



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : B22D 2/00, C21C 1/10 G01N 25/04 // B22D 46/00 C22C 33/08, G01N 33/20	A1	(11) International Publication Number: WO 92/06809 (43) International Publication Date: 30 April 1992 (30.04.92)
(21) International Application Number: PCT/SE91/00685 (22) International Filing Date: 11 October 1991 (11.10.91) (30) Priority data: 9003289-7 15 October 1990 (15.10.90) SE (71) Applicant (for all designated States except US): SINTER-CAST LTD. [GB/GB]; 44/45 Chancery Lane, London WC2A 1JB (GB). (72) Inventor; and (75) Inventor/Applicant (for US only) : BÄCKERUD, Stig, Lennart [SE/US]; 963 Stratford Lane, Bloomfield Hills, MI 48304 (US). (74) Agents: BERG, S., A. et al.; H. Albihns Patentbyrå AB, Box 3137, S-103 62 Stockholm (SE).		(81) Designated States: AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH (European patent), CI (OAPI patent), CM (OAPI patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GA (OAPI patent), GB (European patent), GN (OAPI patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL (European patent), NO, PL, RO, SD, SE (European patent), SN (OAPI patent), SU*, TD (OAPI patent), TG (OAPI patent), US. Published <i>With international search report.</i>
(54) Title: A METHOD FOR THE PRODUCTION OF COMPACTED GRAPHITE CAST IRON		
(57) Abstract A method relating to the production of cast iron castings with compacted graphite crystals. The method comprises controlling and correcting the composition of the cast iron melt and securing the necessary amount of structure modifying agent. A sample of the melt is taken with a sample vessel provided with two thermocouples, one positioned so as to be in the centre of the sample and the other positioned so as to be in the vicinity of the vessel wall. The vessel wall contains or is coated with a layer of a substance which will lower the concentration of dissolved elementary magnesium in the melt in the vicinity of the vessel wall by at least 0.003 %. The temperature/time values obtained through two temperature responsive means are recorded. The occurrence of a plateau temperature will provide information as to the precipitation of flaky graphite in the vicinity of the vessel wall, therewith enabling corrections to be made to the concentration of the modifying agent and to ensure the formation of compacted graphite crystals during the whole of the pouring time required in the foundry process concerned.		

+ DESIGNATIONS OF "SU"

Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

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A METHOD FOR THE PRODUCTION OF COMPACTED
GRAPHITE CAST IRON

The present invention relates to a method for the
5 production of compacted graphite cast iron. The method
is based on a test-method to determine the structural
characteristics of a melt for casting compacted gra-
phite cast iron and means to control the structure and
properties of the material produced.

10 US-A-4 667 725 describes a method for producing cast-
ings with a predetermined graphite structure. The
method comprises taking a sample from a bath of molten
iron and then allowing the sample to solidify over a
15 period of from 0.5 to 10 minutes. During the solidifi-
cation period, recordings are made of the temperature
changes that take place in the centre of the sample
volume and near the inner wall of the sample vessel.
The sample vessel should substantially be in thermal
20 equilibrium at a temperature above the crystallization
temperature of the bath and be allowed to solidify
fully over a period of from 0.5 to 10 minutes. The
temperature-time sequence is measured by two tem-
perature responsive means, of which one is placed in
25 the centre of the sample quantity and the other in the
molten material at a location close to the wall of the
vessel. The degree of dispersion of the graphite phase
in relation to known reference values for the same
sampling and testing process with respect to finished
30 castings is assayed with the aid of the temperature
measured during the first nucleation events of the
eutectic reaction measured at said vessel wall as the
minimum undercooling temperature at the vessel wall,
the recalescence of the vessel wall, the positive
35 difference between the temperature that prevails at the
vessel wall and in the centre of the sample and the

derivative of the temperature decrease at said vessel wall during the time for constant eutectic growth temperature in the centre of the sample quantity, alternatively the highest negative values of the temperature difference between the eutectic maximum growth temperature and the eutectic temperature. If the bath has an insufficiency of crystallization nuclei, a graphite nucleating agent is introduced thereinto and conversely when the crystallization nucleants are present in excess the degree of dispersion is lowered by holding the bath for a length of time sufficient to reduce the amount of nuclei in the bath prior to casting, by assessing the morphology of the graphite precipitation in relation to corresponding data obtained with the same sampling and testing technique as that applied with cast iron of known structure, with the aid of supercooling that takes place in the centre of the molten material, the recalescence in the centre of the sample vessel and the maximum growth temperature, and by correcting the quantity of structure-modifying agent in response thereto, so that graphite precipitation takes place in a predetermined form upon solidification of the molten cast iron subsequent to casting. The obtained values are used to determine the amount of modifying agent and the presence of graphite nucleating agent in the melt concerned and for the equipment used. The production equipment used has to be calibrated and possibly necessary additions of modifying element and nucleating agent have to be made in relation to the calibration of the best equipment.

