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(54) **Method for improving layers of zinc**

(57) The present invention relates to a method for galvanizing a workpiece comprising steel, comprising steps for:

- bringing the workpiece into contact with liquid zinc with a temperature in a first temperature range of 420-800 degrees Celsius in order to obtain a number of alloy layers on the steel surface, characterized by

- heating the workpiece for a time period of 1 second to 24 hours at a temperature in a second temperature range of 420-800 degrees Celsius in order to obtain new layer compositions with a desired composition obtained by the treatment.

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Description

[0001] The present invention relates to treating workpieces comprising steel. Steel workpieces are often provided with a protective layer of another metal.

[0002] Such a process can be carried out by immersing a steel workpiece in a bath of molten zinc. The method creates a number of alloy layers as well as a layer of pure zinc on top of these layers. Such layers are shown in figure 1. Reference numeral 1 here designates the steel of the workpiece. The γ (gamma) layer 2 present thereon comprises a mixture of iron and zinc. Situated thereon is δ (delta) layer 3, which comprises a different composition of iron and zinc. A further layer, the ζ (zeta) layer 4, comprises a further mixture of iron and zinc. Finally, the η (eta) layer comprises practically pure zinc.

[0003] The galvanization produced by the above described layers is carried out at a temperature of about 450-465 degrees Celsius. The combined layer thickness here is usually 50 to 150 micrometers.

[0004] Workpieces which obtain an above described layer composition on the surface according to the above stated galvanizing method are very widely applicable in many technical environments where the protective action of the layers of zinc is important, such as for instance in the building industry or applications where steel is exposed to weather influences, such as for instance the use of containers. In addition, galvanized steel grids are often used in fields of application such as (petrochemical) factories or in other environments such as for instance walking surfaces.

[0005] A drawback of such zinc layers is that for instance in the case of fire or other incidents where the temperature rises above the melting point of zinc, the zinc will melt off the surface to which it is applied. The generally thickest outer layer of pure zinc will certainly melt away rapidly.

[0006] In order to obviate such a drawback, the present invention provides a method for galvanizing a workpiece comprising steel, comprising steps for:

- bringing the workpiece into contact with liquid zinc with a temperature in a first temperature range of 420-800 degrees Celsius in order to obtain a number of alloy layers on the steel surface,
- heating the workpiece for a time period of 1 second to 24 hours at a temperature in a second temperature range of 420-800 degrees Celsius in order to obtain new layer compositions with a desired composition obtained by the treatment.

[0007] The above described prior art layers result from the chemical and physical reaction between the surface of the workpiece and the molten zinc during the step for bringing the workpiece into contact with the zinc to obtain a transition zone comprising layers of different compositions of both metals.

[0008] Further chemical and physical reactions are

brought about between the metals during heating. Zinc particles herein diffuse further into the iron 1 and iron particles further diffuse into the zinc top layer 5. Thus is achieved that iron particles will occur right up to the surface of zinc layer 5. The connections between iron and zinc particles in this modified top layer will result in this top layer not being prone to melting away, even at very high temperatures. Tests have shown that, even at temperatures of 1500 degrees wherein the metal emits cherry-red light, no run-off or melt-off occurred.

[0009] A further advantage of the treatment according to the present invention is that the surface of the workpiece is "clean". This means that no zinc droplet residues, surface thickening, hard-zinc grains or skins or rough elements occur on the surface such as are normally present after the removal of a workpiece from a zinc bath.

[0010] The second temperature range is preferably 420-600 degrees Celsius and more preferably 440-560 degrees Celsius. As will be further described hereinbelow, tests have been performed in these ranges which have brought satisfactory results, wherein the above described advantages have been achieved.

[0011] Use is preferably made of a predetermined atmosphere during heating of the workpiece. A preferred embodiment hereof is that the atmosphere comprises a reducing gas. An alternative embodiment is that the atmosphere comprises oxygen.

[0012] The workpiece preferably comprises a number of perforations or openings. As described in the foregoing, the layers are changed by the heat treatment so that the layers comprising zinc become thicker overall.

