus, when the mixture contains n different photochromic compounds where n is an integer number, it can be irradiated by n laser radiations, each radiation having a given wavelength able to cause the transformation of one and only one photochromic compound amongst the n compounds. In other words, the n photochromic compounds are sensitive respectively and solely to the n wavelengths of the laser radiations irradiating the carrier. More particularly, where the card body contains three colourless photochromic compounds in their first state and, respectively, green

or yellow, magenta red and cyan blue in their second state, the irradiation is effected by three radiations of different wavelengths in the UV region, in particular the aforementioned region ranging from 200 to 400 nm, a first radiation causing the transformation of the first compound into its green or yellow form, a second radiation causing the transformation of the second compound into its magenta red form and a third radiation causing the transformation of the third compound into its cyan blue form. The printing is then polychromic.

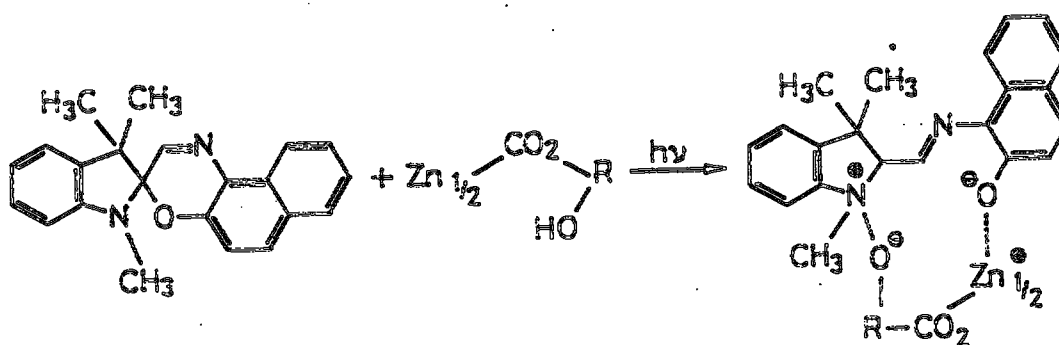
The irradiation is effected by laser radiations, successively or simultaneously. It is directed to precise points on the surface of the layer to be printed, according to the desired pattern. To this end, the irradiation is effected point by point, using a laser beam of given diameter, or through a filter. It being a case of the relative movement of the laser radiations with respect to the layer to be printed on the card body, different cases are possible: either the manufacturing support for the layer moves with respect to the laser radiations which remain in a fixed position, or the laser radiations move with respect to the said fixed support, or the manufacturing support and the radiations move at the same time. These movements are controlled and coordinated by a computer provided with suitable software.

The irradiation is effected before or after a step of pre-polymerisation or polymerisation of the spread mixture and/or evaporation of the solvent, in the case of thermoplastics. Thus, according to circumstances, the irradiation is effected on the mixture spread in a more or less viscous liquid state, or in a pre-polymerised solid state, that is to say partially polymerised, or polymerised.

Where the polymerisation and/or solvent evaporation step has not been effected before irradiation, it is effected afterwards. This polymerisation can be supplemented by a post polymerisation or post-crosslinking which results in a manufacture of crosslinked, interpenetrated or semi-interpenetrated lattices, starting from a combination of two types of successive reactions proceeding from different mechanisms.

Another step of the method of the invention is the fixing, irreversible, of the photochromic compounds in their second coloured state, so that the printing pattern is preserved and notably cannot change in sunlight. Return to the initial transparent form is thus prevented. This fixing is effected, for example, by the fixing reagent.

In one example, a spirooxazine, spironaphthooxazine, is blocked, in its second state, by a metallic complex $\text{Zn}_{1/2}\text{CO}_2\text{ROH}$ in the following fashion:



In another step of the method of the invention, the colourless form of the photochromic compounds which have not changed state is fixed irreversibly. This fixing can be effected by means of a reagent. The colourless form can also be destroyed by a rise in temperature and under UV, with a wavelength less than approximately 200 nm. For example, in the case of spirooxazines, very short UV rays, around 100 nm, result in a destruction of the bonds. As previously, the power of the UV can be modulated so as to modulate the fixing of the colourless form of the photochromic compounds.