The above-mentioned method permits the skilled person to predict how the graphite precipitation will take place in the melt concerned and also how to control the composition of the melt to obtain desired results. The test method gives results which cannot be obtained with

other analysis methods. Although a chemical test will, for instance, disclose the total amount of magnesium present, it will provide no information as to how much magnesium there is in solution and thus active as a modifying agent. This latter information is of great importance since the amount of magnesium in solution in an iron melt will change relatively quickly due to physical and chemical reactions that take place within the melt and due to contact with the surroundings and consequently although a conventional chemical analysis may have given the correct results in respect of the melt concerned at the time of making the analysis may well have changed its status at the time of receiving the analysis results to such an extent that this result can no longer be used to control the solidification process, when casting cast iron objects.

The amount of dissolved elemental magnesium is essential for controlling the graphite precipitation. In addition to magnesium or instead of magnesium the structure modifying agent can contain cerium and other rare earth metals. The modifying agent (and the nucleating agent) will fade with time and there are characteristic rates for this fading, contingent on the process and equipment used. A good control method will enable an exact determination to be made of the amount of modifying and inoculating agents present and will also enable a calculation to be made as to how much of these agents are needed to obtain acceptable results for a casting process during the following say 10 to 15 minutes. This has not, however, been possible hitherto. The method described earlier can only inform us that the melt at the sample extraction moment will solidify with specific graphite crystal form.

The undercooling in a melt where flaky graphite crys-

tals develop is relatively small ($<5^{\circ}\text{C}$) and the minimum represents the situation where a certain number of graphite crystals (together with the austenite phase) have attained a growth rate at which the latent heat evolved balances the heat extracted from the system. After this point, the liquid melt is actually heating up to a new balance point representing the "steady state growth condition", which in the case of a well nucleated liquid with A-graphite is close to the equilibrium temperature, T_E , say $1-2^{\circ}\text{C}$ below the equilibrium temperature of the eutectic reaction in normal Fe-C-Si-alloys. In the present document, the equilibrium temperature is set at 1155°C . This means that the instruments have been calibrated to a $T_E = 1155^{\circ}\text{C}$ and temperature differences calculated in relation therewith. Thermodynamic calculations in the literature give other, somewhat higher values, but for practical reasons T_E is in this connection set at 1155°C .

If modifying agents such as magnesium and rare earth metals are added and dissolved in a liquid cast iron melt, the growth in specific crystallographic directions is restricted and the morphology changed from flaky via compacted to nodular graphite crystals with increasing amounts. From type IV to I in the graphite classification scale.

If there are sufficient graphite precipitation nuclei present and a proper amount of modifying elements is present, the cast iron will solidify as compact graphite cast iron. In this case, the undercooling is much higher than is observed for gray iron before the rate of growth of compacted graphite crystals generates enough heat to counteract and heat-extraction from the system.

The reheating (recalescence) takes a longer time, due to growth restrictions, and the steady state growth temperature will stay from 5 to 10°C below the equilibrium liquidus temperature, T_E .

5

The relationship between the growth habit of these two graphite morphologies and the thermal analysis results and curves have long been known.

10 The successive change in morphology from flaky to compacted graphite as a result of increasing additions of modifying elements is, however, of interest because of its great importance in enabling thermal analysis to be used as a process control instrument.

15

This change is by no means a linear function of the concentration of modifying additives, for the following reasons:

20 Here, magnesium is referred as an example of the modifying agent used and when adding a modifying agent, the magnesium will react with any sulphur and oxygen that may be present while forming MgS and MgO. The remainder of the magnesium will dissolve in the cast iron melt
25 and is defined as $Mg_{(L)}$.

In a set of experiments, it has been found that a $Mg_{(L)}$ -level of 0.008% Mg will give a fully compacted graphite structure and an $Mg_{(L)}$ -level below 0.006% Mg
30 will give a fully flaky structure in a slightly hypoeutectic cast iron (the carbon equivalent CE of 4.0-4.2). A level of dissolved magnesium below 0.006% will not be sufficient to prevent the formation of flaky graphite. This formation will release latent heat
35 at such a high rate as to reduce the degree of undercooling, and the growth of compacted graphite crystals

is never triggered. At this lower degree of undercooling, some crystals may, however, be influenced by the modifying agent to such an extent that they develop in a somewhat unspecified modified form.

