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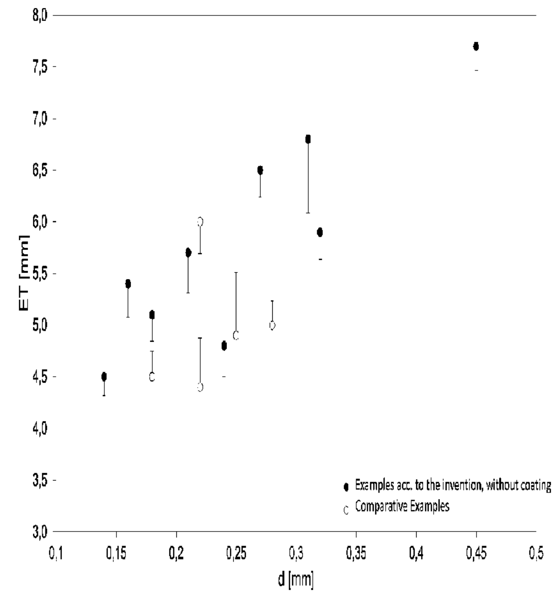

(57) Abrégé/Abstract:
The invention relates to a flat steel product for packaging, comprising a cold-rolled steel sheet with a thickness (d) of less than 0.5 mm and with the following composition in relation to the weight: - C: more than 0.03 %, preferably more than 0.04 %, - Si: less than 0.10 %, - Mn: 0.10 to 0.60 % - P: less than 0.10 %, - S: less than 0.03 %, - Al: less than 0,05 %, preferably less than 0.018 %, - N: more than 0.014 %, preferably more than 0.015 %, - with the rest being iron and unavoidable impurities, wherein the sum of the carbon content (C) and the nitrogen content (N) in relation to the weight is at least 0.050 % and the flat steel product has a tensile strength (Rm) of at least 600 MPa and an Erichsen indentation depth, according to the thickness (d in mm), the carbon content (C in wt.%), the nitrogen content (N in wt.%) and the tensile strength (Rm in MPa) of the sheet steel, of ET # 11.1 • (C + N) + 11.01 mm • d - 0.00864 • Rm + 7.524, wherein ET is the Erichsen indentation depth in mm. The flat steel product is characterised by high level of strength and by a high and isotropic forming capacity within the sheet plane of the flat steel product, and is therefore very well suited to the production of packaging.

Abstract:

The invention relates to a flat steel product for packaging, comprising a cold-rolled steel sheet with a thickness (d) of less than 0.5 mm and with the following composition in relation to the weight: - C: more than 0.03 %, preferably more than 0.04 %, - Si: less than 0.10 %, - Mn: 0.10 to 0.60 % - P: less than 0.10 %, - S: less than 0.03 %, - Al: less than 0,05 %, preferably less than 0.018 %, - N: more than 0.014 %, preferably more than 0.015 %, - with the rest being iron and unavoidable impurities, wherein the sum of the carbon content (C) and the nitrogen content (N) in relation to the weight is at least 0.050 % and the flat steel product has a tensile strength (Rm) of at least 600 MPa and an Erichsen indentation depth, according to the thickness (d in mm), the carbon content (C in wt.%), the nitrogen content (N in wt.%) and the tensile strength (Rm in MPa) of the sheet steel, of ET # 11.1 · (C + N) + 11.01 mm · d - 0.00864 · Rm + 7.524, wherein ET is the Erichsen indentation depth in mm. The flat steel product is characterised by high level of strength and by a high and isotropic forming capacity within the sheet plane of the flat steel product, and is therefore very well suited to the production of packaging.

Cold rolled flat steel product for packaging

The invention relates to a flat steel product for packaging made of a cold-rolled steel sheet with a thickness of less than 0.5 mm.

For reasons of resource efficiency and cost reduction, efforts are being made to reduce the thickness of flat steel products (steel sheets and steel strips) for the production of packaging (hereinafter also referred to as packaging steel). Usual thicknesses of cold-rolled packaging steels are in the ultra-fine range, i.e. between 0.1 and 0.5 mm. However, since a reduction in thickness results in a reduction in the stiffness of the material, the strength of the packaging steel must be increased so that the material can withstand the cold formability requirements in forming processes in the manufacture of packaging, such as deep drawing or ironing. At the same time, however, the formability of the steel sheet must also be maintained during cold forming. There is therefore a need for high-strength steel sheets with a tensile strength of more than 600 MPa which, at the same time, even at low thicknesses in the range from 0.14 to 0.5 mm and in particular between 0.20 and 0.35 mm, have good characteristics for formability, such as a high elongation at break and/or a high Erichsen value (also referred to as Erichsen indentation in accordance with DIN 50101, measured in accordance with the Erichsen cupping test standardized in DIN EN ISO 20482; the terms "Erichsen indentation" and "Erichsen index" or "Erichsen value" are regarded as synonymous).

From EP 2 835 438 B1, a readily formable steel sheet for tear-off lids of cans is known, which has a carbon content of 0.020 to 0.040 wt.% and a nitrogen content of 0.013 to 0.017 wt.%, as well as a tensile strength in a rolling direction of at least 520 MPa and an Erichsen index (Erichsen value) of at least 5.0 mm, the steel sheet containing a coating of a resin film having a thickness of 5 to 100 μm. In the examples, steel sheets coated with a resin film are disclosed which have tensile strengths of up to 591 MPa with an Erichsen index of more than 5 mm. However, tensile strengths of less than 600 MPa are not sufficient for many applications of packaging steels and, in particular, cold-rolled steel sheet with a thickness of less than 0.3 mm to be able to produce stable packaging therefrom in forming processes with very high degrees of deformation. In particular for the production of easy-open ends (EOE) or aerosol cans or aerosol can components, such as aerosol can bases, steel sheets in the thickness range from 0.14 to 0.28 mm (for tear-off lids) and in the thickness range from 0.22 to 0.49 mm (e.g. for aerosol can bases) with tensile strengths of more than 600 MPa and an Erichsen index of at least 4.3

mm for tear-off lids and with an Erichsen index of more than 5 mm for aerosol can bottoms are required to meet the requirements for formability of the starting material and stability of the end product.

There are numerous possibilities for increasing the strength of steel sheets, such as strain hardening, solid solution strengthening (by adding carbon, nitrogen, phosphorus, manganese and/or silicon), precipitation strengthening, strength increase by setting a multiphase steel structure or fine grain hardening. However, many of these measures to increase the strength of steels have undesirable side effects.

With increasing work hardening, for example, longitudinal and transverse differences in the production of cold-rolled steel sheets and consequently the anisotropy increase and at the same time the ductility decreases disproportionately.

In solid solution strengthening, foreign atoms (e.g. N, C, P, Mn, Si) are interstitially or substitutionally incorporated into the host lattice of the steel. However, many of the possible alloying elements have negative side effects (e.g. P is a steel pest, Mn and Si deteriorate the surface quality), which is why increasing strength by adding these alloying elements is not expedient.

Although the addition of carbon increases the strength of the steel with increasing carbon content, at the same time a pronounced anisotropy in the form of zeolicity occurs during processing of the steel sheet, as the carbon is mainly present in the form of cementite due to the low solubility in the ferrite lattice of the steel. Furthermore, with increasing carbon content, the surface quality deteriorates and the risk of slab cracking increases as the peritectic point is approached. Furthermore, with increasing carbon content, the forming behavior of the steel deteriorates. It is therefore advisable to limit the carbon content to a maximum of 0.1% by weight, as this is the only way to effectively prevent the formation of slab cracks and the resulting point oxidation (diffusion of oxygen into cracks) as well as an excessive reduction in slab depth.

Prior art steel sheets for packaging and processes for their production are known in which a sufficient amount of carbon and nitrogen is added to the steel melt for solid solution strengthening to achieve strengths of more than 500 MPa. For example, US 2011/0076177 A1 shows a high-strength steel sheet for can making with a carbon content by weight of 0.02% to 0.10% and a nitrogen content of 0.012% to 0.0250%, which has tensile strengths of more than 500 MPa, the unbound weight fraction of nitrogen, i.e. interstitially incorporated in the steel, being at least 0.0100% by weight. In the examples of US 2011/0076177 A1, steel sheets are listed which, after an aging process, exhibit tensile strengths of up to 540 MPa with an elongation at break of at least 10%. It was found that unbound nitrogen in particular contributes to an increase in the strength of the steel by solid solution strengthening and age hardening. However, the strength increase achievable by interstitial incorporation of nitrogen is limited on the one hand by partial bonding of the nitrogen to nitrides, in particular to AlN, and on the other hand by the fact that at a nitrogen content of more than 0.025% by weight the risk of slab fractures during hot rolling increases considerably.

In the case of precipitation hardening, e.g. by adding Ti or Nb, one problem is that precipitates already are formed during hot rolling due to the high temperature. Consequently, these are involved in all subsequent production stages, such as cold rolling, annealing and, if necessary, re-rolling or skin-passing, and develop a pronounced anisotropy in the process, comparable to cementite, especially if precipitation occurs preferentially on grain boundaries. Furthermore, the precipitants Ti and Nb contribute to an increase in the recrystallization temperature.

The increase in strength through the formation of a multiphase structure in the steel is very limited from the outset in the case of packaging steel due to the normative specifications relating to the alloying constituents of the steel. Conventional multiphase steels, such as those used in the automotive industry, therefore cannot be used for packaging steel because, for example, the alloying constituents used to form a multiphase microstructure, such as manganese and silicon, can only be used in packaging steels up to a maximum weight proportion due to the normative specifications in the packaging steel standard (DIN EN 10202). It is possible to achieve a multiphase microstructure in packaging steel by means of a special cooling technique. However, the resulting microstructural states are characterized by high instability and the increase in strength is usually accompanied by a reduction in formability. If the multiphase microstructure is largely based on the alloying element carbon, there is also a risk that the anisotropy of the cementite will be passed on to the multiphase microstructure and thus become even more pronounced.

