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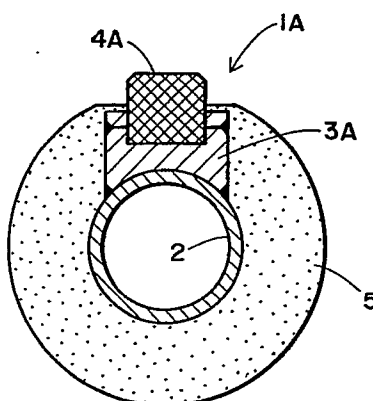
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Skid member using Fe/Cr dispersion strengthened alloys.

A skid rail for use in a furnace operating at high temperature is prepared by using an oxide-dispersion strengthened type heat resistant alloy, which consists essentially of 10-40% Cr and the balance of Fe and contains 0.1-2% of fine particles of high melting point metal oxide such as  $Y_2O_3$  dispersed in the ferrite matrix. The alloy optionally further contains up to 5% Al, or up to 5% Al and up to 5% Ti, and constitutes skid members (4A) of the rail.

The skid rail exhibits excellent properties against hot deformation, oxidation resistance, abrasion resistance, sulfidation resistance and thermal shock resistance.

FIG. 3



## SKID MEMBER USING FE/CR DISPERSION STRENGTHENED ALLOYS

The present invention concerns skid rails having a component which is exposed to furnace atmospheres made of a heat-resistant alloy having good strength, and corrosion and oxidation properties at high temperature.

Steel plates and steel wires are produced by rolling steel pieces called slabs or billets after uniformly heating them in a heating furnace such as a walking beam furnace or pusher furnace. If the temperature of the steel piece is lower at the position where the steel piece contacts the furnace bed than at the remaining positions, then uneven thickness of the rolled steel plate or even cracking may occur. In order to avoid these troubles, it is necessary to raise the temperature of the furnace bed at the position of contact with the heated piece to a temperature near the average heating temperature. Thus, at the highest temperatures of use the furnace bed metal attains a high temperature such as 1300°C or higher.

As a typical material for the furnace bed withstanding a high temperature of 1150°C or higher, there has been used a solid solution strengthened type heat-resistant casting alloy, which contains, in addition to Fe, 20-35% Cr, 15-35% Ni and 5-50% Co as the main components, and 0.5-5% Mo, 0.5-5% W and 0.2-4.0% Ta as the solid solution strengthening elements. However, skid rails in the soaking zone of a furnace are subjected to such a high temperature as 1200-1350°C, and suffer from heavy strain and abrasion. The above mentioned conventional heat-resistant casting alloy, of the solid solution strengthened type, is not satisfactory as a material for the skid rails at these high temperatures.

It has been proposed to use ceramics having high heat-resistance and anti-abrasion properties as the material of the furnace bed metal (for example, Japanese Utility Model Publication No. 35326/1989). So-called fine ceramics materials such as SiC and Si<sub>3</sub>N<sub>4</sub>, preferable from the viewpoint of high shock-resistance, which is one of the properties needed in the skid rails, are easily damaged by oxidation when used in a strongly oxidative atmosphere.

On the other hand, it has been disclosed that super alloys of the oxide-dispersion strengthened type, i.e., Ni-based super alloys in which fine particles of an oxide having a high melting point such as Y<sub>2</sub>O<sub>3</sub> are dispersed, are useful as components in gas-turbines and jet-engines (for example, Japanese Patent Publication No. 38665/1981). As to high temperature furnaces, it has been proposed to use an oxide-dispersion strengthened type super alloy of the composition consisting of 12.5-20% Cr, up to 1% Al, up to 0.1% C and up to 0.5% (volume) Y<sub>2</sub>O<sub>3</sub>, the balance being Ni, as the material for mesh belts (Japanese Patent Publication No. 9610/1984).

In furnaces using heavy oil as the fuel, however, Ni-based super alloys are easily corroded owing to high temperature sulfidation attack by the sulfur in the heavy oil. Furthermore, Ni-based alloys are expensive, and therefore, it is desirable to construct the skid rails with a less expensive alloy. If an Fe-based alloy having equal performance in skid rail service to that of a Ni-based alloy were available, the above desire would be satisfied.