5

Compacted graphite crystals are formed in the range between 0.008-0.016% dissolved magnesium. No flaky crystals are formed in this range, but towards the higher end of this range a certain formation of nodular crystals can be observed.

10

The absolute values of the content of dissolved elemental magnesium may vary from one foundry to another and with constituents in the base melt, but in one actual case the following figures were obtained, which may serve as an example:

15

0 - 0.008% Mg, flaky graphite
0.008 - 0.016% Mg, compacted graphite
0.016 - 0.030% Mg, mix of compacted and
nodular graphite
0.030 - 0.035% Mg, 80-100% nodular graphite
>0.035 % Mg, fully nodular graphite
(Mg in excess)

20

25

From one practical application, it was found that for the process and equipment used, the fading of magnesium was about 0.001% Mg every five minutes. During a casting period of 15 minutes, the content of dissolved elemental magnesium thus decreased with 0.003%. If the original percentage was 0.010% Mg, one would obtain after 15 minutes a content of 0.007% and a large portion of flaky graphite will thus be formed by the end of the casting period, while a sample that originally contains say 0.012% Mg will form only compacted graphite crystals over the whole casting period. If the

30

35

melt had been tested according to US-A-4 667 725, it would have been found in both cases, quite correctly, that both melts would solidify as compacted graphite cast iron. The method does not permit a discrimination to be made between magnesium contents of 0.010% and 0.012%. As graphite flakes have to be completely avoided, has so far been necessary to use a certain excess of magnesium in order to secure a desired result, with the risk of obtaining a certain amount of nodular graphite crystals in the material being produced.

The decrease of the content of dissolved elementary magnesium below about 0.008% will result in a very rapid increase of the amount of flaky graphite due to the fact that an insufficient amount of magnesium permits the growth of flakes of graphite and that a decrease of the magnesium content below the borderline will result in a drastic transformation of the solidification structure with regard to the graphite precipitation. This will be obvious from the Figure, where the amount of compacted graphite and flaky graphite is shown along the ordinate and the percentage of dissolved magnesium along the abscissa. The curve shows the drastic change that occurs, when the magnesium content drops below 0.008% magnesium. Other modifying agents have similar threshold concentrations.

Once the growth habit of the graphite crystals is fully compacted, the test will result in mutually identical signals from the analysis equipment within the range concerned, i.e. between 0.008-0.16% $Mg_{(L)}$. A chemical analysis is not useful since there is no fast method known of discriminating between total and dissolved magnesium quantities.

According to the present invention, compacted graphite

iron can be produced consistently.

Thus, a melt of suitable composition and structure is prepared and a modifying and nucleating agent is added to the melt in an amount which is expected to be sufficient to produce compacted graphite cast iron. A sample is then extracted from the melt in a sample vessel, the wall of which contains or is covered on its inside surface with a layer consisting of a material which will react with dissolved elementary magnesium present in the vicinity of said wall. The layer material or the wall constituents should be present in such amounts that the magnesium concentration of the sample melt in the vicinity of the wall will be lowered by 0.003%. The sample vessel must have two thermocouples, one placed in the centre of the melt amount and the other in the vicinity of the vessel wall. The temperatures are recorded both from thermocouples and the general information is used in accordance with the teachings of US-A-4 667 725. When the magnesium content is as low as about 0.010%, the curve obtained from the thermocouple placed in the vicinity of the vessel wall will show a level of temperature at which precipitation of flaky graphite occurs, since the local Mg-content is $<0.008\%$ Mg. This is an indication that the magnesium content has to be adjusted by adding magnesium. This can be done by adding further structure modifying agent to the melt, such as to compensate for the fading loss of structure modifying agent during the whole of the casting operation. Normally, this addition can be made without any further control of the solidification properties, which also permits the structure modifying agent to be added directly when casting.

In a practical embodiment of the present invention, the sampling vessel is produced from oxides which react

with the modifying agent, i.e. magnesium, in the cast iron melt. The vessel can be made of a mixture of aluminium oxide and the chamotte. The reaction rate determining compounds in such a material are silicon dioxide, small amounts of alkali metal oxides and the sulphur impurity level. The more stable oxides, such as aluminium oxide and calcium oxide, are not likely to take part in the magnesium reduction process during the short contact period between melt and crucible.