In fine-grain hardening, the strength of the steel can be increased by adjusting the fine-grain microstructure while maintaining the formability, whereby the fine-grain microstructure can be achieved in the process by means of a low coiling temperature (coiling temperature after hot rolling), high cold rolling rates and by annealing the cold-rolled steel sheet in continuous annealing. Furthermore, the formation of a fine-grained microstructure can be achieved by microalloying and influencing the precipitation behavior in the hot strip. However, the alloying elements required are expensive and increase the annealing temperature necessary for recrystallization. In addition, due to an increased basic strength of the hot strip, the cold-rollability deteriorates and the surface of the steel sheet becomes more susceptible to defects.

The above-mentioned possibilities for increasing the strength of steel sheets, while retaining formability, thus lead to problems, particularly with regard to isotropy, i.e. with regard to the directional dependence of the material properties. Since packagings, such as aerosol cans, beverage cans or food cans, are mostly (rotationally) symmetrical components, the steel sheets used for the production of packaging are often available in the form of blanks (i.e. a flat, circular sheet blank) which are formed into a cylindrical can body or a circular can base or lid by deep-drawing and stretch-forming processes. Due to the symmetry of the end product, therefore, material properties that are as isotropic as possible are required for the sheets, i.e. the properties of packaging sheets should be as uniform as possible in all directions of the sheet plane. In the case of cold-rolled steel sheets, which are in the form of a steel strip due to the production process, this is very demanding because the direction of rolling during hot rolling and cold rolling always results in a directional dependence of the material properties due to the production process. Cold-rolled steel sheets therefore always exhibit a pronounced anisotropy due to the manufacturing process. This is mainly due to the high degree of cold rolling, which in turn is necessary to achieve the extremely thin plate thicknesses. As the processing of cold-rolled steel sheet in the manufacture of packaging is basically independent of the rolling direction, difficulties frequently arise in the forming process, since, for example, the strength and formability are not homogeneous over the circumference of the blank.

There is therefore a need for a packaging steel in the form of a cold-rolled flat steel product which is characterized on the one hand by a high strength of more than 600 MPa and on the other hand by a high and preferably isotropic forming capacity within the sheet plane of the steel flat product. In the context of continuous thickness reduction of the flat steel product and the necessary strength increase, this represents a contradictory objective which is difficult to achieve. Furthermore, in addition to the isotropic properties of the steel flat product, there are other requirements to be met by the packaging steels in the manufacture of packaging, in particular with regard to the flexibility of the forming processes and the shapes of the packaging, the reduction of material scrap and the realization of the most uniform and homogeneous properties possible of the packaging required for this purpose.

One task of the invention is therefore to provide a high-strength flat steel product for the production of packagings with the highest possible isotropic forming capacity, from which packagings with superior isotropic properties and with a wide variety of geometries and in various forming processes can be produced with the lowest possible material scrap.

Since packaging steel is processed into finished packagings in an aged condition, i.e. after a longer storage period and possibly after painting and drying, material optimization must take into account the effects of aging of the material, which occur after a longer storage period and/or after lamination of a plastic film or painting with subsequent drying. The technological parameters of packaging steels are therefore determined after artificial aging of the material, which, according to the DIN EN 10202 standard, can be performed, for example, by heating the sample to 200°C for 20 minutes. Since the (natural or artificial) aging of steel sheets particularly affects the strength and formability, the aging effects must be taken into account when optimizing the material properties.

Improving the material properties of cold-rolled steel sheets in terms of strength and formability is achieved at the expense of the isotropy of the material properties due to the reasons listed above. Various metallurgical and process engineering options exist for achieving isotropic properties of steel sheets in the production of cold-rolled steel sheets. One option for specifically improving the isotropy of cold-rolled steel sheets is the addition of boron. However, boron has a negative effect on the processability of the steel and the end product (steel sheet). For example, the addition of boron increases the annealing temperature required for recrystallization of the steel sheet after cold rolling, the weldability of the material deteriorates and the aging potential (i.e. the increase in strength when the steel sheet ages) decreases.

A further task of the invention is therefore to demonstrate packaging steels and processes for their manufacture which can be produced inexpensively and simply in terms of process technology and which, on the one hand, exhibit the highest possible strength while maintaining a sufficiently good formability for deep drawing and ironing and a weldability of the material necessary for the manufacture of three-piece cans and, on the other hand, the highest possible isotropy of the material properties with respect to strength and formability in the aged state of the material.

The above-mentioned tasks are solved according to the invention with a flat steel product having the features of claim 1. In this context, a flat steel product is understood to be a sheet- or strip-shaped steel plate with a thickness in the ultrafine sheet range, in particular in the thickness range from 0.14 mm to 0.49 mm.

The invention is based on the knowledge that solid solution strengthening by means of interstitially incorporated alloying constituents of the steel enables simultaneous improvement of strength, formability and isotropy and that solid solution strengthening by carbon and nitrogen proves to be particularly effective in this respect, provided that bonding of the carbon and nitrogen to carbides and nitrides can be at least largely suppressed by process technology. The formation of carbides and nitrides would promote the formation of anisotropic properties.

A further finding underlying the invention is that the introduction of nitrogen by nitriding a cold-rolled flat steel product in an annealing furnace in the presence of a nitrogen donor, at the end of the packaging steel production route, is particularly suitable both for realizing effective solid solution strengthening by nitrogen and for improving the isotropy of the material properties relevant for further processing of the flat steel product in the production of packagings, in particular tensile strength or the yield strength, the elongation at break and the Erichschsen value (i.e. the Erichschsen index). Indeed, it has been shown that, unlike increasing the nitrogen content by introducing nitrogen into the molten steel, nitriding in an annealing furnace essentially leads to an interstitial and homogeneous incorporation of nitrogen without the nitrogen setting to nitrides.

Surprisingly, it was found that the nitrogen interstitially incorporated in the cold-rolled flat steel product during nitriding in the annealing furnace (in particular in a continuous annealing furnace before or during recrystallization annealing) has a positive effect on the formability and the isotropy of the material properties and that, despite the comparatively high carbon content, a high iron deepening can be achieved. Due to a uniform distribution of nitrogen in the (ferrite) lattice of the steel, the interstitial incorporation of nitrogen apparently causes an outstanding isotropy of the mechanical properties of the flat steel product and, as a result, a high forming capacity, which is reflected in a high Erichsen value of the uncoated steel sheet. In particular, the Erichsen value is at least 4.3 mm for a thickness of the steel sheet in the range from 0.14 to 0.25 mm and at least 5.3 mm for a thickness of the steel sheet in the range from 0.26 to 0.49 mm. Furthermore, during nitriding in the annealing furnace, the tensile strength is increased due to solid solution strengthening caused by the incorporation of free (i.e. unbound) nitrogen, and due to the homogeneity of the nitrogen distribution in the steel flat product, also the Erichsen index is increased.

A further contributing factor is that, in the case of interstitial incorporation of nitrogen, compared with carbon, the position of the peritectic point is shifted to higher alloy contents and therefore an incorporation of large amounts of nitrogen on interstitial sites of the steel lattice is much less critical than with carbon in terms of surface quality and the risk of slab cracking. To avoid slab cracking, the weight fraction of carbon in the flat steel product according to the invention is preferably limited to 0.10%. For the incorporation of nitrogen, on the other hand, there is a limit to the nitrogen content only with regard to the solubility limit of nitrogen in the ferrite lattice of the steel as well as the economy of the production process, which, taking into account the solubility limit of nitrogen in the ferrite lattice of approx. 0.1 wt.% and a partial binding of the nitrogen in nitrides in the presence of strong nitride formers such as Al, Ti, Nb and/or B, is a maximum of 0.120 wt.% in the steel. From the point of view of process technology, the nitrogen content of the nitrided flat steel product of the invention is preferably not more than 0.070% by weight, since nitriding the cold-rolled flat steel product in the (continuous) annealing furnace beyond this level can only be achieved at very high technological expense, which in any case is not economically viable at present. For process technology and economic reasons, the proportion of nitrogen by weight is therefore preferably 0.050% or less.

It is particularly advantageous to add the nitrogen to the flat steel product in the manufacturing process as late as possible, in order to prevent different material properties from forming in and transverse to the rolling direction after nitriding, in particular as a result of cold rolling operations along a rolling direction. The nitriding of the flat steel product according to the invention can be carried out, for example, after (primary) cold rolling before or during annealing in a continuous annealing furnace.

Due to the fact that the nitriding takes place only after the (primary) cold rolling, the nitrogen is not part of the processing steps hot rolling and (primary) cold rolling, which cause a massive anisotropy of the material properties. Interstitial incorporation of the nitrogen in the iron lattice (ferrite lattice) during or after recrystallization annealing additionally promotes the homogeneity of the packaging steel according to the invention. In particular, there is no risk of nitride precipitation, which would increase the directionality of the material properties during re-rolling.

Due to a higher basic strength of the steel, which is achieved by solid solution strengthening through the interstitially incorporated nitrogen, the degree of re-rolling during the second cold rolling can be reduced and thus also the anisotropy caused by this can be minimized. The degree of re-rolling during the second cold rolling can thus preferably be limited to 20% or less and is in particular between 7% and 16%.