The general object of the present invention is to provide metal components for furnace construction, particularly, skid rails, of higher performance by using the above mentioned heat-resistant oxide-dispersion strengthened iron-based alloy (or steel).

The furnace component according to the present invention comprises a furnace atmosphere contacting surface made of an oxide-dispersion strengthened type alloy consisting essentially of 10-40% Cr and the balance of Fe, and containing 0.1-2% of fine particles of a high melting point metal oxide dispersed in the ferrite matrix.

The alloy may further contain up to 10% Al, advantageously up to 5% Al, or up to 5% Al and up to 5% Ti.

A preferable range of Cr content is 20-40% and a more preferable range is 20-35%. Percentages are by weight.

The high melting point metal oxide may be one or more selected from Y<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. Y<sub>2</sub>O<sub>3</sub> gives the best results.

Skid members or rails embodying the invention have been found to exhibit, when used in various furnaces such as heating furnaces for hot processing of steel, excellent properties against heat deformation, oxidation resistance, abrasion resistance, sulfidation resistance and thermal shock resistance, and therefore, can be used for long periods of time. This will decrease maintenance labor of the heating furnaces and facilitates continuous operation thereof. Decreased costs for energy and maintenance result in lower production costs in the hot processing of steel.

In order to produce the above mentioned oxide-dispersion strengthened type alloy, so-called mechanical alloying technology developed by INCO (The International Nickel Co., Inc.) is useful. The technology

comprises subjecting powders of metal components and fine crystals of a high melting point metal oxide in a ball mill, for example, a high kinetic energy type ball mill, so as to produce by repeated welding and fracturing a granular product comprising an intimate and uniform mixture of very fine particles of the components. The product prepared by mechanical alloying is then compacted and sintered by hot extrusion or hot isostatic pressing and, if necessary, machined to provide the component of the skid rail,

A typical embodiment of the skid rail of the present invention is, as shown in Figure 1 to Figure 3, a skid rail 1A made by welding metal saddles 3A on a water-cooled skid pipe 2, attaching skid members 4A made of the oxide dispersion strengthened heat-resistant alloy to the saddles and covering all the members except for the skid members 4A with refractory insulator 5.

The skid rails may be of other configurations. For example, a skid structure may use cylindrical saddles to attach button shaped skid members.

In general, nickel-based oxide-dispersion strengthened type super alloys are stable even at a high temperature, and the above mentioned known nickel-base alloys have alloy compositions suitable for uses such as turbine blades (Japanese Patent Publication No. 56-38665) or mesh belts (Japanese Patent Publication No. 59-9610) and contain suitable amounts of oxide particles. However, these known nickel-base alloys do not have sufficient corrosion-resistance against high temperature sulfidation attack occurring in furnaces having atmosphere resulting from combustion of heavy oil.

By using a skid member made of the above described iron-base oxide-dispersion strengthened alloy it is possible to achieve a high compression creep strength, as shown in the working example described later, in addition to the heat-resistance and oxidation-resistance. Thus, less expensive, but more durable skid members are provided.

Criteria associated with the selected alloy compositions employed in the skid members of the present invention are as follows:

In the heat-resistant alloy of the basic composition,

Cr: 10-40%

If the content of Cr is less than the lower limit, the desired heat-resistance is not obtained. On the other hand, if it exceeds the upper limit, an intermetallic compound called "sigma phase" is formed and the material becomes brittle.

Preferable range of Cr content is 20-40%, particularly, 20-35%.

In the heat-resistant alloy containing optionally added elements,

Al: Up to 10%

In case where a better anti-oxidation property is desired, for example, in the material for the skid rails to be used in heating furnaces with atmosphere containing a relatively large quantity of oxygen (up to several %), up to 5% Al is advantageous for oxidation resistance. Further additions of Al up to 10% also give improved results. Addition of higher amounts will cause occurrence of harmful large inclusions.

Ti: Up to 10%

Ti also contributes to the strength of the alloy and, therefore, is optionally added preferably in amounts up to 5%. Additions in amounts over 10% also causes formation of large inclusions.