One example of commercial products which can be used for the production of sample vessels useful when practicing the present invention is 50% SECAR^R 71, (Lafarge S.A.) which mainly consists of a 71% Al_2O_3 , 27% CaO and less than 2% total impurities, among which 0.35% SiO_2 , 0.35% Na_2O , 0.25% Fe_2O_3 , 0.05% H_2O and 0.15% SO_3 can be mentioned, and 50% Refag (Alfa Aggregates Ltd., Newcastle), mainly consisting of 52% SiO_2 , 41.5% Al_2O_3 , 3% Fe_2O_3 , 0.5% K_2O and 0.1% Na_2O .

It will be understood that both sampling temperature and the time lapse between sampling and the start of solidification (= liquid cooling rate) plays a part in establishing the desired concentration profile.

The inventive method results in an increased yield of acceptable castings. The method, according to US-A-4 667 725, gives in one practical case about 90% acceptable castings, i.e. with more than 80% compacted graphite. According to the present invention, these figures have been increased in practice to above 99.5%.

The invention will now be explained in more detail with reference to the Figures.

Figure 1 is a diagram, which shows the percentage of

graphite in compacted form with the remainder being flaky graphite and from which it will be seen that above about 0.008% $Mg_{(L)}$ the graphite is fully compacted and below about 0.006% is almost fully flaky. Between 0.006% and 0.008% $Mg_{(L)}$, there exists a sharp transition region with different proportions of the two graphite structures.

Figure 2 is a diagram inserted in a schematic illustration of a sample vessel and defining the percentage of dissolved magnesium in the sample vessel from the vessel wall towards the centre of the sample vessel. The sample vessel wall is indicated on the left of the Figure and an assumed level of dissolved $Mg_{(L)}$ in the centre is indicated by a dotted horizontal line (0.008% $Mg_{(L)}$). The $Mg_{(L)}$ level at a thermocouple in the vicinity of the sample wall is indicated by another dotted line 5 (0.005% $Mg_{(L)}$). The region where flaky graphite crystals are formed is indicated by the area 4.

Figure 3 shows the temperature/time curves for a thermocouple in the centre I and the thermocouple in the vicinity of the sample vessel wall II. Curve I is a typical curve for the compacted graphite solidification in the centre of the sample. Curve II shows at A an inflexion which is typical of a flaky graphite solidification. The relative stay time on the first plateau (A) is proportional in relation to the amount of flakes in the area in the vicinity of the sample wall.

The following example elucidates the invention. The example assumes that there is used a production line in which the Mg fading rate is estimated to be 0.001% Mg for each 5 minutes and that the last moulds in said line are filled with melt about 15 minutes after the sample was taken.

EXAMPLE

Production of compacted graphite cast iron. The true
Mg-level at the moment of sampling was 0.010% of free,
5 dissolved elementary magnesium. A thermal analysis made
from the centre of the sample showed that the melt will
result in a substantially compacted graphite material,
while the thermocouple in the vicinity of the wall
showed a tendency towards flake formation. The informa-
10 tion thus obtained indicated that the remaining Mg-
level would be reduced to 0.008% after a time period of
about 10 minutes and that the last third of the cast-
ings would contain graphite in flaky form, provided
that the Mg-level was not increased. The need for
15 additional amounts of magnesium was obvious from the
temperature-time-curve obtained from a thermocouple
located in the vicinity of the vessel wall.