It is therefore an object of the invention to provide a
a flat steel product for packaging comprising a cold rolled steel sheet having a thickness (d) of less than 0.5 mm and the following composition by weight:

- C: more than 0.03%, preferably more than 0.04%,
- Si: less than 0.10%,
- Mn: 0.10 to 0.60%
- P: less than 0.10%,
- S: less than 0.03 %,
- Al: less than 0.05%, preferably less than 0.018%,
- N: more than 0.014%, preferably more than 0.015%,
- Residual iron and unavoidable impurities,

the sum of the carbon content (C) by weight and the nitrogen content (N) by weight being at least 0.050%, and the flat steel product having a tensile strength (Rm) of at least 600 MPa and an Erichsen value, which is dependent on the thickness (d in mm), the carbon content (C in % by weight), the nitrogen content (N in % by weight) and the tensile strength (Rm in MPa) of the steel sheet, of

$$ET \geq 11.1 \cdot (C + N) + 11.01 \cdot d - 0.00864 \cdot Rm + 7.524 \qquad \text{(Formula 1)},$$

where ET is the Erichsen value in mm.

The Erichsen value (ET) is a measure of the forming capacity of the steel sheet. The Erichsen value depends on the thickness of the steel sheet, as it is determined in the Erichsen cupping test at high thinning. The higher the plate thickness (d), the more material is available for flow and the higher the Erichsen indentation. For the uncoated steel sheets according to the invention, the Erichsen value is at least 4.3 mm when the thickness of the steel sheet is in the range of 0.14 to 0.25 mm and at least 5.3 mm when the thickness of the steel sheet is in the range of 0.26 to 0.49 mm. In order to obtain an Erichsen value of at least 4.3 mm while maintaining high tensile strengths of at least 600 MPa, the thickness of the steel sheet is preferably more than 0.14 mm. Steel sheets with a thickness of 0.14 to 0.28 mm are used, for example, for the production of easy open ends (EOE).

The Erichsen value also depends on the strength (Rm) of the steel sheet, since the strength is increased by increased cold forming, which causes a reduction in the forming capacity. Therefore, a higher strength results in a lower draw depth. Furthermore, the Erichsen indentation depends on the sum of the carbon content and the nitrogen content of the steel sheet (C + N). When the nitrogen content is at least 0.014 wt%, the interstitial atoms provided by carbon and nitrogen provide a more locally uniform movement of the dislocations. These dislocations do not concentrate at a particular location, thus delaying the development of local thinning and thereby cracking, which is why Erichsen indentation increases linearly with the sum of the carbon content and the nitrogen content. Nitrogen and carbon thus have a strengthening effect on the one hand, and on the other hand cause an equalization of the mechanical properties. The sum of the carbon content by weight and the nitrogen content of the steel sheet is therefore at least 0.050% in the flat steel product according to the invention. The C and N atoms are present in a proportion as high as possible in dissolved form as interstitial atoms in the lattice of the steel.

The flat steel product according to the invention is therefore characterized by a high tensile strength (Rm) of at least 600 MPa recorded in the rolling direction and, at the same time, by good and homogeneous forming properties. In addition, the flat steel product according to the invention has a good elongation at break (A) of preferably more than 5% in the rolling direction.

The thickness of the steel sheet is preferably greater than 0.14 mm and is in particular in the range from 0.18 mm to 0.49 mm. Thicknesses of less than 0.35 mm are preferred. This enables packagings to be produced from steel sheets that are as thin as possible but sufficiently stable for the forming processes used.

To increase corrosion resistance, the flat steel product may have a metallic coating, in particular of tin and/or chromium/chrome oxide, applied electrolytically. Instead of or in addition to the metallic coating, the steel sheet may have an organic coating, in particular a polymer coating of a thermoplastic or a paint coating. In particular, the organic coating may be a polymer coating or a polymer film made of a thermoplastic such as a polyester, in particular polyethylene terephthalate (PET), or of polyethylene (PE) or polypropylene (PP) or a mixture thereof. The organic coating may also comprise a varnish, in particular a BPA-NI varnish or a water-soluble varnish. Preferably, the organic coating has a coating thickness of 5 to 100 μm. Such an organic coating significantly improves the corrosion resistance of the flat steel product without impairing the forming properties. The organic coating can be applied to one or both sides of the steel sheet. In the case of a coating applied to only one side, the coated side of the flat steel product is expediently used as the inside of a packaging container to be made from it, e.g. a can.

An organic coating on one or both surfaces of the flat steel product also improves the forming capacity and therefore increases the Erichsen value. The Erichsen value (ET) of the flat steel product coated with an organic coating according to the invention is, for example, at least 0.1 mm greater than the Erichsen value of the uncoated steel sheet.

The flat steel product according to the invention can be produced as follows from a steel having the following composition by weight:

- C: more than 0.03%, preferably more than 0.04% and less than 0.10%,
- Si: less than 0.10%,
- Mn: 0.10 - 0.60%
- P: less than 0.10%,
- S: less than 0.03 %,
- Al: less than 0.05%, preferably less than 0.018%,
- N: less than 0.014 %,
- Residual iron and unavoidable impurities,

wherein a steel slab cast from the molten steel is hot rolled at a preheating temperature of at least 1200°C up to a final rolling temperature of at most 900°C and in particular between 800°C and 900°C to produce a hot strip, the hot strip is coiled into a roll (coil) at a coiling temperature of 670°C or less, preferably of 590°C or less, and after cooling to room temperature, preferably after pickling and degreasing, is cold-rolled with a cold rolling degree of at least 80% to produce a cold-rolled steel sheet (primary) and then annealed in an annealing furnace, in particular in a continuous annealing furnace recrystallizing at an annealing temperature between the recrystallization temperature of the steel and 700°C, preferably at less than 670°C and in particular between 600°C and 670°C, and finally re-rolled with a re-rolling degree between 7% and 20%, wherein, to increase the nitrogen content to more than 0.014 wt. % and preferably to more than 0.015 wt.%, the steel sheet is nitrided in the annealing furnace, wherein the nitriding can take place before, during or after the recrystallizing annealing.

The steel sheet is nitrided in the annealing furnace, for example, by the at least temporary presence of a nitrogen donor, which is formed in particular by an ammonia-containing gas atmosphere in the annealing furnace. At the high temperatures in the annealing furnace, atomic nitrogen, which acts as a nitrogen donor, is formed from the ammonia gas on the surface of the steel sheet by a catalytic effect and can diffuse from there into the steel sheet, thus enriching the nitrogen content of the steel sheet.

During annealing in the annealing furnace at annealing temperatures, which are preferably above 630°C (temperature of the steel flat product) to ensure complete recrystallization, the nitrogen diffuses into the cold-rolled steel flat product. This results in uniform distribution and interstitialization of the diffused nitrogen in the lattice of the steel. The uniform distribution of the interstitially incorporated nitrogen results in a high isotropy of the mechanical properties of the nitrided flat steel product influenced by the nitriding process, in particular with regard to elongation at break, tensile strength and yield strength as well as Erich indentation.

Uniform distribution of the nitrogen introduced into the annealing furnace over the cross section of the steel sheet can be achieved if the nitrogen donor, e.g. ammonia gas, is not only uniformly distributed in the annealing furnace but also directed onto the surfaces of the steel sheet, e.g. by spraying with spray nozzles.

The most homogeneous possible distribution of the nitrogen stored in the annealing furnace also results from longer residence times of the flat steel product in the annealing furnace and in particular from longer annealing times for recrystallization annealing. Preferably, therefore, the residence times of the flat steel product in the annealing furnace are more than 10 seconds, more preferably more than 30 seconds and in particular in the range from 30 seconds to 250 seconds, for example in the range from 100 to 180 seconds. These annealing conditions ensure that as high a proportion as possible of the N atoms is diffused in during the nitriding process and also of the C atoms already contained in the steel melt are deposited on interstitial sites in the lattice of the steel and the nitrogen present in the steel sheet is thus present in dissolved form to the greatest possible extent.

With dwell times of more than 400 seconds, the throughput speed of the strip-shaped flat steel product in a continuous annealing furnace would have to be set so low for a typical length of the throughput section that the efficiency of the process is no longer feasible for economic reasons, which is why annealing times longer than 400 seconds can best be set in a batch-type annealing process.

After annealing, the cold-rolled steel sheet is preferably cooled at a cooling rate of between 2 K/s and 25 K/s, and particularly preferably between 5 K/s and 20 K/s. With slower cooling, i.e. at cooling rates of less than 2 K/s, part of the nitrogen incorporated during nitriding would lose its strength-increasing and homogenizing effect on the mechanical properties due to precipitation into nitride particles. In the case of faster cooling with cooling rates of more than 25 K/s, distortions can occur in the steel, which cause anisotropies of the mechanical properties and unevenness in the steel sheet.

The isotropy of the material properties relevant for cold forming, such as tensile strength and yield strength as well as elongation at break and Erich indentation, achieved in the flat steel product according to the invention by nitriding after cold rolling can be achieved despite a grain elongation of the steel grains, which cannot be avoided by (double) cold rolling. In the flat steel product according to the invention, the grains of the steel structure preferably have an average chord length of 3.0 to 6.0 μm and a direction-dependent grain elongation (S) which, for example, is at least 1.4 in the rolling direction (0°) in longitudinal sections of the flat steel product and at least 1.1 in planar sections of the steel flat product. It therefore follows that, despite grain elongation due to the manufacturing process, homogeneous, preferably direction-independent properties with regard to tensile strength, yield strength and elongation at break and Erich indentation in the sheet plane can be achieved in the flat steel product according to the invention, and thus isotropic forming properties are obtained.