High Melting Point Metal Oxide: 0.1-2%

The most preferred metal oxide is, as noted above,  $Y_2O_3$ . In skid rails used in heating furnaces of relatively low temperature (up to about 1200°C), the whole or a portion of the  $Y_2O_3$  may be replaced with  $ZrO_2$  or  $Al_2O_3$ . Of course, combined use of two or three of  $Y_2O_3$ ,  $ZrO_2$  and  $Al_2O_3$  is possible. Contents of the high melting point metal oxide should be 0.1% or more. Otherwise, the effect of stabilizing the alloy at a high temperature will not be satisfactory. As the content increases, the effect slows down at about 1% and saturates at 2%, and therefore, a suitable content in this range should be chosen. It should be noted that during processing originally added  $Y_2O_3$  may convert to various yttria-alumina compounds (e.g., YAG) if alumina is copresent.

Figure 1 to Figure 3 illustrate a typical embodiment of the skid rail using an alloy embodying the invention:

Figure 1 being a plan view;

Figure 2 a side elevation view; and

Figure 3 a cross-sectional view.

Oxide-dispersion strengthened type alloys INCOLOY MA956 and improved MA956 groups and having the composition as shown in Table 1 (weight %, the balance being Fe) were prepared by the above noted mechanical alloying process, and the alloys were hot extruded and machined to give testing materials.

The above obtained materials and a conventional skid rail material "TH101" (0.1C-32Cr-21Ni-23Co-2.5W-Zr) were subjected to compression creep test at a very high temperature for determining their durability as a material for the skid rail. The compression creep test is carried out by cramping a columnar test piece of 3mm in diameter and 6.5mm high between a fitting plate and a receiving plate, and applying compressing load at a high temperature. After a certain period of time, the height of the test piece is measured, and the deformation is calculated as the percentage of decrease in height.

Deformation (%) of the materials at various testing conditions are as shown in Table 2.

From reference to the case of alloy No. 1, temperature 1300°C, stress 0.4 kgf/cm<sup>2</sup> and testing period 30 hours, it is seen that deformation of the conventional material reached 6.14%. In contrast, deformation of the material used in skid rails or skid rail members of the present invention was as small as 0.30%. Thus, the good results were ascertained.

In practical use in soaking zones of steel heating furnaces, the life of a skid rail embodying the present invention was more than 10 times that of the conventional products.

In the case of alloys No. 3 and No. 4 where a portion of Y<sub>2</sub>O<sub>3</sub> was replaced with ZrO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>, when compared to the case of Y<sub>2</sub>O<sub>3</sub> used alone the extent of deformation is smaller even at longer testing periods, and the performance is much higher than that of the conventional material. Further, it is expected that, even if whole of Y<sub>2</sub>O<sub>3</sub> is replaced with ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> or a combination thereof, the resulting oxide-dispersion reinforced super alloy can be used at a relatively low heating furnace temperature up to around 1200°C.

Table 1

| <u>No.</u> | <u>C</u> | <u>Cr</u> | <u>Al</u> | <u>Ti</u> | <u>Metal Oxide</u>             |     |
|------------|----------|-----------|-----------|-----------|--------------------------------|-----|
| 1          | 0.05     | 20        | 4.5       | 0.5       | Y <sub>2</sub> O <sub>3</sub>  | 0.5 |
| 2          | 0.05     | 15        | 5.0       | 3.0       | Y <sub>2</sub> O <sub>3</sub>  | 0.8 |
| 3          | 0.05     | 25        | 4.0       | 1.5       | Y <sub>2</sub> O <sub>3</sub>  | 0.7 |
|            |          |           |           |           | ZrO <sub>2</sub>               | 0.3 |
| 4          | 0.05     | 33        | 4.0       | 0.4       | Y <sub>2</sub> O <sub>3</sub>  | 0.7 |
|            |          |           |           |           | Al <sub>2</sub> O <sub>3</sub> | 0.3 |
| 5          | 0.05     | 25        | 5.5       | 0.5       | Y <sub>2</sub> O <sub>3</sub>  | 0.5 |

