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Multi-layer heat-sealable packaging material, a food package made thereof and a method of packaging

5 The present invention relates to multi-layer heat-sealable packaging material, especially for food packages. The packaging material is based on a middle layer of fibre material, such as cardboard, besides which it contains one or several protective layers for extending the durability time of the packed product, and heat sealing polymer on the surface of the material for closing the package. In addition, the invention relates to a method based on the use of the packaging material, a food
10 package closed by heat sealing, and the use of the packaging material for food packages, such as heat-sealed milk and juice cartons.

It has been tried to make the packages for perishable liquid foods, such as milk products and juices, oxygen and aroma proof for improving the durability. The traditional procedure has been to provide the fibre-based packaging material with a
15 grey aluminium foil, which provides an efficient protection against the penetration of oxygen in the air and the escape of aromas in the packed product. However, the use of aluminium foil used for a long time is now decreasing due to its high costs, environmental hazards, and regulations concerning the recycling of materials. Aluminium is undecomposable on dumping areas, and it is difficult to regenerate
20 packaging cardboard lined with aluminium.

Aluminium used as an oxygen and aroma barrier in food packages has been replaced by polymers to an increasing extent; the most important polymers being ethyl vinyl alcohol copolymer (EVOH), polyamide (PA), and polyethylene terephthalate (PET). By combining these polymers with binding agents and heat
25 sealing polymers, multi-layer cardboard has been formed, with which sealing characteristics almost comparable with aluminium have at best been achieved.

Another trend also depending on material costs and tightening environmental regulations has been to decrease the amount of polymer used for the coating of packaging cardboard. One known polymer-coated food packaging cardboard, in
30 which good oxygen and aroma barrier and low material amounts in polymeric sealing and binding agent layers have simultaneously been achieved, has been described in the publication print FI-96752. The advantageousness of the packaging cardboard of the publication is substantially based on the low heat sealing temperature of about 250°C, with which it is possible to prevent the formation of



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holes in the polymer layer at the closing stage of the package and the resulting weakening of the gas barrier. Also the risk of the taste and smell of the product being harmed is reduced, as the heat sealing temperature is as low as possible.

5 According to the publication FI-96752 it is possible to incorporate glimmer into the EVOH sealing layer for improving the adhesion of the layer to cardboard. It has also been shown that the glimmer effects the gas barrier and reduces the permeability of ultraviolet light. The patent application FI-980086 further describes a multi-layer packaging cardboard, in which a considerable amount of talcum has been added to the polymer in the gas barrier layer. Also this application discloses a
10 UV protection generated with a sealing layer, according to the application by adding to the layer, besides talcum, also a dye pigment comprising at most 5% of the weight of the layer.

If the packaging cardboard and its polymeric coating layers are thick, they form a relatively good protection against the transmission of both ultraviolet radiation and
15 visible light. The fact that the ultraviolet radiation used as heat sealing polymer has a weakening effect on polyethylene is mainly an advantage, as it promotes the material decomposition on dumping areas. However, as it has been the trend to thin the packaging material, the consequence has been that the transmission of visible light has increased. This is especially the case when bleached sulphate pulp is used
20 in the material, which is best suitable for food packages because of its organoleptic properties. Unbleached pulp efficiently absorbs light, but its use in food packages is avoided because of its possibly detrimental effect on smell and flavour. No transmission of light or UV radiation occurred in traditional packaging materials provided with aluminium foil.

25 The present invention is partially based on the observation that the multi-layer packaging cardboard according to the publication FI-96752 and respective modern packaging cardboard can let through even 10% of visible light coming across it, and partly on the observation that, similar to oxygen, also this light may have a detrimental effect on the durability and quality of packed food. The measurements
30 carried out show that the light penetrating the packaging material splits ascorbic acid in juice, thus reducing its amount to about one third of the original during a storage time of five weeks. In an otherwise similar preservation test, in which the effect of light was eliminated, about 75% of the ascorbic acid remained after the end of the test.

Due to the said surprising observations, it is the object of the invention to provide a solution, with which the detrimental transmission of light through the packaging material can be prevented. The invention thus comprises a heat-sealable packaging material which contains, besides the middle layer of fibre material, at least one gas proof polymeric sealing layer protecting the packed product and at least one polymeric heat sealing layer as the surface layer of the material; the invention is characterised in that the heat sealing layer contains a pigment that absorbs light for protecting the product from visible light.