The fineness of the grains of the steel structure can be influenced by the cooling and temperature conditions after hot rolling up to coiling. Particularly fine grains can be obtained if the hot strip is cooled from the final rolling temperature to the coiling temperature (coiler temperature) at a cooling rate of at least 15 K/s. The resulting grain refinement improves the isotropy of the mechanical properties of the steel structure. The resulting grain refinement improves the isotropy of the mechanical properties of the steel sheet in the sheet plane. A uniform grain size, i.e. a narrow half-width of the grain size distribution, which also contributes to improving the isotropy of the mechanical properties of the steel sheet in the sheet plane, can be achieved if the coiling temperature is at least 500°C.

Since the solid solution strengthening produced by the nitriding of the flat steel product is most efficient when the introduced nitrogen is interstitially incorporated in interstitial sites of the steel (in particular of the ferrite lattice), it is expedient if the alloy composition of the steel contains as few strong nitride-forming elements as possible, such as Al, Ti, B, and/or Nb, in order to prevent the nitrogen from being bound in the form of nitrides. Therefore, the alloy composition of the steel preferably has the following upper limits for the weight proportion of these strong nitride-forming alloying constituents:

- Al: < 0.05%, preferably less than 0.018%;
- Ti: < 0.01%, preferably less than 0.002%;
- B: < 0.005%, preferably less than 0.001%;
- Nb: < 0.01%, preferably less than 0.002%;

Preferably, the total weight fraction of the nitride formers is less than 0.05 %. In particular, this allows a weight fraction of the unbound nitrogen of more than 0.01 % to be produced.

The steel sheet of the flat steel products according to the invention may optionally contain, in addition to the alloying constituents already listed above and the maximum amounts of nitride formers mentioned, the following further elements which may be added during the production of the molten steel, in particular by the addition of scrap:

- Cr: less than 0.1%, preferably 0.01 - 0.05%,
- Ni: less than 0.1%, preferably 0.01-0.05%,
- Cu: less than 0.1%, preferably 0.002 - 0.05%,

- Mo: less than 0.02 %,
- Sn: less than 0.03 %.

The weight fraction of unbound nitrogen in the hot strip N_{free} (hot strip) can be described by the following *formula 2*, assuming that any nitride-formers Al, Ti, B, and Nb present in the steel within the above limits are completely bound with nitrogen to form nitrides:

$$N_{free} \text{ (hot strip)} = \frac{1}{2} (N_0 - Ti / 3.4 - B / 0.8 - Nb / 6.6 - \text{Al factor} + | N_0 - Ti / 3.4 - B / 0.8 - Nb / 6.6 - \text{Al factor} |)$$

(*Formula 2*),

where N_0 is the weight fraction of nitrogen in the melt of the steel, the Al factor is defined as a function of the coiling temperature HT (coiling temperature of the hot strip) and the aluminum content Al (in % by weight) as follows:

- if HT < 640 °C: Al factor = 0;
- if $750 \geq HT \geq 640$ °C: Al factor = $N_0 - N_0$ x (-0.682 HT + 536) / 100 = N_0 x (1 - (-0.682 HT + 536)/100);

and the summand

$$| N_0 - Ti / 3.4 - B / 0.8 - Nb / 6.6 - \text{Al factor} |$$

is defined as the amount of the difference "N_0 - Ti / 3.4 - B / 0.8 - Nb / 6.6 - Al factor". In formula 2, this sum of magnitudes takes into account that at most only the total nitrogen actually present in the hot strip (i.e. in the molten steel) can be bound by the nitride formers present in the hot strip (i.e. in the molten steel).

The total weight content of free nitrogen in the cold-rolled flat steel product is the sum of the free nitrogen content in the hot strip (N_{free} (hot strip) according to formula 2 above) and the nitrogen content in the continuous annealing furnace due to the nitriding process.
added nitrogen ΔN:

$$N_{free} = N_{free} \text{ (hot strip)} + \Delta N \qquad \text{(formula 3)}$$

It is assumed that the nitrogen content ΔN introduced in the continuous annealing furnace during nitriding is at least essentially interstitially deposited in interstitial spaces. The upper limit for the weight fraction of free nitrogen in the cold-rolled flat steel product is determined by the solubility limit of nitrogen in the ferrite lattice of the steel, which is approx. 0.1% by weight.

The total weight fraction of free nitrogen in the cold-rolled flat steel product (N_{free}) is preferably more than 0.01%. In order to introduce as high a proportion as possible of the nitrogen in unbound form into the cold-rolled steel flat product, the majority of the total proportion by weight of the nitrogen is preferably introduced by nitriding in the continuous annealing furnace, the proportion by weight of ΔN preferably being at least 0.002% by weight and particularly preferably more than 0.008% by weight.

The flat steel product can be nitrided in the continuous annealing furnace before, during or after recrystallizing annealing. For example, it is possible to nitride the flat steel product in the continuous annealing furnace in a first zone of the continuous annealing furnace at a first temperature below the recrystallization temperature in the presence of a nitrogen donor and then to heat the flat steel product in a second zone of the continuous annealing furnace downstream in the strip running direction for recrystallizing annealing at a second temperature above the recrystallization temperature. This sequence of nitriding and recrystallizing annealing can also be reversed. Such a decoupling of the nitriding and recrystallizing annealing in different zones of the continuous annealing furnace has the advantage that the optimum temperature can be set for the respective process, with the optimum temperature for nitriding being lower than for recrystallizing annealing. For economic reasons, however, simultaneous nitriding and annealing of the flat steel product in the continuous annealing furnace at a temperature above the recrystallization temperature in the presence of a nitrogen donor is preferable.

Preferably, the hot strip already has an initial nitrogen content N_0 in the range from 0.001 wt.% to a maximum of 0.014 wt.% in order to maximize the total nitrogen content in the cold-rolled flat steel product and thereby the solid solution strengthening caused by the nitriding of the cold strip. In order to prevent the formation of slab cracks during slab casting and hot rolling, and to avoid already increasing the strength of the hot strip to such an extent that it is no longer cold-rollable with conventional cold-rolling equipment, the proportion by weight of nitrogen in the molten steel from which the hot strip is produced should not exceed 0.014%. The total nitrogen content of the flat steel product of the invention, which is the sum of the initial nitrogen content N_0 and the nitrogen content ΔN introduced during nitriding in the annealing furnace, is adjusted during annealing of the cold-rolled flat steel product by the presence of the nitrogen donor in the annealing furnace, in that dissociated atomic nitrogen of the nitrogen donor diffuses into the cold-rolled flat steel product at the annealing temperatures, thereby increasing the nitrogen content by ΔN. Preferably, the nitrogen fraction ΔN introduced during annealing in the annealing furnace is at least 0.002 wt%, thereby increasing the total nitrogen fraction of the flat steel product to more than 0.014 wt% if the initial nitrogen fraction N_0 in the molten steel was lower than this value. Particularly preferably, the cold-rolled flat steel product in the continuous annealing furnace is nitrided to more than 0.020 wt% nitrogen content. The total nitrogen content of the flat steel product nitrided in the continuous annealing furnace can (at least theoretically) reach the solubility limit of nitrogen in the (ferrite) lattice of the steel of about 0.1 wt.%.

The nitrogen donor can be, for example, a nitrogen-containing gas atmosphere in the annealing furnace, in particular an ammonia-containing atmosphere, or a nitrogen-containing liquid which is applied to the surface of the cold-rolled flat steel product before it is heated in the annealing furnace. The nitrogen donor should be designed to provide atomic nitrogen in the annealing furnace by dissociation, which can diffuse into the steel flat product. In particular, the nitrogen donor may be ammonia gas. In order for this to dissociate in the annealing furnace to form atomic nitrogen, furnace temperatures of more than 400°C are preferably set in the annealing furnace when nitriding the cold-rolled steel flat product.

Due to the increase in strength brought about by solid solution strengthening as a result of the nitriding of the flat steel product during annealing in the (continuous) annealing furnace in the presence of the nitrogen donor, the flat steel product according to the invention does not require rerolling with a high rerolling degree in order to additionally increase the strength by work hardening. The degree of re-rolling can therefore preferably be limited to a maximum of 20%, whereby a deterioration in the isotropy of the material properties can be avoided by a second cold rolling with high rerolling degrees. Preferably, the rerolling degrees are less than 16%.

The properties of the flat steel product produced in this way are established after aging of the re-rolled steel strip, which can be brought about either artificially by heating to 200°C for 20 minutes or by painting with subsequent paint drying of the steel flat product.

After the second cold rolling (re-rolling), a coating can be applied to one or both sides of the surface of the flat steel product to improve corrosion resistance, e.g. by electrolytic deposition of a tin layer and/or a chromium/chrome oxide layer and/or by painting with an organic paint, e.g. polyester or epoxyphenol paint, or by laminating on a polymer film of a thermoplastic, in particular a film of PET or of PP, PVC or PE or mixtures thereof. In the case of coatings, the preferred thicknesses are in the range of 2 to 15 μm per side. The thickness of laminated polymer films is expediently in the range of 10 to 25 μm. Organic overlays such as coatings or laminated polymer films increase formability. Thus, depending on the layer thickness of the overlay, the Erich value of painted flat steel products or flat steel products coated with a polymer film according to the invention is about 0.1 mm or more higher than the Erich value of the uncoated steel sheet.

