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D E C I S I O N
of 21 November 1996

Case Number: T 0857/92 - 3.3.2

Application Number: 88115550.1

Publication Number: 0309902

IPC: C03C 17/245

Language of the proceedings: EN

Title of invention:
Chemical vapor deposition of tin oxide on float glass in the tin bath

Applicant:
PPG INDUSTRIES, INC.

Opponent:
-

Headword:
Chemical vapor deposition/PPG INDUSTRIES

Relevant legal provisions:
EPC Art. 56

Keyword:
"Inventive step (yes)"

Decisions cited:
-

Catchword:
-

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Case Number: T 0857/92 - 3.3.2

D E C I S I O N
of the Technical Board of Appeal 3.3.2
of 21 November 1996

Appellant: PPG INDUSTRIES, INC.
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Pennsylvania 15272 (US)

Representative: Sternagel, Hans-Günther, Dr.
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Decision under appeal: **Decision of the Examining Division of the European Patent Office posted 13 April 1992 refusing European application No. 88 115 550.1 pursuant to Article 97(1) EPC.**

Composition of the Board:

Chairman: P. A. M. Lançon
Members: M. M. Eberhard
J. van Moer

Summary of Facts and Submissions

I. European patent application No. 88 115 550.1 was refused by a decision of the Examining Division. The decision was based upon the set of amended claims filed on 13 August 1991.

II. The ground for the refusal was that the subject matter of the amended claims 1 to 11 did not involve an inventive step over the disclosure of the citations US-A-3 674 453, EP-A-0 186 481 and WO 87/01970 (hereinafter D1, D3 and D4 respectively).

The Examining Division held that the claimed method differed from the process of D1 essentially by the use of air as carrier medium for depositing the metal oxide. However, as the deposition of tin oxide on glass by a CVD method using air as a carrier medium and a reactant (cf. D3 or D4) was known, the skilled person whose aim was to coat glass by a CVD method would have applied the useful information contained in D3 to solve his technical problem. The Appellant's arguments stressing the importance of maintaining a non-oxidising atmosphere over the tin bath despite the use of air in the coating chamber were not accepted.

III. The Appellant lodged an appeal against this decision. Several sets of amended claims were filed during the appeal proceedings in reply to communications of the Board. Oral proceedings were held on 21 November 1996. At the hearing, the Appellant submitted two sets of amended claims as main and auxiliary request respectively. Claim 1 of the main request reads as follows:

"A method for depositing a low emissivity tin oxide film onto a continuous glass substrate conveyed through a coating station by:

a. supporting a glass substrate on a molten metal bath;

b. maintaining a nonoxidising atmosphere over the molten metal bath and glass substrate;

c. contacting said glass substrate in a coating station on the surface which is not supported on said molten metal bath with a mixture of air as carrier gas and a tin-containing coating reactant in vapor form while maintaining the surface being coated free from a reducing atmosphere; and

d. thermally reacting said coating reactant to provide said glass with a tin oxide film and

e. removing unreacted coating reactant, undeposited reaction product and reaction by-products and carrier gas from the coating site."

IV. The Appellant's arguments submitted in writing can be summarised as follows:

The closest prior art was D3, since this document was also concerned with the problem of production of a tin oxide coating having a low surface resistance and hence a low emissivity. With respect to D3, the problem to be solved was to provide a method for depositing a tin oxide coating resulting in an improved coating uniformity, reduced reflected distortion and an improved process efficiency without compromising low surface resistance and hence low emissivity.

The solution to this problem, namely performing the vapour deposition while the glass substrate was still supported on a molten metal bath, was not obvious in view of D1. The only purpose for using the float glass process in D1 was to avoid distortion of the flat glass, which had to be treated at very high temperatures in order to dissolve the metal oxide into the glass surface. Dissolving tin oxide into the glass surface as taught in D1 would have resulted in a surface having a considerably high surface resistance. Accordingly, a skilled person would never have combined the teaching of D1 and D3.