[0013] The perforations or openings which become (partially) blocked during the thermal galvanization are further unblocked by the heat treatment. The unblocked surface of the perforations or openings also obtains the same surface layer as the rest of the surface of the workpiece. The perforations do not therefore have to be cleared by means of a post-treatment, which is an expensive operation.

[0014] It further occurs that steel in the form of small particles (hard zinc particles) enters a zinc bath during the thermal galvanization, and that such particles adhere to the surface of a workpiece when the workpiece is removed from the zinc bath. These hard zinc particles are removed from the surface by the heat treatment, which for instance takes place in that the metal hereof is absorbed into the surface of the workpiece. These particles do not therefore have to be removed mechanically or manually, which is a long and (partly for this reason) costly treatment. The same problem is solved in the case bulges or droplets are present which are left behind on the surface of the workpiece during the thermal galvanization.

[0015] In a further embodiment the workpiece comprises a fence or grid-like element. The hard zinc particles also occur in such workpieces and are also removed by the treatment.

[0016] In a further embodiment the workpiece comprises a building component or construction element for use in the building industry, wherein the heat treatment provides similar advantages as in the foregoing embodiments. An example of such a construction element is a lintel.

[0017] A further aspect of the present invention relates to a galvanized product obtained by means of a method as described in the foregoing or in the appended claims.

[0018] Further advantages, features and details of the present invention will be further described with reference to the annexed figures, in which:

- fig. 1 is a schematic representation in cross-section of a number of alloy layers which result during a galvanizing process;
- fig. 2 shows a view of a workpiece galvanized according to the prior art (fig. 2a) and a workpiece galvanized using the present invention (fig. 2b);
- fig. 3 is a perspective view of a further galvanized workpiece.

[0019] There are diverse methods for galvanizing a steel workpiece. Known among others are thermal galvanization, centrifugal galvanization, Sendzimir galvanization, Sherard galvanization, spraying zinc wire or zinc powder, electrolytic galvanization or mechanical galvanization. An embodiment of a method according to the present invention comprises follow-on steps for improving galvanized products or workpieces according to the prior art. Each of the prior art methods results in the galvanization of a number of layers of different alloys on the surface of the steel workpiece.

[0020] In the case of for instance thermal galvanization (fig. 1), four alloy layers are created on the steel 1. These layers each have a specific zinc-steel ratio or zinc-steel alloy. The compositions of these layers are known. Layer 1 is the steel of the workpiece. Layer 2, also referred to as the γ (gamma) layer, comprises 21-28% Fe. Layer 3, also referred to as the δ (delta) layer, comprises 7-11.5% Fe. Layer 4, also referred to as the ζ (zeta) layer, comprises 6.0-6.2% Fe. Layer 5, also referred to the η (eta) layer, comprises about 0.08% Fe. This top layer is therefore an almost pure layer of zinc.

[0021] This almost pure layer of zinc 5 melts off for instance in the case of fire where the temperature rises above 420 degrees Celsius. The workpiece, for instance a grid floor, thereby becomes unusable. If dripping zinc falls onto warm stainless steel, the zinc will begin to alloy with the steel. Nickel possibly present in stainless steel enhances the formation of such alloys. If there are conduits made for instance of stainless steel, these can be damaged hereby and begin to leak. In such cases both the galvanized workpieces and the damaged conduits must be replaced.

[0022] A drawback of the top layer 5 of almost pure zinc is therefore the thermal vulnerability.

[0023] An embodiment according to the present invention is that a galvanized workpiece with the above described alloy layers is heated, for instance in a furnace, to a temperature of for instance 420 to 550 degrees Celsius. This is for instance carried out for an hour.

[0024] In a test two thermally galvanized strips are brought to a temperature of 550 degrees Celsius for one hour in a closed electric furnace. Before the start of this treatment the surface layers had a thickness of $\pm 60 \mu\text{m}$. The strips had a smooth exterior, which is normal after thermal galvanization. A few zinc droplets and sharp protrusions are situated on the galvanized surface of the strips before they are placed in the furnace.

[0025] After the heat treatment in the oven the strips were discoloured to a dull grey strip. The zinc layers were about $100 \mu\text{m}$ in cross-section. Instead of being shiny, the surface had become somewhat matt/rough. The droplets and rough elements had disappeared. Further analyses must be carried out in respect of the composition of the iron-zinc layer, which had become thicker.