Table 2

| 5  | Alloy | Testing Conditions      | Period (Hrs) |      |      |      |
|----|-------|-------------------------|--------------|------|------|------|
|    |       |                         | 20           | 40   | 60   | 80   |
|    | TH101 |                         | 3.63         | 6.94 | 9.95 | 13.2 |
| 10 | No. 1 |                         | 0.07         | 0.14 | 0.21 | 0.28 |
|    | No. 2 | 1200°C                  | 0.06         | 0.13 | 0.20 | 0.27 |
|    | No. 3 | 0.9 kgf/mm <sup>2</sup> | 0.07         | 0.15 | 0.20 | 0.28 |
| 15 | No. 4 |                         | 0.06         | 0.14 | 0.20 | 0.28 |
|    | No. 5 |                         | 0.07         | 0.14 | 0.20 | 0.28 |
| 20 | TH101 |                         | 4.72         | 7.21 | 9.83 |      |
|    | No. 1 |                         | 0.12         | 0.24 | 0.36 |      |
| 25 | No. 2 | 1250°C                  | 0.10         | 0.22 | 0.34 |      |
|    | No. 3 | 0.6 kgf/mm <sup>2</sup> | 0.11         | 0.23 | 0.35 |      |
| 30 | No. 4 |                         | 0.10         | 0.23 | 0.35 |      |
|    | No. 5 |                         | 0.12         | 0.24 | 0.37 |      |
| 35 |       |                         | Period (Hrs) |      |      |      |
|    |       |                         | 10           | 20   | 30   |      |
| 40 | TH101 |                         | 2.31         | 4.43 | 6.14 |      |
|    | No. 1 |                         | 0.10         | 0.20 | 0.30 |      |
|    | No. 2 | 1300°C                  | 0.09         | 0.17 | 0.25 |      |
| 45 | No. 3 | 0.4 kgf/mm <sup>2</sup> | 0.08         | 0.16 | 0.24 |      |
|    | No. 4 |                         | 0.10         | 0.19 | 0.28 |      |
| 50 | No. 5 |                         | 0.11         | 0.20 | 0.31 |      |

**Claims**

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1. A skid member for use in a furnace operating at high temperatures having at least one surface exposed to high temperature furnace atmosphere, characterized in that the skid member is made of an oxide-dispersion strengthened type heat-resistant alloy, which consists essentially of 10-40% (by weight) Cr

and the balance of Fe, and contains 0.1-2% of fine particles of high melting point metal oxide dispersed in the ferrite matrix.

- 5     **2.** A skid member for use in a furnace operating at high temperatures having at least one surface exposed to high temperature furnace atmosphere, characterized in that the skid member is made of an oxide-dispersion strengthened type heat-resistant alloy, which consists essentially of 10-40% Cr, up to 5% Al and the balance of Fe, and contains 0.1-2% of fine particles of high melting point metal oxide dispersed in the ferrite matrix.
- 10    **3.** A skid member for use in a furnace operating at high temperatures having at least one surface exposed to high temperature furnace atmosphere, characterized in that the skid member is made of an oxide-dispersion strengthened type heat-resistant alloy, which consists essentially of 10-40% Cr, up to 5% Al, up to 5% Ti and the balance of Fe, and containing 0.1-2% of fine particles of high melting point metal oxide dispersed in the ferrite matrix.
- 15     **4.** A skid member according to any one of claims 1 to 3, wherein the high melting point metal oxide in said heat resistant alloy comprising  $Y_2O_3$ .
- 20     **5.** A furnace skid rail comprising skid members (4A) in accordance with any one of claims 1 to 4 attached along a skid pipe (2) by saddles (3A).
- 25     **6.** Use of an oxide dispersion-strengthened-type heat resistant alloy, comprising 10-40 wt% Cr, 0-5 wt% Al, 0-5 wt% Ti and substantially the balance Fe, with 0.1-2 wt% of fine particles of high melting point metal oxide dispersed therein, as a member subject to heat and abrasion in a high-temperature furnace.
- 30     **7.** Use according to claim 6 in which the metal oxide is  $Y_2O_3$ ,  $ZrO_2$ ,  $Al_2O_3$ , or a combination thereof.