The excellent isotropic mechanical properties of the steel sheets according to the invention enable the production of tear-off lids of cans ("easy-open-ends" EOE) or of aerosol cans or aerosol can components, such as aerosol can bottoms or lids, with isotropic properties over the entire surface of the tear-off lids or the aerosol cans and their components. Particularly in the case of round or oval tear-off lids and round aerosol can bottoms or lids, the isotropic properties of the steel sheets according to the invention prove to be advantageous, since virtually constant mechanical properties are present over the entire circumference of the respective product. The isotropic mechanical properties of the steel sheets of the invention also prove advantageous in deep-drawing applications in which a round sheet part (round blank) is formed, for example to produce a can body for a two-piece can, since here consistent mechanical properties of the formed sheet part around its circumference can be achieved as well and no thinned-out areas with reduced sheet thickness are produced during forming.

These and other properties, features and advantages of the flat steel product according to the invention are disclosed in the embodiments described in more detail below with reference to the accompanying drawings and tables. The drawings show:

Fig. 1: A diagram of the values of Erichsen indentation (ET in mm) measured on flat steel products according to the invention and on comparison samples of cold-rolled steel sheets not according to the invention plotted against the thickness of the flat steel products (d in mm), where the dots represent the values of the Erichsen indentation measured on the specimens and the lines connected thereto by a connecting line represent the value of the Erichsen indentation calculated by calculation in accordance with formula (1), an upward deviation characterizing a higher calculated value and a downward deviation characterizing a lower calculated value in comparison with the measured value;

Fig. 2: A plot of the difference (ΔET) between the measured values of the Erichsen indentation (ET) and the values of the Erichsen indentation (ETb) calculated from formula (1), plotted against the number of the respective example from tables 1 to 3;

For the production of flat steel products according to the invention, a slab is cast from a steel melt and hot-rolled into a hot strip. The alloy composition of the molten steel is suitably based on the limit values specified by standards for packaging steel (as defined, for example, in ASTM A623-11 "Standard Specification for Tin Mill Products" or in "European Standard EN 10202"). The components of the steel from which flat steel products according to the invention can be made are explained in detail below:

<u>Composition of the steel:</u>

- <u>Carbon, C: at least 0.03% and at most 0.1%, preferably</u> more than 0.04% and/or <u>less than 0.085%</u> by weight;

Carbon has a hardness- or strength-increasing effect. Therefore, the steel contains at least 0.03 wt.%, preferably more than 0.04 wt.% carbon. In order to ensure the rollability of the flat steel product during primary cold rolling and, if necessary, in a second cold rolling step (re-rolling or skin-passing) and not to reduce the elongation at break, the carbon content should not be too high. Furthermore, as the carbon content increases, a pronounced anisotropy in the form of latency occurs during the production and processing of the steel flat product, since the carbon is present mainly in the form of cementite due to its low solubility in the ferrite lattice of the steel. In addition, with increasing carbon content, the surface quality deteriorates and the risk of slab cracking increases as the peritectic point is approached. Furthermore, with increasing carbon content, the forming behavior of the steel deteriorates. It is therefore necessary to limit the carbon content to a maximum of 0.1% by weight, as this is the only effective way to avoid the formation of slab cracks and the resulting point oxidation (diffusion of oxygen into cracks) as well as an excessive reduction of the Erichsen value. Particularly preferably, the carbon content is in the range of 0.04 to 0.085 wt.%.

- Manganese, Mn: minimum 0.10% and maximum 0.60%;

Manganese also increases hardness and strength. In addition, manganese improves the weldability and wear resistance of steel. Furthermore, the addition of manganese reduces the tendency to red fracture during hot rolling by binding sulfur to less harmful MnS. Furthermore, manganese leads to grain refinement and manganese can increase the solubility of nitrogen in the iron lattice and prevent diffusion of carbon to the surface of the slab. Therefore, a manganese content of at least 0.10 wt.% is preferable. To achieve high strengths, a manganese content of more than 0.2 wt.%, in particular 0.30 wt.% or more, is preferred. However, if the manganese content becomes too high, this is to the detriment of the corrosion resistance of the steel and food compatibility is no longer guaranteed. In addition, if the manganese content is too high, the strength of the hot strip becomes too high, which means that the hot strip can no longer be cold rolled. Therefore, the upper limit for the manganese content is 0.60% by weight.

- Phosphorus, P: less than 0.10%.

Phosphorus is an undesirable by-product in steels. A high phosphorus content leads in particular to embrittlement of the steel and therefore deteriorates the formability of steel flat products, which is why the upper limit for the phosphorus content is 0.10 wt.%. Preferably, the phosphorus content is 0.03 wt.% or less.

- Sulfur, S: more than 0.001% and not more than 0.03%.

Sulfur is an undesirable accompanying element that deteriorates ductility and corrosion resistance. Therefore, no more than 0.03% by weight of sulfur should be present in the steel. On the other hand, complex and cost-intensive measures have to be taken to desulfurize steel, which is why a sulfur content of less than 0.001 wt.% is no longer justifiable from an economic point of view. The sulfur content is therefore preferably in the range from 0.001 wt.% to 0.03 wt.%, particularly preferably between 0.005 wt.% and 0.01 wt.%.

- Aluminum, Al: more than 0.002% and less than 0.05%.

Aluminum is required in steel production as a deoxidizing agent for steel quenching. Aluminum also increases scale resistance and formability. For this reason, the aluminum content is preferably more than 0.002% by weight. However, aluminum forms aluminum nitrides with nitrogen, which are disadvantageous in the flat steel products of the invention because they reduce the amount of free nitrogen. In addition, excessively high aluminum concentrations can lead to surface defects in the form of aluminum clusters. For this reason, aluminum is used in a maximum concentration of 0.05% by weight. Preferably, the aluminum content is less than 0.018 wt.% to ensure the highest possible proportion of unbound free nitrogen (N_{free}).

- Silicon, Si: less than 0.10%;

Silicon increases scale resistance in steel and is a solid solution hardener. In steel production, Si serves as a deoxidizing agent. Another positive effect of silicon on steel is that it increases tensile strength and yield strength. Therefore, a silicon content of 0.003 wt% or more is preferable. However, if the silicon content becomes too high, and in particular exceeds 0.10 wt.%, the corrosion resistance of the steel may deteriorate and surface treatments, in particular by electrolytic coatings, may become more difficult. Preferably, the silicon content is between 0.005 wt.% and 0.03 wt.%.

- Optional: Nitrogen, N_0 : less than 0.014%, and preferably more than 0.001%.

Nitrogen is an optional component in the molten steel from which the steel for the flat steel products according to the invention is produced. Indeed, nitrogen acts as a solid solution strengthener to increase hardness and strength. However, an excessively high nitrogen content in the steel melt of more than 0.014% by weight means that the hot strip produced from the steel melt is more difficult to cold-roll. Furthermore, a high nitrogen content in the molten steel increases the risk of defects in the hot strip, since at nitrogen concentrations of 0.014 wt.% or more the hot forming capability becomes lower. In accordance with the invention, it is envisaged to subsequently increase the nitrogen content of the flat steel product by nitriding the cold-rolled flat steel product in an annealing furnace. Therefore, the introduction of nitrogen into the molten steel can also be dispensed with entirely. However, to achieve a high solid solution strengthening, it is preferable that the steel melt already contains an initial nitrogen content of more than 0.001% by weight, particularly preferably 0.010% by weight or more.

To introduce an initial nitrogen content N_0 into the flat steel product prior to nitriding in the annealing furnace, nitrogen can be added to the molten steel in appropriate quantities, for

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example by blowing in nitrogen gas and/or by adding a solid nitrogen compound such as calcium cyanamide or manganese nitride.

- optional: nitride formers, especially niobium, titanium, boron, molybdenum, chromium:

Nitride-forming elements such as aluminum, titanium, niobium, boron, molybdenum and chromium are disadvantageous in the steel of the flat steel products according to the invention because they reduce the proportion of free nitrogen through nitride formation. In addition, these elements are expensive and therefore increase the manufacturing costs. On the other hand, the elements niobium, titanium and boron, for example, have a strength-increasing effect via grain refinement as microalloying constituents without reducing toughness. Therefore, the aforementioned nitride formers can advantageously be added within certain limits as alloying constituents of the steel melt. The steel can therefore (optionally) contain the following nitride-forming alloying constituents by weight:

- Titanium, Ti: preferably more than 0.002%, but less than 0.01% for cost reasons,
- Boron, B: preferably more than 0.001%, but for cost reasons less than 0.005%, and/or
- Niobium, Nb: preferably more than 0.001%, but less than 0.01% for cost reasons, and/or
- Chromium, Cr: preferably more than 0.01% to allow the use of scrap in the production of the molten steel and to impede the diffusion of carbon on the surface of the slab, but not more than 0.1% to avoid carbides and nitrides, and/or
- Molybdenum, Mo: less than 0.02% to avoid excessive increase in recrystallization temperature;

To avoid a reduction in the proportion of free, unbound nitrogen N_{free} due to nitride formation, the total proportion by weight of said nitride formers in the molten steel is preferably less than 0.05%.

Other optional components:

In addition to the residual iron (Fe) and unavoidable impurities, the molten steel may also contain other optional constituents, such as

- optionally copper, Cu: more than 0.002 to allow the use of scrap in the production of molten steel , but less than 0.1% to ensure food compatibility;

- optionally nickel, Ni: more than 0.01 to allow the use of scrap in the production of the molten steel and to improve toughness, but less than 0.1% to ensure food compatibility, preferably the nickel content is between 0.01 and 0.05% by weight;
- optional Tin, Sn: preferably less than 0.03%;

Manufacturing process of the steel flat product:

The steel composition described is used to produce a molten steel which is first continuously cast and after cooling is cut into slabs. The slabs are then reheated to preheating temperatures of more than 1100°C, in particular 1200°C, and hot-rolled to produce a hot strip with a thickness in the range from 1 to 4 mm.