[0026] After this treatment a test was performed to test the heat resistance of the new layer. An untreated strip, i.e. not treated in the oven, with the prior art zinc layer and a treated strip according to an embodiment of the present invention were heated with a burner with a red-yellow flame. The prior art strip displayed melting-off of the zinc. The strip treated according to an embodiment of the present invention became red hot but no zinc dripped from it. The red glow of the heated strip was cherry-red, which indicates a temperature of about 1500 degrees Celsius.

[0027] In a further test a perforated plate was galvanized by means of thermal galvanization according to the prior art. The result was a galvanized plate with a shiny surface with zinc droplet residues and sharp protrusions. In addition, a large number of the holes or perforations had become clogged by a thin zinc membrane. Fig. 2a shows a graphic representation of the perforated plate 22. A few holes or perforations 24 were open after the treatment. A few holes 25 were wholly provided with a zinc membrane. A few holes 26 were partly provided with a zinc membrane. Zinc droplets or sharp protrusions 23 were further discernible on the surface. The plate was then placed for ten minutes in a furnace at 550 degrees Celsius with a temperature distribution of 10 degrees Celsius. The result is shown in fig. 2b. Plate 20 has a somewhat matt, roughened surface. The coarse unevenness has however disappeared. All openings or perforations are further provided in nicely uniform manner with a galvanized surface and are completely open. This has the advantage that after galvanization the perforations do not have to be opened up or cleaned. This opening or cleaning is very labour-intensive work. The removal of surface unevenness 23 is likewise very labour-intensive.

[0028] A similar result can be seen in fig. 3. Fig. 3a shows a workpiece 32 with surface roughness 34. This

surface roughness comprises droplets and sharp protrusions. The steel beam 30 of fig. 3b treated according to an embodiment of the present invention has a somewhat matt, lightly roughened surface but is otherwise uniform.

[0029] The workpieces of fig. 2b and 3b have a thicker alloy layer on the surface than the workpieces of fig. 2a and 3a. This is the result of a further exchange of Fe particles from the workpiece to the layers of zinc.

[0030] The surfaces of the heat-treated workpieces of fig. 2b and 3b are very suitable for applying a further coating, such as for instance an organic cover layer such as a powder coating. The adhesion to such surfaces is very good. In the tests a zinc oxide layer was found to form on the workpiece. In order to prevent this, nitrogen can for instance be used as shielding gas in the furnace.

[0031] A further test involved a workpiece being heated for twelve hours at 380 degrees Celsius and for fifteen minutes at 450 degrees Celsius. After this treatment the surface was coarse and displayed the features of an Si-steel. When a coating was then applied, slightly more degassing occurred than usual. The adhesion was however good. Prior to filing of this application no accurate analyses have as yet been performed relating to the percentages of Fe and Zn in the newly formed top layers. It has been determined that the alloy layers are overall substantially 20-50%, or about 30% thicker than before the heat treatment in the furnace. The top layer before the treatment comprises about 0.08% Fe. After the treatment the layer preferably comprises at least 5% Fe or the quantity of Fe as in the above \bar{o} (delta) layer 3 or ζ (zeta) layer 4.

[0032] The present invention is not limited to the above described preferred embodiment; the rights sought are defined by the following claims, within the scope of which many modifications can be envisaged.