The invention thus requires that a pigment blending with heat sealing polymer be used, which absorbs the visible light on the wavelength area of 400 - 700 nm. Most efficient pigments are black pigments absorbing over the entire wavelength area, such as carbon black, which is not toxic and which is thus suitable for food packages. Carbon black also provides an efficient protection against ultraviolet radiation penetrating the package.

Incorporating the pigment into the heat sealing layer is first of all due to the fact that the heat sealing layer generally is considerably thicker than the other polymeric coating layers in the multi-layer cardboard; the pigment achieves a smoother overlap in the polymeric layer without stripes disturbing the appearance of the layer. Secondly, the sealing characteristics of polymers in the oxygen barrier layer often depend on their purity, due to which one tends to avoid adding foreign components to these. Pigments blend well with polyolefins typically used as heat sealing polymer, and in the concentrations used, they do not hinder the extrudability or heat-sealability of the polymer.

Especially advantageously the heat sealing layer of the food package material according to the present invention has been tinted grey by mixing appropriately a black pigment and a white pigment. The white pigment reflects light from the surface of the material and thus reduces the transmission of light of the material. However, a more important advantage is the appearance of the material which has been pigmented grey; the grey surface layer namely looks like the aluminium foil traditionally used in food packages, which consumers have got accustomed to in course of time. This matter is very important for getting the material approved in the market. Black pigment in itself would produce a nondescript dark, aesthetically questionable material surface, which could be resented by markets although the material would be functional in every aspect from the technical point of view.

In practice, the transmission of light in wavelengths of visible light can be made to fall almost to zero by adding a rather small amount of black pigment into the heat seal polymer. The amount of pigment in the heat sealing layer can be between about 0.05 and 0.5 wt. %, preferably about 0.10 – 0.30 wt. %, and most preferably about 0.10 – 0.20 wt. %. 0.2 wt. % is a limit, the exceeding of which does not improve the absorption in practice, but which may be exceeded for achieving a suitable level of grey. Considering the suitable level of grey, the amount of white pigment has to be considerably bigger than the amount of black pigment, such as about 5 – 25%, preferably about 10 – 20%, and most preferably about 10 – 15% of the weight of the heat sealing layer. By blending 0.15 wt. % of carbon black and 12 wt. % of titanium dioxide with a low-density polyethylene (PE-LD), an optimal heat sealing concentration has been found, which on cardboard deceptively resembles aluminium foil.

The density of low-density polyethylene in the heat sealing layers may be 912 – 935 kg/m³, preferably 915 – 930 kg/m³, and the melt viscosity (MFR₂) 0.5 – 20 g/10 min., preferably 3 – 10 g/10 min. In addition to pigments, at most 0.5% of molecular sieve, such as sodium aluminium silicate, can be incorporated into the heat sealing layer as deodoriser.

The packaging material of heat-sealable packages is normally provided with a polymeric heat sealing layer on both sides. Only the heat sealing layer remaining inside the packages is then pigmented in accordance with the invention. The heat sealing layer on the outer surface of the package is left colourless so that it would not cover the printings on the cardboard.

Relating to the oxygen sealing layer of the package material of the invention, reference is made especially to the publication print FI-96752. In the said publication, the oxygen barrier polymer can be EVOH, PET or PA, the latter blended with EVOH; in addition to these, also PA as such; separate EVOH and PA layers adhered to each other; and sealing polymers blended with minerals, such as talcum, may also come to question. In all cases, the oxygen and aroma barrier and protection against visible light are combined in the same packaging material according to the invention.

The invention further comprises heat-sealable packaging material, which contains, besides the middle layer of fibre material, at least one polymeric-based protective layer tinted grey by blending into it light-absorbing black pigment, such as carbon black, and white pigment, such as titanium dioxide, so that the black pigment

provides the packed product with protection against visible light, the said grey protective layer acting simultaneously as the heat sealing layer for the material. The blend proportions of pigments in the protective layer can be as presented above. The material is suitable for a packed product which has to be, above all, protected from light during its storage.