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FIG. 1

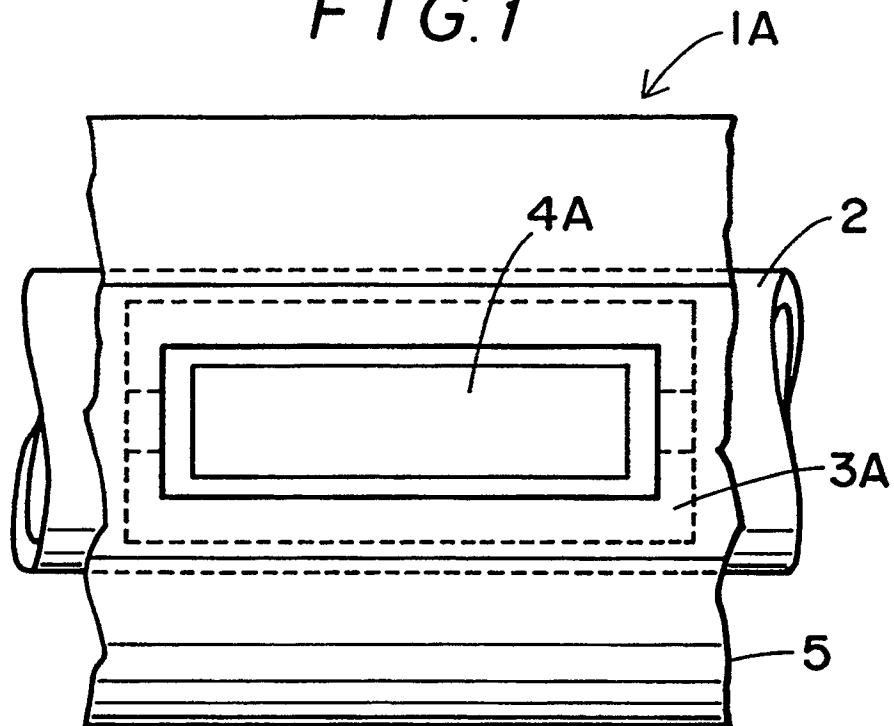


FIG. 2

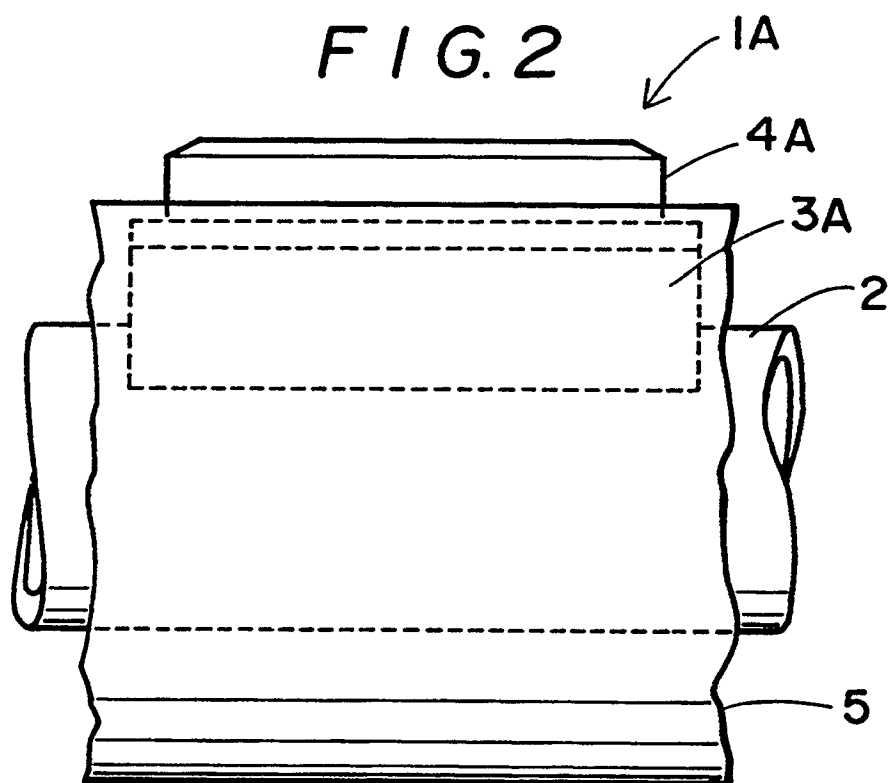
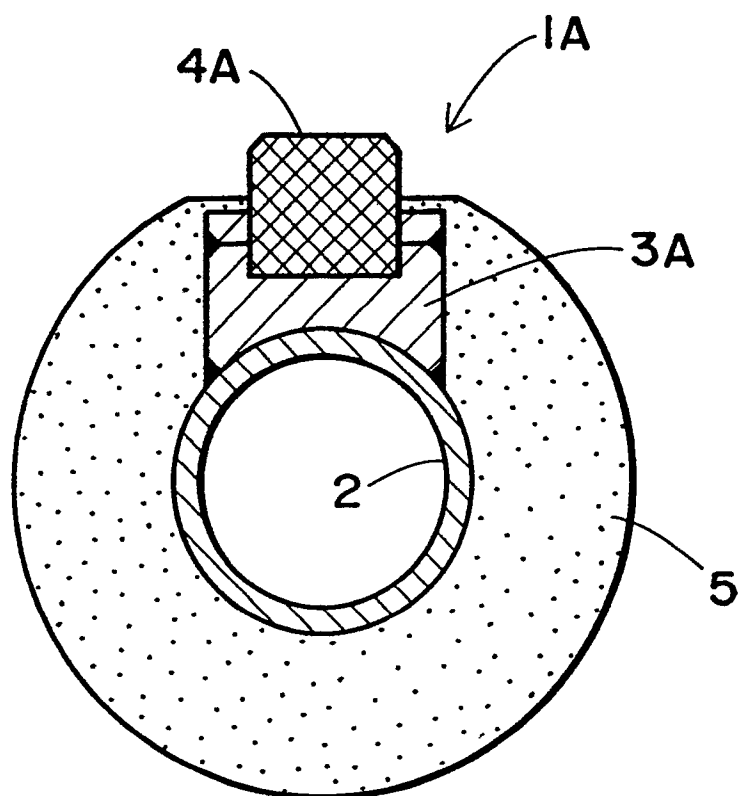