Claims

1. Method for galvanizing a workpiece comprising steel, comprising steps for:
 - bringing the workpiece into contact with liquid zinc with a temperature in a first temperature range of 420-800 degrees Celsius in order to obtain a number of alloy layers on the steel surface, **characterized by**
 - heating the workpiece for a time period of 1 second to 24 hours at a temperature in a second temperature range of 420-800 degrees Celsius in order to obtain new layer compositions with a desired composition obtained by the treatment.
2. Method for treating a galvanized steel workpiece, comprising steps for heating the galvanized workpiece for a time period of 1 second to 24 hours at a temperature in a second temperature range of 420-800 degrees Celsius in order to obtain new layer compositions with a desired composition obtained by the treatment.
3. Method as claimed in one or more of the foregoing claims, wherein the second temperature range is 420-600 degrees Celsius and more preferably 440-560 degrees Celsius.
4. Method as claimed in one or more of the foregoing claims, wherein the first temperature range is 400-550 degrees Celsius and preferably 440-460 degrees Celsius.
5. Method as claimed in one or more of the foregoing claims, wherein the time period lies in the range of 5-1000 minutes, preferably 6-300 minutes and more preferably 10-60 minutes.
6. Method as claimed in one or more of the foregoing claims, comprising steps for cooling the workpiece to at least a predetermined temperature between placing of the workpiece into contact with the liquid zinc and heating thereof.
7. Method as claimed in one or more of the foregoing claims, wherein use is made of a predetermined atmosphere during heating of the workpiece.
8. Method as claimed in claim 7, wherein the atmosphere comprises a reducing gas.
9. Method as claimed in claim 7, wherein the atmosphere comprises oxygen.
10. Method as claimed in one or more of the foregoing claims, wherein the time duration of the heating is such that at the applied temperature an iron content of 2-14%, preferably 4-12% and more preferably 6-11% is present in the upper surface layer.
11. Method as claimed in one or more of the foregoing claims, wherein the heating takes place in a furnace.
12. Method for coating a workpiece after undergoing a method as claimed in one or more of the foregoing claims.
13. Method as claimed in one or more of the foregoing claims, wherein the workpiece comprises a number of perforations or openings, such as for instance in a perforated steel plate.
14. Method as claimed in one or more of the claims 1-12, wherein the workpiece comprises a fence or

grid-like element.

15. Method as claimed in one or more of the claims 1-12, wherein the workpiece comprises a building component or construction element for use in the building industry. 5

16. Method as claimed in claim 15, wherein the construction element is a lintel. 10

17. Galvanized product obtained by means of a method as claimed in one or more of the foregoing claims. 15

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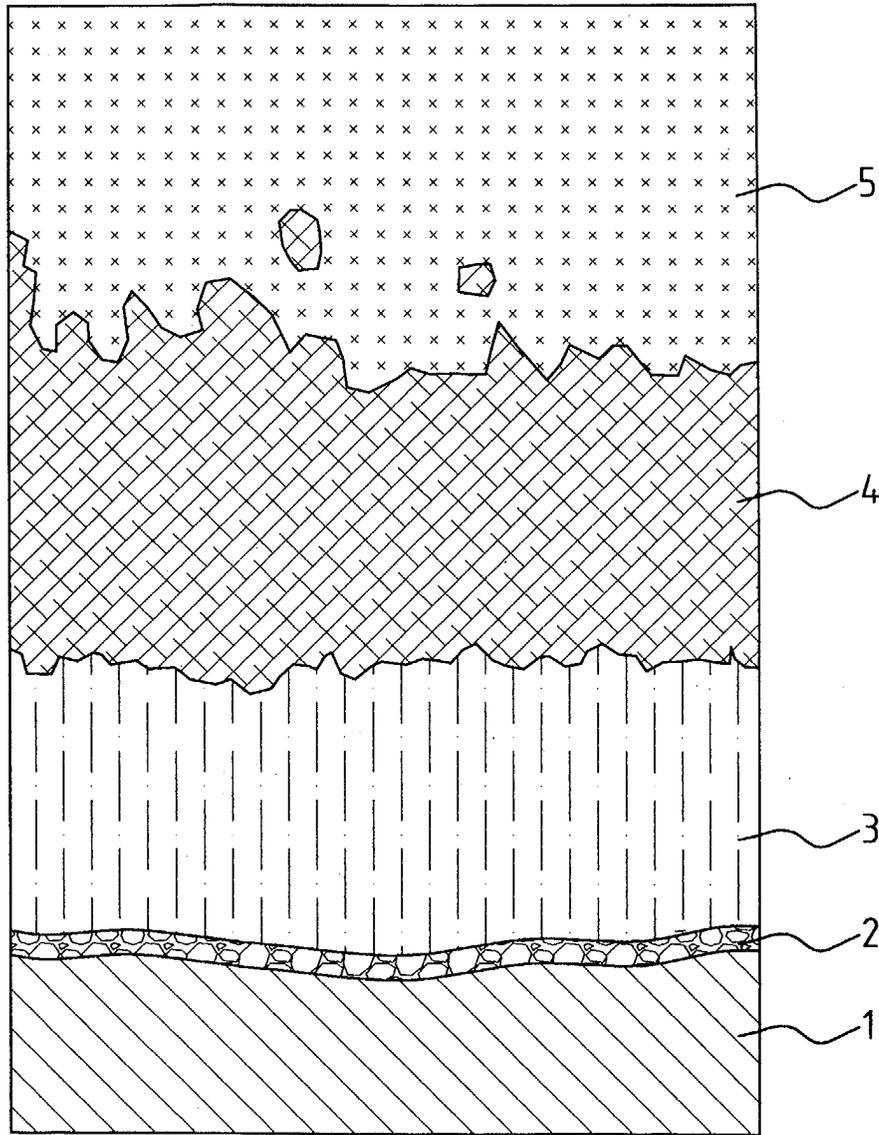