It is characteristic of the method of the invention for the packaging of food, in which a carton or case is bent from packaging material comprising a middle layer of cardboard, at least one gas proof polymeric sealing layer and at least one polymeric heat sealing layer, into which food is closed by heat sealing, that the heat seal layer is blended with light-absorbing pigment for protecting the food from visible light. The heat sealing layer is preferably tinted grey by using pigments, as is described above. The carbon black and titanium dioxide pigments used in the invention do not disturb the heat sealing of the package, so that about 250°C is sufficient for the heat sealing temperature. Thus, the technology known from the publication FI-96752 can in itself be utilised in the invention without losing any of the advantages mentioned in the publication.

In relation to the finished food package of the invention and the use of the packaging material of the invention, reference is made to the enclosed claims, especially to claims 13 – 18.

The invention is next explained in more detail by way of example, referring to the enclosed drawings, in which

Figures 1 – 5 schematically present five different laminated packaging materials of the invention; and

Figures 6 and 7 describe the transmission of light as a function of the wavelength of light, measured from some packaging materials of the invention and some packaging materials representing the known state of technology.

Figures 1 – 5 are examples of multi-layer heat-sealable packaging materials of the invention principally for the packaging of food. The packaging material 1 consists in both cases of a heat-sealable surface layer 2 of low-density polyethylene (PE-LD), which forms the outer surface for the finished, closed package. This is followed by a middle layer 3 of fibre material, which may be, for example, cardboard of bleached sulphate pulp. Next in Figures 1 – 3 is a polymeric, oxygen and aroma proof sealing layer 4, the material of which is ethylene vinyl alcohol copolymer (EVOH), polyethylene terephthalate (PET), or a mixture of ethylene

vinyl alcohol copolymer (EVOH) and polyamide (PA). The packaging materials of Figures 4 and 5 comprise two sealing layers 4, 5 adhered to each other, the materials of which are EVOH and PA; in Fig. 4, PA is placed against cardboard and EVOH is adhered to PA, and in Fig. 5, EVOH is against cardboard and PA is adhered to EVOH. The sealing layer 4 or layers 4, 5 is followed by a binding agent layer 6, which is, for example, low-density polyethylene modified with maleic anhydride, and the purpose of which is to bind the sealing layer to the heat sealing layer 7 of low-density polyethylene (PE-LD) forming the inner surface of the package.

In the package materials 1 shown, one or several pigments have been incorporated into the heat sealing layer 7 forming the inner surface of the package according to the invention, the intention being to prevent visible light from penetrating into the closed package, in which light could harm the packed product. Preferably the pigment used in accordance with the invention is carbon black, which already in low concentrations provides an almost perfect protection against light. According to the invention, also white pigment, such as titanium dioxide, can be added into the heat sealing layer 7, which has some effect on the light protection but which, above all, provides the heat sealing layer with an aesthetically pleasant appearance resembling an aluminium foil.

In the packaging materials 1 shown, the weight of the middle layer 3 of cardboard is at least 170 g/m², preferably 200 – 400 g/m². The superimposed polymeric layers 4 – 7 can be placed to the cardboard 3 as one stage by coextrusion. The amount of material of the sealing layers 4, 5 and the binding agent layer 6 are 1 – 10 g/m² per layer, preferably 2 – 5 g/m². The amount of material of both the heat sealing layers 1, 7 is 5 – 60 g/m², preferably 20 – 50 g/m², and most preferably 30 – 40 g/m². The share of carbon black in the heat sealing layer 7 forming the inner surface of the package is 0.05 – 0.5 wt. %, preferably about 0.15 wt. %, and the share of titanium dioxide is 5 – 25 wt. %, preferably about 12 wt. %, respectively.

The packaging material of the invention manufactured as a continuous web can be die cut as blanks, which again can be bent and heat-sealed to form closed food packages. The heat sealing temperature is at most about 250°C. Packed products may be especially liquid foods, for example, juices and milk products, such as milk, cream, sour milk, yoghurt, and ice-cream. Likewise box-like packages for dry foods are possible, such as packages for flour, powders, flakes, cereal, and animal food. Further, closed dishes for ready-prepared foods can be provided, in which both the dish and its lid are made of light-impermeable packaging material of the invention.