The final rolling temperature during hot rolling is preferably above the Ar3 temperature to remain austenitic, and is preferably below 900°C, in particular between 800°C and 900°C.

The hot strip is wound into a coil at a predetermined and suitably constant coiling temperature (coiler temperature, HT). The coiling temperature is preferably below Ar1 in order to remain in the ferritic region, in particular less than 670°C and preferably below 630°C, particularly preferably less than 590°C and especially in the range from 500°C to 590°C, in order to avoid precipitation of AlN. For economic reasons and to achieve a uniform grain size, the take-up temperature should be higher than 500°C. Formation of iron nitrides on the surface of the hot strip can be avoided by cooling the hot strip after completion of hot rolling until coiling at higher cooling rates of more than 15 K/s.

To produce a packaging steel in the form of a thin flat steel product in the thickness range of less than 0.5 mm (thin sheet thicknesses) and preferably with a thickness in the range from 0.14 to 0.35 mm, the hot strip is cold rolled, with a reduction in thickness (reduction ratio or cold rolling ratio) of at least 80% and preferably in the range from 85% to 95%. To restore the crystal structure of the steel destroyed during cold rolling, the cold-rolled steel strip is then annealed in an annealing furnace to recrystallize it. This is peformed, for example, by passing the flat steel product in the form of a cold-rolled steel strip through a continuous annealing furnace in which the steel strip is heated to temperatures above the recrystallization temperature of the steel. Before or preferably simultaneously with the recrystallization annealing or after complete recrystallization, the cold-rolled flat steel product is nitrided by heating the flat steel product or by maintaining a suitable niotriding temperature in the annealing furnace in the presence of a nitrogen donor. The nitriding is preferably carried out simultaneously with the recrystallization annealing in the annealing furnace by introducing a nitrogen donor, in particular in the form of a nitrogen-containing gas, preferably ammonia (NH_3), into the annealing furnace and heating the flat steel product to an annealing temperature above the recrystallization temperature of the steel and holding it at the annealing temperature for a holding time of preferably 30 to 180 seconds, preferably in the range from 50 to 150 seconds. The annealing temperature is preferably between the recrystallization temperature of the steel and 700°C, preferably above 600°C, in particular between 630°C and 670°C, for example in the range from 650°C to 670°C. The nitrogen donor is selected so that, at the temperatures in the annealing furnace, atomic nitrogen is formed by dissociation of the nitrogen donor and can diffuse into the steel flat product. Ammonia has proved suitable for this purpose. In order to prevent oxidation of the surface of the flat steel product during annealing, it is expedient to use an inert gas atmosphere in the annealing furnace. Preferably, the atmosphere in the annealing furnace consists of a mixture of the nitrogen-containing gas acting as a nitrogen donor and an inert gas such as HNx, the volume fraction of the inert gas preferably being between 90% and 99.5% and the remainder of the volume fraction of the gas atmosphere being formed by the nitrogen-containing gas, in particular ammonia gas (NH_3 gas).

<ins>Embodiments:</ins>

Embodiments of the invention and comparative examples are explained below.

Flat steel products (steel sheets) were produced from steel melts with the alloy compositions listed in **Table 1** by hot rolling followed by cold rolling, where N0 indicates the nitrogen content in the steel melt.

The cold-rolled steel sheets were then subjected to recrystallizing annealing in a continuous annealing furnace by holding the flat steel products at annealing temperatures of 630°C to 673°C for a holding time of 38 to 48 seconds. In the case of the flat steel products according to the invention, before or during annealing in the continuous annealing furnace, a nitriding was carried out by means of an ammonia-containing gas atmosphere in the annealing furnace consisting of an HNx protective gas and ammonia gas with an ammonia equilibrium content of 0.5 to 5.0% by volume.

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The ammonia gas acting as a nitrogen donor was additionally directed onto the surface of the steel sheets by means of spray nozzles. The resulting concentration of nitrogen in the nitrided steel sheets according to the invention is shown in Table 1 as N (in % by weight). The total nitrogen content N was recorded in accordance with the standard DIN EN ISO 14284 (in particular item 4.4.1), if necessary after removal of a superficial iron nitride layer formed on the surface of some samples during the nitriding process. In the case of the flat steel products according to the invention, the total nitrogen content by weight is composed of the initial nitrogen content of the steel melt (N0) and the nitrogen content $\Delta N = N - N0$ (Table 1) introduced by the nitdriding process in the continuous annealing furnace, with a significant proportion of the total nitrogen content N_{free} being in unbound form and the remainder in bound form as nitride, see formula (2). From the weight proportion of the nitride formers present in the steel, the weight proportion of the free nitrogen N_{free} can be estimated via formula (2).

In the case of the flat steel products not according to the invention, which were produced for comparison purposes, no nitrogen was added in the continuous annealing furnace (i.e. 100% HNx protective gas atmosphere in the continuous annealing furnace during annealing). The nitrogen concentration N of the reference samples therefore corresponds to the initial nitrogen concentration N0 in the molten steel.

After thermal treatment in the continuous annealing furnace, the cold-rolled and recrystallizing annealed flat steel products were subjected to re-rolling. The process parameters of the manufacturing processes, including the re-rolling degrees (NWG) of the second cold rolling, are listed in **Table 2.** Here, T_E denotes the final rolling temperature of the hot strip, T_H denotes the coiling temperature (take-up temperature of the hot strip), T_G denotes the annealing temperature in the annealing furnace, t_G denotes the total annealing time of the steel sheet in the annealing furnace, t_H denotes the holding time during which the steel sheet was held at the annealing temperature, v_K denotes the cooling rate after annealing in the annealing furnace, and NWG denotes the re-rolling degree in secondary cold rolling. Finally, after re-rolling, an artificial aging of the flat steel products was produced by heating the sample to 200°C for 20 minutes.

Tensile tests were carried out on the aged specimens to determine the tensile strength in the direction of rolling (Rm in MPa, measured in accordance with DIN EN ISO 6892-1) and the

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Erichsen value (ET in mm, measured in an Erichsen cupping test in accordance with the standard DIN EN ISO 20482 (2003-12)). The material properties of the post-rolled steel sheets, including the final thickness (d) after the second cold rolling, are given in **Table 3,** where

- d is the thickness of the steel sheet (in mm),
- ET is the Erichsen value measured on the specimens (in mm),

and

- Rm is the tensile strength (in MPa) in the rolling direction.

Table 3 shows, in addition to the the Erichsen value (ET) measured by the cupping test on the specimens of the steel sheets according to the invention and the steel sheets not according to the invention, also the calculated Erichsen value (ET_b) obtained from the formula

$$ET_b = 11.1 \cdot (C + N) + 11.01 \cdot d - 0.00864 \cdot Rm + 7.524 \qquad \text{(formula 1')}$$

and the difference between the measured and the calculated Erichsen values ($\Delta ET = ET - ET_b$).

After measuring the mechanical properties, in particular the thickness d, the tensile strength Rm and the Erichsen value ET, the samples were provided with organic coatings, namely a BPA-free polyester varnish with a varnish film thickness of 5 µm on each side or a PET film with a film thickness of 12 µm. Subsequently, the Erichsen value was measured again in a cupping test. The results are shown in the columns "Delta Paint" and "Delta Film" of Table 3, which indicate the difference between the Erichsen values of the uncoated steel sheet and the Erichsen values of the painted or film-coated steel sheet.

The values of the Erichsen indentation (ET in mm) measured on the uncoated flat steel products (i.e. without paint or film coating) are plotted in Figure 1 against the thickness of the flat steel products (d in mm), the dots representing the values of the Erichsen indentation measured on the individual specimens and the transverse bars connected to them by a connecting line representing the value of the Erichsen indentation calculated according to formula (1'). An upward deviation characterizes a higher calculated value (ET_b) and a downward deviation characterizes a lower calculated value in comparison to the measured value of the Erichsen value (ET). It can be seen from Figure 1 that the flat steel products according to the invention, whose measured Erichsen value is marked with a filled dot, each have a measured value which is above the Erichsen value (ET_b) calculated according to formula (1'), i.e. the samples according to the invention satisfy the condition of formula (1). In contrast, the reference specimens not according to the invention, whose measured Erichsen value ET is marked with a circle in each case, have a measured value that is below the calculated Erichsen value (ET_b) according to formula (1'), i.e. the reference specimens not according to the invention do not fulfill the condition of formula (1).

This is illustrated by Figure 2, in which in each case the difference ΔET (in mm) of the Erichsen values (ET) measured on the samples from Tables 1 to 3 and the calculated Erichsen value (ET_b) according to formula (1') is shown and plotted over the number of the respective example from Tables 1 to 3, where

$$\Delta ET = ET - ET_b$$

and ET is the measured Erichsen value (in mm) and ET_b is the Erichsen value calculated according to formula (1') from the properties of the specimens according to Table 3. As can be seen from Figure 2, all the samples of Examples 6 to 14 according to the invention satisfy the condition of Formula (1), while all the comparative examples, with the exception of Example 5, do not satisfy this condition. It can be seen from Table 3 that the specimens of Example 5, however, have a tensile strength of $Rm < 600$ MPa, which is too low, and therefore cannot be characterized as being according to the invention.

The invention thus can be used to manufacture flat steel products and to characterize them in terms of their suitability for the manufacture of packagings, such as aerosol cans, or parts thereof (such as, for example, tear-off lids), taking into account, via the relation of formula (1), in particular the relationship between the formability, characterized by the Erich value, and the mechanical properties, namely the thickness and the strength (especially the tensile strength in the rolling direction). By applying formula (1), the suitability of the flat steel products for the production of specific packaging or parts thereof can be determined. For example, it can be determined whether, for a given thickness of the steel sheet and a given tensile strength, there is a sufficiently high forming capacity to produce a particular package or part thereof in a forming process suitable for this purpose.