FIG. 1

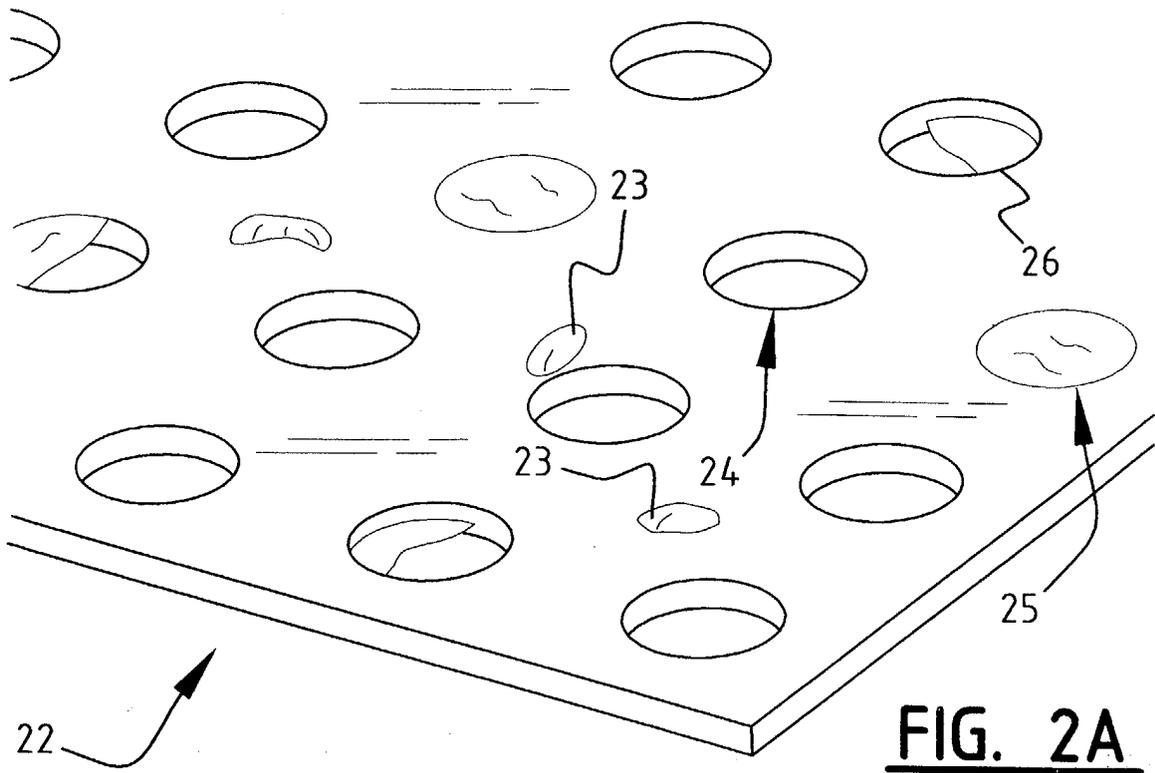


FIG. 2A

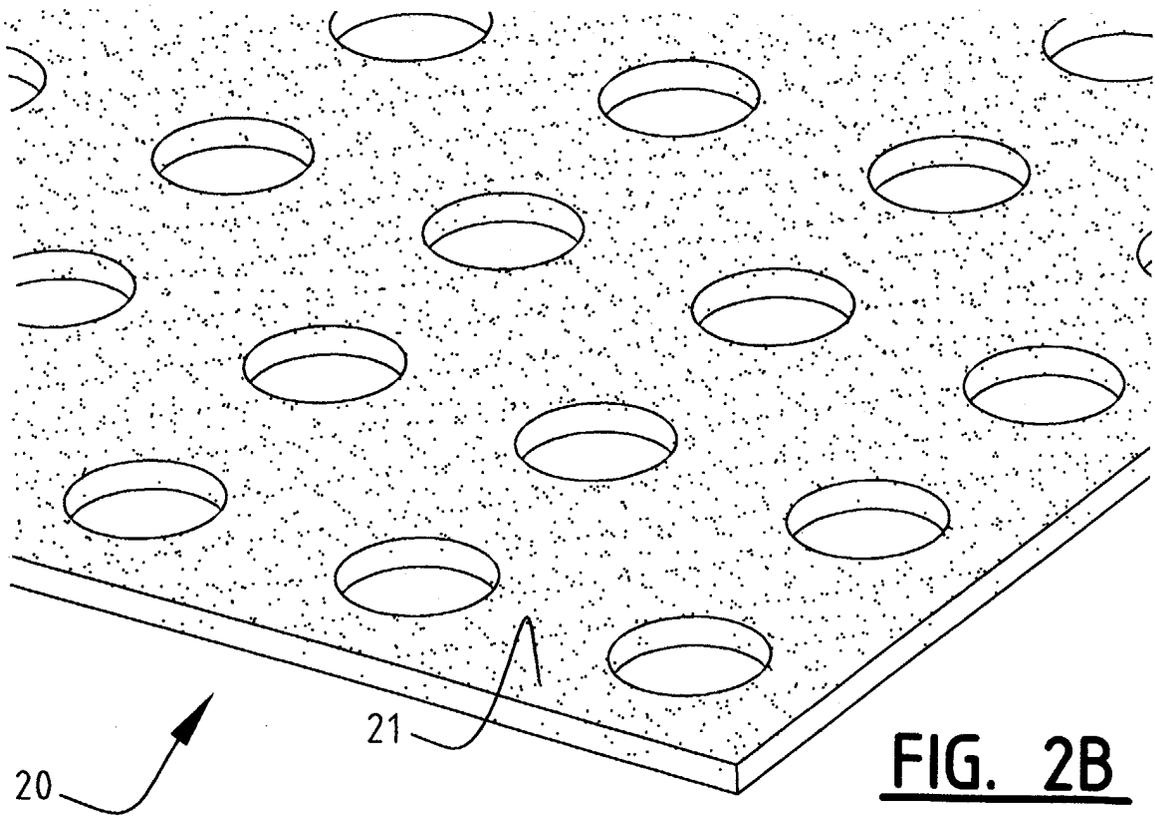
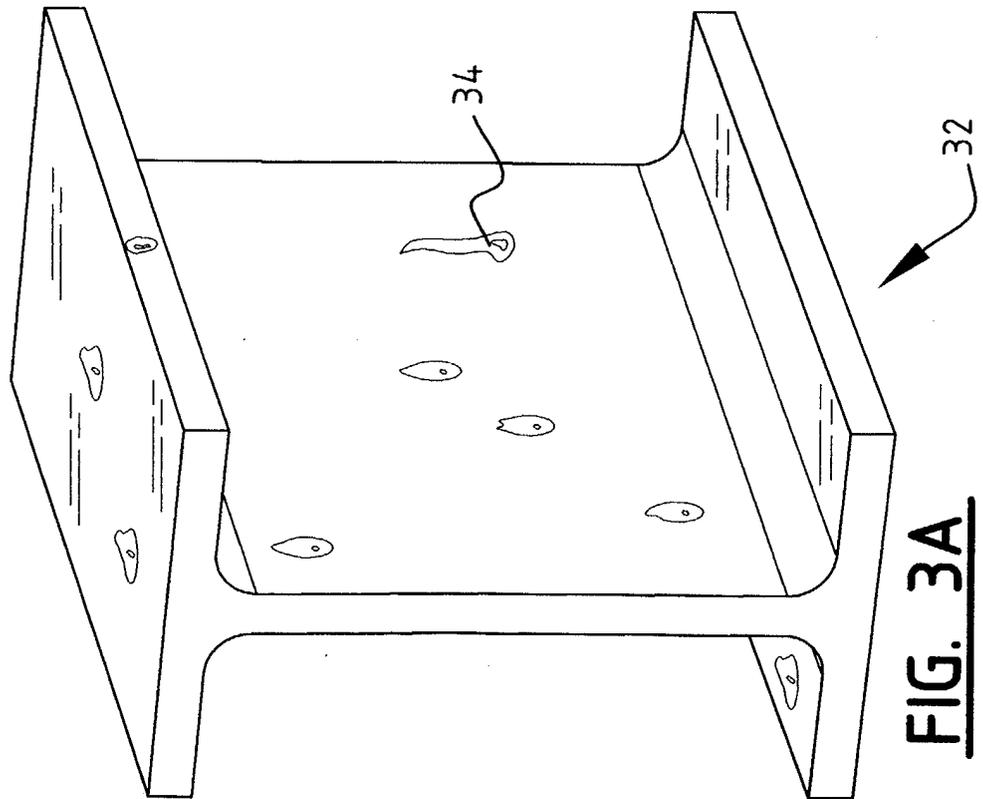