The definitive fixing or blocking of the coloured and non-coloured forms of the photochromic compounds can be effected or improved by the polymerisation or

post-polymerisation of the mixture, for example under the effect of UV insolation of short wavelength. This UV insolation can also trigger the blocking by the fixing reagents without triggering post-polymerisation.

The aforementioned fixing and/or blocking steps can be performed at the same time. The blocking of the coloured and non-coloured forms can also be simply mechanical, by evaporation of the solvents.

Thus the printed patterns do not show any degradation over time or under the effect of heat or light.

The post-polymerisation can be localised. It will move substances and will give rise to a difference in refractive index, the substance then appearing in polychromatic relief.

Finally, the printed card can be dried with evaporation of solvents so as to obtain a finished product.

By virtue of the method of the invention, it is possible to print, directly and positively, approximately 20,000 visible layers or card faces per hour, which remain intact after printing. In addition, the definition of the printed patterns is, in theory,

molecular. In practice, it is limited, where the irradiation is carried out through a filter, to the dimensions of the frame of the said filter and, where the irradiation is effected point by point, to the dimensions of the beam at the surface of the irradiated layer.

CLAIMS

1. A method for printing a visible thermoplastic or setting polymerised layer on a portable information carrier body, characterised in that it includes the following steps:

- mixing

a thermoplastic or setting polymerisable binder, and

at least one photochromic compound sensitive to laser radiation of a given wavelength so as to change from a first state to a second coloured state,

with a view to forming a mixture;

- irradiating the mixture by means of a laser radiation of a given wavelength,

- fixing the second coloured state; and

- polymerising the mixture so as to form the polymerised layer of the carrier body.

2. A method according to Claim 1, characterised in that the mixing step comprises the mixing of a



reagent intended to fix the second coloured state of the photochromic compound, the fixing of the second coloured state thus being caused by the reagent.

3. A method according to Claim 1, characterised in that the first state of the photochromic compound is colourless.

4. A method according to one of Claims 1, 2 or 3, characterised in that the mixing step is effected with n different photochromic compounds where n is an integer number, and in that the irradiation step is effected by laser irradiation with n different wavelengths, each wavelength being intended to cause one and only one photochromic compound to change from a first state to a second coloured state.

5. A method according to Claim 4, characterised in that n is equal to 3 and in that a first compound has a second green or yellow coloured state, a second compound has a second magenta red coloured state and a third compound has a second cyan blue coloured state.

6. A method according to one of Claims 4 or 5, characterised in that the irradiation of the n photochromic compounds by means of the n laser radiations is effected simultaneously.



7. A method according to one of Claims 4 or 5, characterised in that the irradiation of the n photochromic compounds by the n laser radiations is effected successively.
8. A method according to one of the preceding claims, characterised in that the mixture also contains additives for separating the excitation bands of the photochromic compounds present in the mixture so that there is no interference.
9. A method according to one of the preceding claims, characterised in that the irradiation is effected in the ultraviolet range.
10. A method according to one of the preceding claims, characterised in that it also includes a post-polymerisation step.
11. Application of the method according to one of the preceding claims to the printing of memory cards, notably chip cards.
12. A portable information carrier, having a visible printed thermoplastic or setting polymerised layer on a carrier body, characterised in that the said polymerised layer contains:



- a thermoplastic or thermosetting polymerised binder; and

- at least one photochromic compound fixed in a second coloured state obtained from a first state by irradiation by means of a laser radiation of given wavelength.

13. A portable information carrier according to Claim 12, characterised in that it constitutes a chip card, notably a memory card.



* C L M S *

3-645082