Composition (in % by weight)

No.		C	N0	N	C+N	Al	Mn	Si	P	S
1	Comparison example	0,066	0,0029	0,0029	0,0689	0,037	0,29	0,008	0,015	0,007
2	Comparison example	0,017	0,0035	0,0152	0,0322	0,028	0,19	0,005	0,010	0,009
3	Comparison example	0,045	0,0143	0,0143	0,0593	0,009	0,22	0,005	0,013	0,012
4	Comparison example	0,021	0,0026	0,0026	0,0236	0,035	0,20	0,006	0,012	0,009
5	Comparison example	0,056	0,0042	0,0144	0,0704	0,022	0,22	0,007	0,014	0,009
6	According to the invention	0,079	0,0114	0,0225	0,1015	0,011	0,33	0,006	0,014	0,008
7	According to the invention	0,081	0,0128	0,0198	0,1008	0,032	0,32	0,005	0,012	0,008
8	According to the invention	0,072	0,0087	0,0156	0,0876	0,035	0,31	0,008	0,013	0,009
9	According to the invention	0,071	0,0118	0,0352	0,1062	0,015	0,33	0,006	0,011	0,010
10	According to the invention	0,075	0,0135	0,0417	0,1167	0,017	0,35	0,006	0,012	0,008
11	According to the invention	0,070	0,0133	0,0249	0,0949	0,012	0,32	0,007	0,013	0,008
12	According to the invention	0,042	0,0057	0,0211	0,0631	0,031	0,02	0,005	0,013	0,008
13	According to the invention	0,069	0,0123	0,0246	0,0936	0,013	0,32	0,007	0,013	0,009

14	According to the invention	0,067	0,0120	0,0198	0,0872	0,012	0,30	0,006	0,012	0,010

Other constituents: Mo < 0.006 wt%, Cr < 0.032 wt%, Ni < 0.013 wt%, Cu < 0.013 wt%, Ti < 0.001 wt%, B< 0.004 wt%, Nb < 0.002 wt%, Sn < 0.008 wt.%, balance: iron

Table 1

No.		T_E (°C)	T_H (°C)	T_G (°C)	t_G (s)	t_H (s)	v_K (K/s)	NWG (%)
1	Comparison example	875	573	665	157	45	11	13
2	Comparison example	888	635	673	146	42	18	35
3	Comparison example	876	658	621	230000	-	0,005	29
4	Comparison example	891	629	654	132	38	12	40
5	Comparison example	882	667	667	132	38	15	8
6	According to the invention	853	559	642	132	38	15	13
7	According to the invention	863	567	638	167	48	20	14
8	According to the invention	864	582	642	146	42	9	9
9	According to the invention	871	575	640	157	45	13	15
10	According to the invention	848	563	646	132	38	6	16

11	According to the invention	848	569	635	132	38	10	8
12	According to the invention	868	573	639	132	38	11	14
13	According to the invention	866	576	641	132	38	7	12
14	According to the invention	871	571	645	153	44	8	12

Table 2

No.	d (mm)	Rm (MPa)	ET (mm)	ET b (mm)	ΔET (mm)	Delta varnish (mm)	Delta foil (mm)
1	0,18	639	4,5	4,74963	-0,2496	-0,1496	-0,3496
2	0,28	663	5,0	5,2359	-0,2359	-0,1359	0,0359
3	0,25	628	4,9	5,50881	-0,6088	-0,6088	-0,4088
4	0,22	617	4,4	4,87728	-0,4773	-0,37228	-0,1773
5	0,22	583	6,0	5,69052	0,3095	0,2095	0,3095
6	0,14	680	4,5	4,31685	0,1832	0,3831	0,2832
7	0,45	710	7,7	7,46298	0,2370	0,3370	0,5370
8	0,27	605	6,5	6,24186	0,2581	0,5581	0,4581
9	0,32	763	5,9	5,6337	0,266	0,4663	0,3663
10	0,24	806	4,8	4,49793	0,3021	0,5021	0,5021
11	0,16	609	5,4	5,07723	0,3228	0,5228	0,6228
12	0,18	621	5,1	4,84077	0,2592	0,4592	0,3592
13	0,21	644	5,7	5,3109	0,389	0,4891	0,5891
14	0,31	674	6,8	6,08166	0,7183	0,9183	0,9183

Table 3

Claims:

1. A flat steel product for packaging comprising a cold rolled steel sheet having a thickness (d) of less than 0.5 mm and the following composition by weight:
    - C: more than 0.03% and less than 0.1%,
    - Si: less than 0.10%,
    - Mn: 0.10 to 0.60%
    - P: less than 0.10%,
    - S: less than 0.03 %,
    - Al: less than 0.05%,
    - N: more than 0.014%,
    - optionally Cr: less than 0.1%,
    - optionally Ni: less than 0.1%,
    - optionally Cu: less than 0.1%,
    - optional Ti: less than 0.01 %,
    - optional B: less than 0.005 %,
    - optional Nb: less than 0.01 %,
    - optional Mo: less than 0.02 %,
    - optional Sn: less than 0.03 %,
    - Residual iron and unavoidable impurities,

the sum of the carbon content (C) by weight and the nitrogen content (N) by weight being at least 0.050%, and the flat steel product having a tensile strength (Rm) of at least 600 MPa and an Erichsen value, being dependent on the thickness (d in mm), the carbon content (C in % by weight), the nitrogen content (N in % by weight) and the tensile strength (Rm in MPa) of the steel sheet, of

$$ET \geq 11.1 \cdot (C + N) + 11.01 \cdot d - 0.00864 \cdot Rm + 7.524$$

where ET is the Erichsen value in mm.

2. A flat steel product according to claim 1, **wherein** the steel sheet has the following composition by weight:
    - C: more than 0.04% and less than 0.1%,

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- Si: more than 0.003% and less than 0.03%,
- Mn: more than 0.17 and less than 0.5%,
- P: more than 0.003% and less than 0.03%,
- S: more than 0.001% and less than 0.03%,
- Al: more than 0.002% and less than 0.018%,
- N: more than 0.014 and less than 0.07%,
- optionally Cr: less than 0.1%,
- optionally Ni: less than 0.1%,
- optionally Cu: less than 0.1%,
- optional Ti: less than 0.01 %,
- optional B: less than 0.005 %,
- optional Nb: less than 0.01 %,
- optional Mo: less than 0.02 %,
- optional Sn: less than 0.03 %.

3. Flat steel product according to claims 1 or 2, **wherein** the thickness of the steel sheet is greater than 0.14 mm.

4. Flat steel product according to one of claims 1 to 3, **wherein** the flat steel product comprises an organic coating.

5. Flat steel product according to claim 4, **wherein** the organic coating is a polymer coating comprising a polyester, polyethylene terephthalate (PET), polyethylene (PE) or polypropylene (PP), or a mixture thereof.

6. Flat steel product according to claim 4, **wherein** the organic coating comprises a BPA-NI lacquer or a water-soluble lacquer.

7. Flat steel product according to any one of claims 4 to 6, **wherein** the organic coating has a coating thickness of 5 to 100 µm.

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8. Flat steel product according to any one of claims 1 to 7, **wherein** the Erichsen value of the uncoated steel sheet is at least 4.3 mm when the thickness of the steel sheet is in the range of 0.14 to 0.25 mm and at least 5.3 mm when the thickness of the steel sheet is in the range of 0.26 to 0.49 mm.

9. Flat steel product according to any one of claims 4 to 8, **wherein** the steel sheet coated with the organic coating has an Erichsen value that is at least 0.1 mm larger than the Erichsen value of the uncoated steel sheet.

10. Flat steel product according to any one of claims 1 - 9, **wherein** the steel sheet is obtainable by

   - Heating a steel slab to a preheating temperature of at least 1200°C and hot rolling the steel slab to a final rolling temperature of at most 900°C to produce a hot strip,
   - Winding the hot strip at a winding temperature of 670°C or less,
   - Cold rolling of the hot strip with a cold rolling degree of at least 80% to produce a cold-rolled steel sheet,
   - Annealing of the cold-rolled steel sheet in an annealing furnace at an annealing temperature between the recrystallization temperature of the steel and 700°C, ,
   - Nitriding the cold-rolled steel sheet in the annealing furnace, in particular before or during annealing, to a nitrogen content of more than 0.014% by weight,
   - Re-rolling of the nitrided and annealed steel sheet with a degree of re-rolling between 7% and 20%.

11. Flat steel product of claim 10, wherein the hot strip is cooled to the coiling temperature after final rolling at a cooling rate of at least 15 K/s.

12. Flat steel product of claim 10 or 11, wherein the annealing occurs during an annealing period of from 30 seconds to 180 seconds.

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13. Flat steel product according to any one of claims 10 to 12, wherein the cold-rolled steel sheet is cooled after annealing at a cooling rate of from 2 K/s to 25 K/s,.

14. Flat steel product according to any one of claims 10 to 13, wherein the hot strip is pickled before cold rolling and/or degreased after cold rolling.