In Figs. 6 and 7 there are shown light-permeability curves measured in the wavelength range of 400 – 700 nm for visible light, of some multi-layer packaging materials of the invention and the state of the art. In Fig. 6, the curve 8 has been obtained from cardboard of bleached pulp, with a weight of 240 g/m² and with a coating of 20 g/m² of clear, unpigmented polyethylene (PE-LD); curve 9 has been obtained from likewise coated cardboard of bleached pulp, with a weight of 300 g/m²; curve 10 has been obtained from similarly coated cardboard of unbleached pulp, with a weight of 239 g/m², and the curve 11 illustrating the invention has been obtained from cardboard of bleached pulp, with a weight of 240 g/m² and coated with 20 g/m² of polyethylene (PE-LD) which was tinted grey by blending into it 0.12% of carbon black and 7.5% of titanium dioxide.

By comparing the curves 8 and 9 of Fig. 6, the increase of light transmission, which is a consequence of thinning the cardboard manufactured of bleached mass, can be observed. The curve 10 further indicates that if the cardboard is made of unbleached pulp, the problem of light transmission hardly exists. The substantially corresponding light permeability of curve 11 has been achieved by a polymeric coating layer of the invention, tinted grey with the help of white and black pigment.

Figure 7 contains light transmission curves measured as in Fig. 6, illustrating the effect of the amount of titanium dioxide and carbon black to the absorption of light. The curve 9 illustrating the state of the art and the curve 11 illustrating the present invention are similar to those in Fig. 6. The curve 12 has been obtained from cardboard of bleached pulp, with a weight of 300 g/m and coated with 20 g/m² of polyethylene (PE-LD) containing 7.5% of titanium dioxide. The curve 13 was obtained from the same base cardboard, which was coated with 17 g/m² of the said polyethylene bleached white, with 3 g/m² of the said polyethylene tinted grey blended with it. By comparing the curves in Fig. 7, it can be noted that the titanium dioxide has a relatively small effect on the reduction of light transmission, as again the carbon black, even as low concentrations as 0.018%, reduces the light permeating the material to under a third of the value it would be without the adding of pigment.

The invention was further tested by following the change in ascorbic acid concentration in packed apple juice during a five week long durability test in storage temperatures of 9°C and 23°C. The packages were heat-sealed closed cartons, in which packaging cardboard of the invention was used, the weight of which was 240 g/m², and which was coated with 5 g/m² of ethylene vinyl alcohol copolymer, 6 g/m² of polymeric binding agent, and on top 45 g/m² of polyethylene

(PE-LD) blended with 0.12% of carbon black and 7.5% of titanium dioxide, with which the layer was tinted grey. The reference material was a packaging cardboard similarly coated with polymer, but without the pigments added to the topmost heat sealing layer.

- 5 Ascorbic acid concentration was measured from the juices at the moment of packaging and after a storage time of two and five weeks. The results are shown in the following table.

Table

Change in the ascorbic acid concentration (mg/l) in apple juice

Storage time	0	2 weeks	5 weeks
Invention 9°C	450	395	355
Invention 23°C	450	355	340
Reference 9°C	450	375	155
Reference 23°C	450	275	145

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The results show the considerable improvement in the preservation of ascorbic acid in packed juice, achieved by the invention.

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It is obvious for one skilled in the art that the various forms of embodiment of the invention are not restricted to the above examples, but they may vary within the scope of the enclosed claims. Instead of cardboard, also paper may be used as the middle layer of the packaging materials, which is suitable for dry package embodiments. In addition, the polymeric heat sealing layer can be provided only on one side of the packaging material. On the other side of the material, especially on the outer side of dry packages, heat-sealable lacquer can be used.