If the skilled person had nevertheless tried to combine D1 and D3, then he would have had to conduct the process of D1 under conditions such that a tin oxide film be deposited onto the glass surface. This would have required an increase of the oxygen concentration. It was not evident to the skilled person that the measures taken in D1 to avoid the oxygen coming into contact with the molten tin bath would also have worked with a considerably higher oxygen concentration in the treatment zone. If the skilled person had increased the oxygen content in the said zone, he would, in any event, have used a protective atmosphere containing a reducing constituent such as hydrogen, to be on the safe side. D1 also taught in that direction. The use of an inert protective atmosphere was disclosed in D1 only in the context of modifying or developing certain colours. However, with high hydrogen concentration the desired low surface resistance could not have been achieved as shown in the examples of the present invention. It was the merit of the inventor to have recognized that the surface resistance depended on the hydrogen concentration in the protective atmosphere. Neither D1 nor the other cited references taught that a high hydrogen concentration was detrimental to the surface resistance of tin oxide coatings.

At the hearing, the Appellant further argued that the question whether D1 or D3 represented the closest prior art had been reconsidered, and that D1 seemed to be a more appropriate starting point since the process of D1 involved the treatment of a moving glass ribbon still supported on the molten tin bath. The problem to be solved with respect to D1 was to provide a method for depositing a uniform tin oxide film having a low surface resistance and a low emissivity onto the surface of a float glass ribbon. The Appellant stressed that the oxidising atmosphere used in D1 comprised a very low amount of oxygen, i.e. traces up to 6%, so that the risk of interference with the protective atmosphere over the tin bath was relatively low. The skilled person would have been very reluctant to use air as carrier gas in a treatment zone over the molten tin bath since the contact of the latter with air had to be avoided. Furthermore, the exhaust gases in the process of D1 contained no oxygen whereas the use of air as carrier gas would have implied the presence of a relatively high amount of oxygen in the exhaust gases. Moreover, the skilled person would have feared that the difference between the temperature of the glass ribbon and the temperature of the carrier gas caused cracks in the glass ribbon. For all these reasons, he would not have used air as carrier gas to coat the glass ribbon in the float portion.

V. The Appellant requested that the decision under appeal be set aside and that a patent be granted in the following version :

as main request: claims 1 to 8 and description pages 1 to 3, 3a, 3b and 4 to 10, all submitted at the oral proceedings, and drawings as originally filed; or

as auxiliary request: claims 1 to 7 and description pages 1 to 3, 3a, 3b and 4 to 10, all filed at the oral proceedings, and drawings as originally filed.

Reasons for the Decision

1. The appeal is admissible.

Main request

2. The amended claims 1 to 8 are considered to meet the requirements of Article 123(2) EPC. Claim 1 is based on the combination of the features recited in claims 1, 10, 11 and 14 as originally filed with additional features disclosed in the original description (cf. page 4, lines 11 to 14, 19 to 23 and 35 to 36, page 7, lines 15 to 19, page 8, lines 27 to 30 and page 10, lines 27 to 29). The features of the dependent claims 2 to 8 correspond to those of the original claims 2, 3, 5 to 9 respectively. The amendments in the description are also in conformity with the provisions of Article 123(2).

3. The process of claim 1 is novel with respect to the prior art cited in the search report. None of the documents cited therein discloses a process for depositing a low emissivity tin oxide film onto a float glass surface, which comprises the combination of features recited in claim 1.

4. The question arises which of the documents D1 or D3 represents the closest prior art. D3 relates to a process for depositing a tin oxide film having a low sheet resistance onto a glass substrate, by chemical

vapour deposition. However, the film is not deposited onto a moving continuous glass ribbon in the float portion of the float process so that the problem of possible interference between a protective atmosphere over the molten tin bath and the oxidising agent is not dealt with. On the contrary, this problem is addressed in D1 where the process involves the treatment of the surface of a moving continuous glass ribbon in the float region with a vapour of a tin compound and an oxidising agent. In these circumstances, although D1 does not disclose the deposition of a tin oxide film having a low emissivity onto the glass surface, the Board can accept the Appellant's arguments and the Examining Division's approach that D1 constitutes a more appropriate starting point for the definition of the problem underlying the present application.