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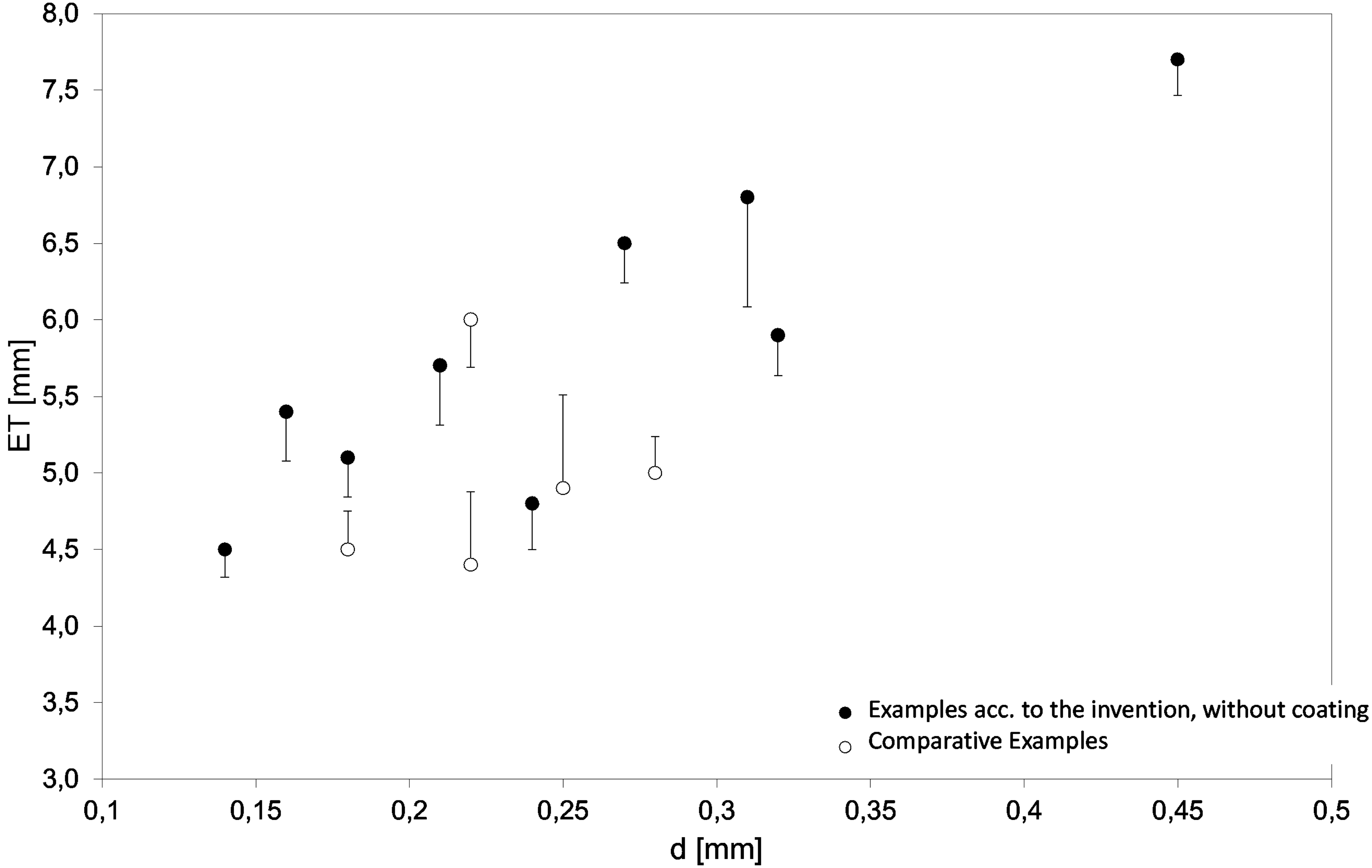
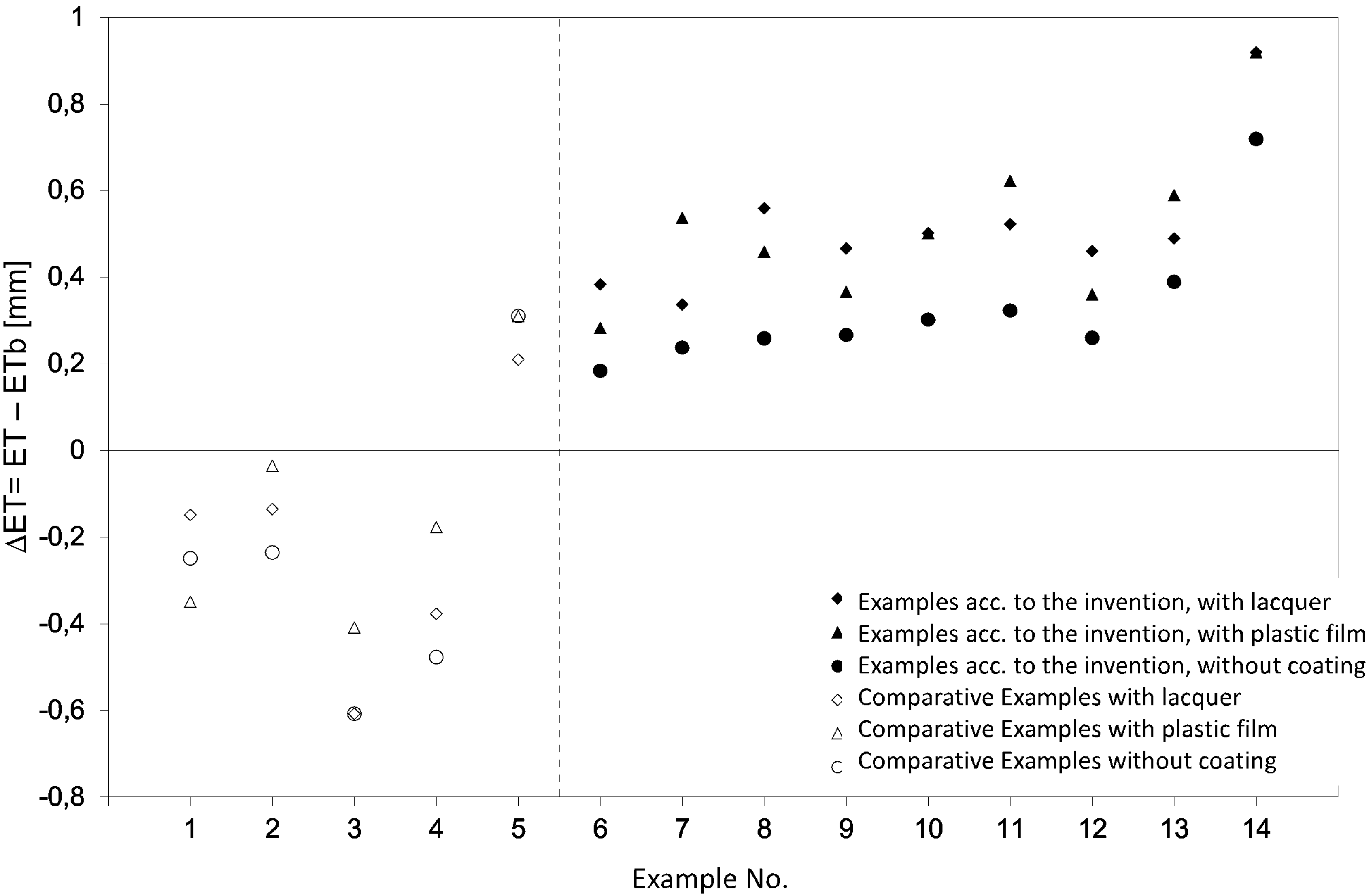


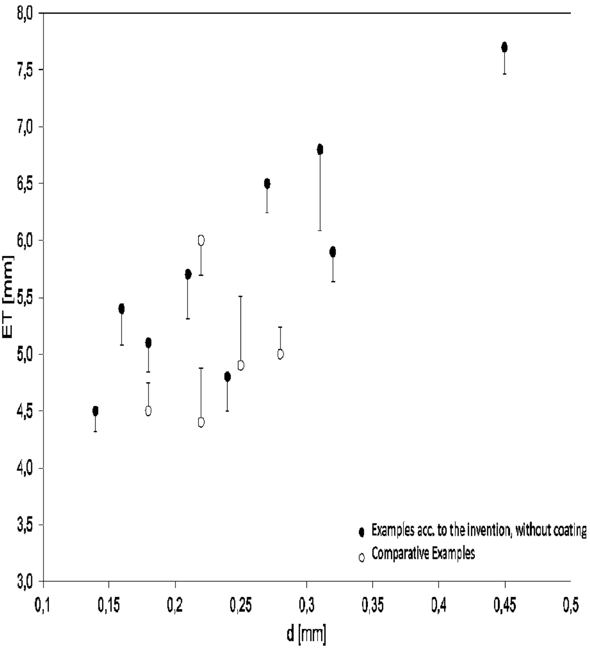
8,0
7,5
7,0
6,5
6,0
5,5
5,0
4,5
4,0
3,5
3,0
ET [mm]
0,1
0,15
0,2
0,25
0,3
0,35
0,4
0,45
0,5
d [mm]
Examples acc. to the invention, without coating
Comparative Examples

Fig. 1



1
0,8
0,6
0,4
0,2
0
-0,2
-0,4
-0,6
-0,8
ΔET= ET – ETb [mm]
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Example No.
Examples acc. to the invention, with lacquer
Examples acc. to the invention, with plastic film
Examples acc. to the invention, without coating
Comparative Examples with lacquer
Comparative Examples with plastic film
Comparative Examples without coating

Fig. 2


8,0
7,5
7,0
6,5
6,0
5,5
5,0
4,5
4,0
3,5
3,0
ET [mm]
0,1
0,15
0,2
0,25
0,3
0,35
0,4
0,45
0,5
d [mm]
Examples acc. to the invention, without coating
Comparative Examples