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Claims

1. Multi-layer heat-sealable packaging material (1) especially for food packages, comprising a body layer (3) of fibre material, at least one gas proof polymeric barrier layer (4, 5) protecting the packed product, and at least one polymeric heat sealing layer (2, 7) as a surface layer of the material; **characterised** in that the material comprises a heat sealing layer (7) containing black and white pigments blended with the heat sealing polymer, the light-absorbing black pigment protecting the product from visible light and the black and the white pigments together lending a grey colour to the heat sealing layer.
2. Packaging material according to claim 1, **characterised** in that the black pigment is carbon black and the white pigment is titanium dioxide.
3. Packaging material according to claim 1 or 2, **characterised** in that the heat sealing layer (7) comprises 0.05 – 0.5%, preferably 0.10 – 0.30% and most preferably 0.10 – 0.20% of black pigment of the amount of polymer.
4. Packaging material according to claims 2 and 3, **characterised** in that the heat sealing layer (7) comprises 5 – 25%, preferably 10 – 20%, and most preferably 10 – 15% of white pigment of the amount of polymer.
5. Packaging material according to one of the preceding claims, **characterised** in that the polymer in the heat sealing layer (7) is polyolefin, such as low-density polyethylene (PE-LD).
6. Packaging material according to one of the preceding claims, **characterised** in that it comprises polymeric heat sealing layers (2, 7) on both sides of the material, and that black and white pigments are provided into the layer (7) on the inner surface of the package.
7. Packaging material according to one of the preceding claims, **characterised** in that the polymer in the gas proof barrier layer (4, 5) is ethylene-vinyl-alcohol-copolymer (EVOH) or polyamide (PA), or a mixture of these.
8. Packaging material according to one of the preceding claims, **characterised** in that the body layer (3) is cardboard, containing bleached sulphate pulp.
9. Multi-layer heat-sealable packaging material (1) especially for food packages, comprising a body layer (3) of fibre material and at least one grey protective layer (7) protecting the packed product; **characterised** in that the protective layer (7)

contains polymer, in which the greyness has been achieved by blending with it light-absorbing black pigment, such as carbon black, and white pigment, such as titanium dioxide, so that the black pigment provides the product with a protection against visible light, and that the polymeric protective layer tinted grey simultaneously acts as the heat sealing layer.

10. Method for packing food, in which a carton or case is bent from a packaging material (1) comprising a body layer (3) of cardboard, at least one gas proof polymeric barrier layer (4, 5) and at least one polymeric heat sealing layer (2, 7), into which food is closed by heat sealing; **characterised** in that black and white pigments are blended into the heat sealing polymer for protecting the food from visible light and lending an aluminium foil-like grey colour to the heat sealing layer (7).

11. Method according to claim 10, **characterised** in that the heat sealing layer (7) is tinted grey by blending with the heat sealing polymer 0.05 – 0.5%, preferably 0.10 – 0.20% of light-absorbing black pigment, such as carbon black, and 5 – 25%, preferably 10 – 15% white pigment, such as titanium dioxide.

12. Method according to claim 10 or 11, **characterised** in that the carton or case is closed by heat sealing at a temperature of at most about 250°C.

13. Food package, which contains perishable food closed into a carton or case formed by bending and heat sealing from packaging material comprising a body layer of cardboard, at least one gas proof polymeric barrier layer and at least one polymeric heat sealing layer; **characterised** in that the packaging material comprises a heat sealing layer containing black and white pigments blended with the heat sealing polymer, the light absorbing black pigment protecting the packed food from visible light and the black and white pigments together lending a grey colour to the heat sealing layer.

14. Food package according to claim 13, **characterised** in that the heat sealing layer has been tinted grey by blending into the heat sealing polymer 0.05 – 0.5%, preferably 0.10 – 0.20% of light-absorbing black pigment, such as carbon black, and 5 – 25%, preferably 10 – 20% of white pigment, such as titanium dioxide.

15. Food package according to claim 13 or 14, **characterised** in that the heat sealing polymer is polyolefin, preferably low-density polyethylene (PE-LD).

16. Food package according to one of the claims 13 – 15, **characterised** in that the barrier layer and the pigmented heat sealing layer are placed to the interior of the body layer and that a colourless polymeric heat sealing layer is provided onto the surface of the package on the outside of the body layer.
- 5 17. The **use** of multi-layer packaging material (1) comprising a body layer (3) of fibre material, at least one gas proof polymeric barrier layer (4, 5) and at least one light-absorbing polymeric heat sealing layer (7) containing black and white pigments blended with the heat sealing polymer, in a heat-sealed product package for food sensitive to light.
- 10 18. The use of multi-layer packaging material (1) according to claim 17 in a package for liquid food, such as a milk or juice carton.