4.1 More precisely, D1 discloses a process for producing a continuous layer of metal oxide dissolved in the surface of float glass, for example tin oxide. This process comprises advancing a continuous glass ribbon along a molten metal bath (for example a molten tin bath) over which a protective atmosphere is maintained, directing a vapour of a metal compound into a treatment zone onto the upper surface of the glass ribbon supported on the float bath, said surface being at a temperature of at least 600°C, supplying an oxidising agent into said metal compound vapour, maintaining the oxidising agent and the vapour in the treatment zone in non-destructive relationship with the protective atmosphere, maintaining the oxidising agent at a concentration in the treatment zone sufficient to oxidise the metal compound only at the hot glass surface so as to produce a metal oxide which is dissolved into a surface layer of the glass, and removing spent vapours from the said treatment zone. According to D1, the protective atmosphere over the molten tin bath usually contains a reducing agent, for

example hydrogen, and in the preferred embodiments it comprises 3 to 5% hydrogen. In the embodiments concerning the dissolution of tin oxide in the glass surface, the tin compound in vapour form is either stannic chloride or stannous oxide, the oxidising agent fed into the treatment zone being then a mixture of 1% oxygen with 99% nitrogen or a mixture of 10% oxygen with 90% nitrogen respectively (see claims 1 and 2, column 1, abstract and lines 49 to 60, column 2, lines 47 to 71, column 4, lines 20 to 23, column 5, lines 34 to 38, column 8, lines 19 to 41, column 8, line 70 to column 9, line 27, Figures 5, 6 and 7).

As pointed out by the Appellant, there is no deposition of a tin oxide film onto the glass surface in this process, instead the treated float glass has its surface modified by the dissolution of the tin oxide into a surface layer of the glass, said layer having a certain depth within the glass. Starting from this prior art, the technical problem underlying the present application can be seen in providing a method for depositing a uniform tin oxide film having a low surface resistance and a low emissivity onto a float glass ribbon.

The present application proposes to solve this problem by the process as defined in claim 1, which differs from that of D1 by the fact that (i) a tin oxide film with a low emissivity is formed on the glass substrate, (ii) air is used as carrier gas for the tin-containing coating reactant and (iii) the surface being coated is maintained free of a reducing atmosphere. Having regard to the examples of the application and to the statement at page 8 of the description (second paragraph), the Board has no reason to doubt that this problem has been solved by the process defined in claim 1.

4.2 According to D1, the amount of oxidising agent introduced into the treatment zone is relatively low. When a mixture of 5 to 10% chlorine in an inert gas is used as reactive gas to form the metal chloride vapour, 0.00001 to 6% oxygen (by volume) is maintained as oxidising agent in the treatment zone (see claim 9). In the embodiment according to Figure 5 where the metal compound vapour is stannous oxide vapour, the oxidising agent fed through the nozzle (56) consists of a mixture of 10% oxygen and 90% nitrogen, which is said to be a "strongly oxidising" mixture (see column 8, lines 33 to 41). The concentration of oxygen in the treatment zone inside the refractory hood (52) is in fact lower than 10% taking into account that the treatment zone also comprises the nitrogen supplied to the tube (54) and the produced stannous oxide vapour. This teaching neither suggests that air might be used as carrier gas for the tin compound in vapour form nor that a non-destructive relationship with the protective atmosphere over the molten tin bath might still be maintained with considerably higher concentrations of oxygen in the treatment zone.

4.3 D3 discloses a chemical vapour deposition method for producing a fluorine-doped tin oxide film on a glass substrate. This process makes it possible to produce coatings having a minimum and constant sheet resistance under different process conditions (see claims 1 and 3, surface resistivity of 25 ohms/sq. at a thickness of about 180-210 nm). In the CVD process disclosed in D3, the deposition is carried out in a deposition chamber where the glass substrate is mounted on a heated plate. The carrier gas for the vapour mixture containing the organotin compound is preferably air (see page 4). The question arises whether in view of D3 the skilled person faced with the problem stated above would have contemplated trying said CVD process in the float glass process of D1, in particular whether he would have

considered using air as carrier gas for the tin-containing reactant to be brought into contact with the glass substrate supported on the molten tin bath.