FIG. 3







European  
Patent Office

## EUROPEAN SEARCH REPORT

Application Number

EP 91 30 0888

| DOCUMENTS CONSIDERED TO BE RELEVANT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                                                                                                                                             |                              |                                               |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------|-----------------------------------------------|
| Category                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | Citation of document with indication, where appropriate, of relevant passages                                                                               | Relevant to claim            | CLASSIFICATION OF THE APPLICATION (Int. Cl.5) |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | EP-A-0 326 371 (DAIDO TOKUSHUKO K.K.)<br>* Page 2, lines 29-41; claims 1-5; figures 1-3 *<br>- - -                                                          | 1-7                          | C 22 C 32/00<br>F 27 D 3/02                   |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | US-A-4 427 447 (EXXON RESEARCH & ENGINEERING CO.)<br>* Claim 1; column 1, lines 8-10 *<br>- - -                                                             | 1-7                          |                                               |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | FR-A-1 509 893 (GENERAL ELECTRIC CO.)<br>* Column 2, lines 1-19; column 3, lines 36-54; column 6, lines 12-14 *<br>- - -                                    | 1,4,5                        |                                               |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                                                             | 2,3,6,7                      |                                               |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | L.L. SHREIR et al.: "Corrosion", vol. 1, Metal/Environment reactions, 2nd edition 1976, Newnes-Butterworths, London, GB, page 7:7, lines 19-38<br>- - - - - | 1-7                          |                                               |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                                                                                             |                              | TECHNICAL FIELDS SEARCHED (Int. Cl.5)         |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                                                                                             |                              | C 22 C<br>F 27 D                              |
| The present search report has been drawn up for all claims                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                                                                                                                             |                              |                                               |
| Place of search                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                                                                                             | Date of completion of search | Examiner                                      |
| The Hague                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                                                                                                             | 25 April 91                  | RIBA VILANOVA M.                              |
| <b>CATEGORY OF CITED DOCUMENTS</b><br>X: particularly relevant if taken alone<br>Y: particularly relevant if combined with another document of the same category<br>A: technological background<br>O: non-written disclosure<br>P: intermediate document<br>T: theory or principle underlying the invention<br><br>E: earlier patent document, but published on, or after the filing date<br>D: document cited in the application<br>L: document cited for other reasons<br>-----<br>&: member of the same patent family, corresponding document |                                                                                                                                                             |                              |                                               |