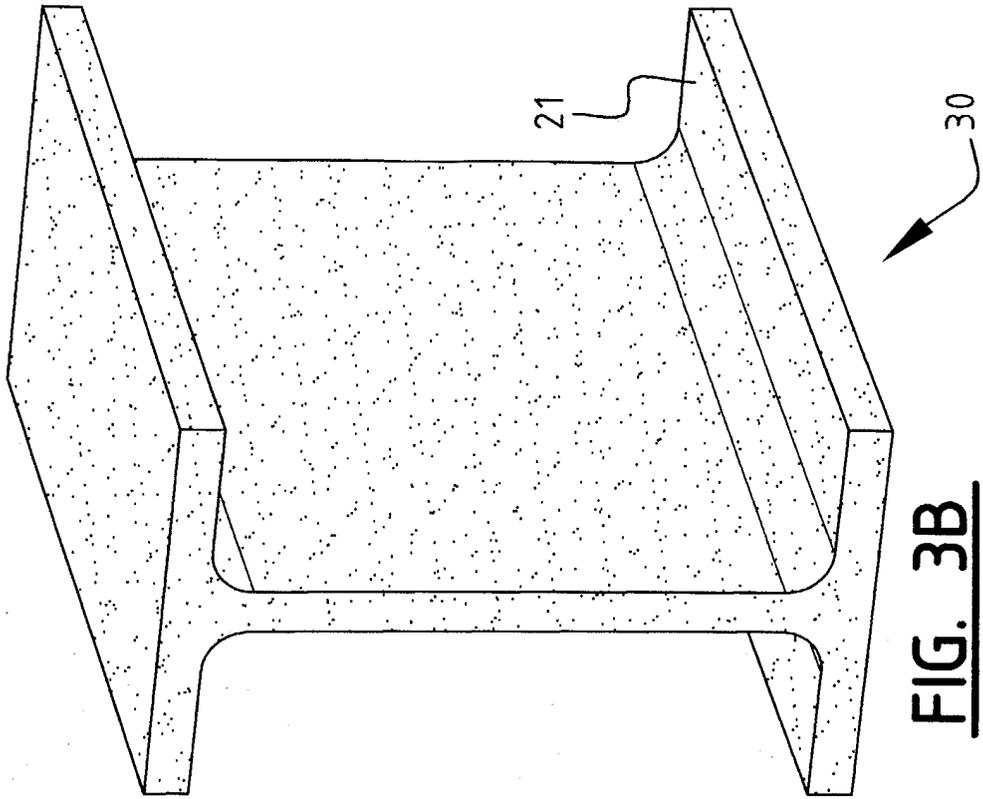


FIG. 2B





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Application Number
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<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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