It was well known before the priority date that a non-oxidising atmosphere must be maintained over the float bath and that ingress of air into the headspace over the bath must be prevented in order to avoid oxidation of the molten tin. It was also well known that this could be achieved by using a small amount of a reducing constituent such as hydrogen in the atmosphere of the headspace and maintaining a positive pressure therein. In the float process of D1, the protective gas in the headspace (25) is for example a reducing gas containing 3% to 5% hydrogen (see column 2, last paragraph, column 5, lines 34 to 43). In view of D1 the skilled person was aware of the fact that it was possible to maintain a non-destructive relationship between the protective atmosphere over the float bath and the oxidising atmosphere in the treatment zone (see column 9, lines 20 to 27, and the embodiments according to Figure 5). However, as indicated above, this teaching concerns relatively low contents of oxygen in the treatment zone, i.e. lower than 10% by volume. Furthermore, as stressed by the Appellant, the spent gases which are removed from the treatment zone through the exhaust duct (61) at the downstream edge of the treatment zone contain themselves a very low amount of oxygen or no oxygen at all. On the contrary, the use of air as carrier gas for the tin-containing reactant would imply that the concentration of oxygen both in the treatment zone and in the exhaust gases would be considerably higher than in D1. In the treatment zone, the concentration of oxygen would be more than doubled with respect to the embodiment of D1 including the highest oxygen content and considered as strongly oxidising. In these circumstances, the Board can accept the Appellant's arguments that the skilled person would

have been very reluctant to perform the CVD process of D3 in the float section, using air as carrier gas for the tin-containing reactant, since he would have expected that with such high amounts of oxygen the non-destructive relationship with respect to the protective atmosphere could not be maintained.

Even if it were assumed that the skilled person would nevertheless have tried the CVD method in the float section of D1, using air as carrier gas, then he would certainly have taken precautions in order to minimize the higher risk of oxidation of the molten tin bath, resulting from the considerably higher amounts of oxygen in the treatment zone and in the exhaust gases. Therefore, although the use of an inert protective atmosphere such as nitrogen is mentioned in column 3, lines 12 to 15, of D1, he would not have chosen nitrogen as protective atmosphere but the reducing atmosphere which is used in the embodiments of D1 (see column 5, lines 34 to 38), all the more so as a slightly reducing atmosphere is usually employed in the float process. Thus, the skilled person would have tried to perform the CVD process while using a reducing protective atmosphere containing at least the hydrogen concentration of 3 to 5% disclosed in D1. Doing so, he could not have solved the problem stated above, since he would have obtained a tin oxide film having a high surface resistivity and a high emissivity as shown in the comparative examples 1 and 2 of the present application.

In order to achieve a tin oxide film exhibiting a low surface resistance and low emissivity when the CVD process is carried out in the float section, the surface being coated must be maintained free from a reducing atmosphere as stated in claim 1 and at page 10 of the description. Neither D1 nor the other cited documents contain information pointing towards this

solution. Although D1 discloses that nitrogen may be employed as protective atmosphere in the headspace over the molten tin bath when reduction of the treated glass surface is not required, the skilled person would not have selected an inert protective atmosphere for the reasons already given in the preceding paragraph and also because he could not infer from D1, D3 or D4 that the small amount of hydrogen contained in the protective atmosphere of the float might be detrimental to the surface resistivity and emissivity of the tin oxide film.

4.4 In the process disclosed in D4, the tin oxide coating is deposited by chemical vapour deposition onto the continuously advancing glass ribbon, using air as carrier gas for the tin compound. However, the corresponding treating station is not situated in the float section but in the **oxidising atmosphere of the lehr** where the problems of oxidation of the molten tin bath and of interference of the protective atmosphere with the oxidising medium used for the deposition of the tin oxide film do not exist. Therefore, the reasons indicated above in connection with the combination of the teaching of D1 and D3 apply analogously to the combination of D1 with D4 or to the combination of these three documents.

4.5 It follows from the above that the process as defined in claim 1 of the main request meets the requirement of inventive step set out in Articles 52(1) and 56 EPC.

5. Claim 1 being allowable, the same applies to the dependent method claims 2 to 8 whose patentability is supported by that of claim 1.

6. As a patent can be granted on the basis of the main request, examination of the auxiliary request was not necessary.

Order

for these reasons it is decided that:

1. The decision under appeal is set aside;

2. The case is remitted to the first instance with the order to grant a patent in the version according to the main request, namely:

Claims: 1 to 8 filed at the oral proceedings;

Description: pages 1 to 3, 3a, 3b and 4 to 10 filed at the oral proceedings;

Drawings: as originally filed.

The Registrar: The Chairman:

P. Martorana P. A. M. Lançon

H.Bo