20 This structure prediction cannot be achieved with the
method known from US-A-4 667 725.

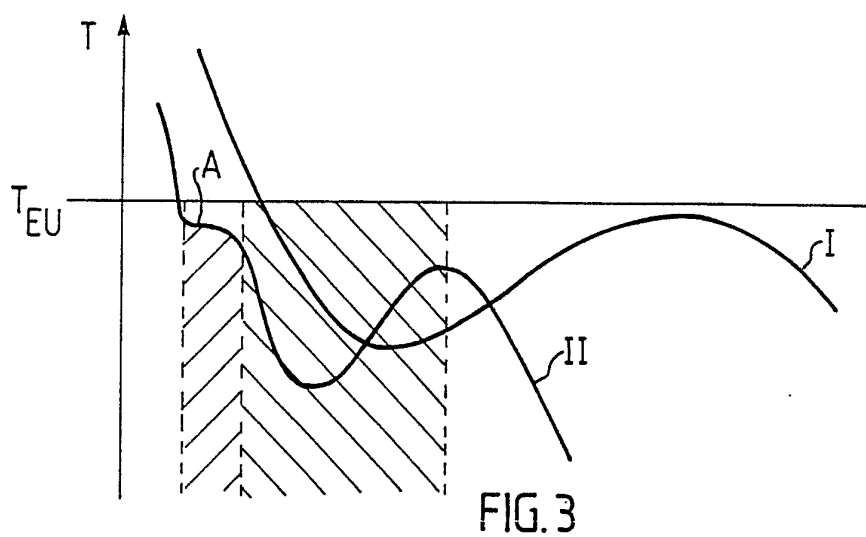
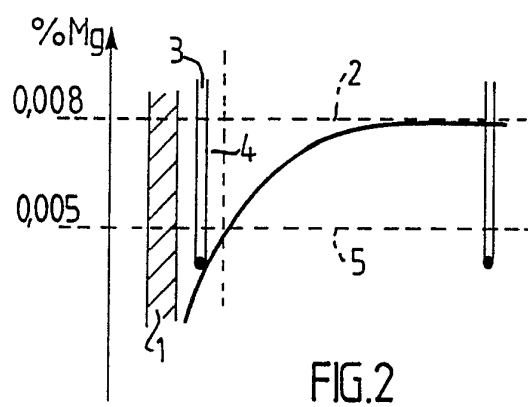
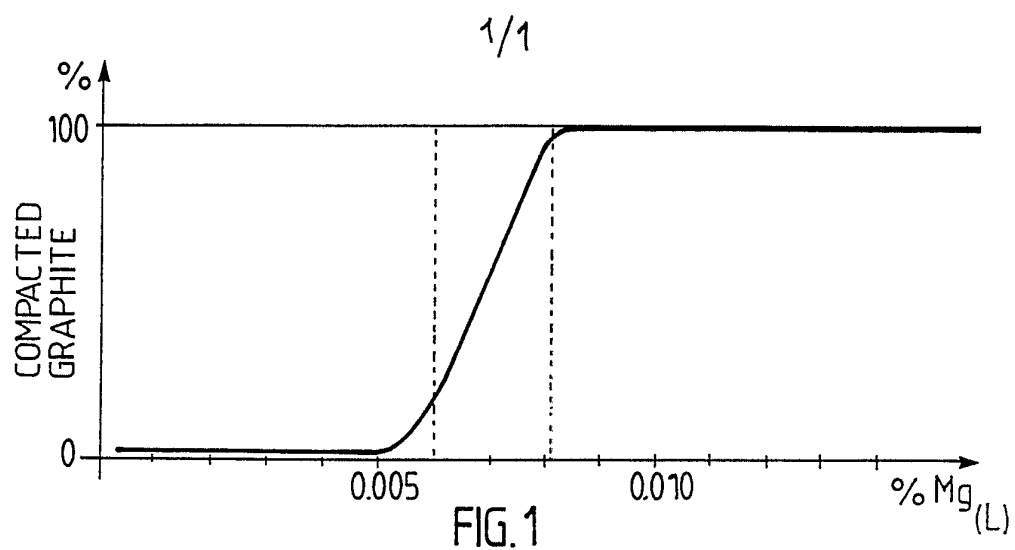
CLAIMS

1. A method relating to the production of cast iron
castings of the kind which contain graphite crystals in
5 compacted form and entailing controlling and correcting
the composition of a cast iron melt, the method comprising
preparing a cast iron melt and adding to the melt
a structure modifying agent and nucleating agent in
amounts according to experience just enough to give
10 fully compacted graphite iron when solidified directly,
c h a r a c t e r i z e d by extracting a sample of
melt from the melt in a sample vessel that is equipped
with two temperature responsive means, one of which is
in the centre of the vessel and the other of which is
15 in the vicinity of the vessel wall and which is permitted
to reach thermal equilibrium with the melt, which
vessel wall consists of a material which contains or is
covered with a layer of a substance which will lower
the concentration of dissolved elementary magnesium by
20 at least 0.003% or a corresponding percentage of some
other modifying agent in the melt in the vicinity of
the wall and in the vicinity of the temperature responsive
means positioned adjacent to said wall, recording
the temperatures registered by the two temperature
25 responsive means; evaluating from the recorded curve in
a manner known per se the characteristics of the melt
and also registering the plateau temperature which
might possibly occur as a result of the precipitation
of flaky graphite crystals around the temperature
30 responsive means located in the vicinity of the vessel
wall; and correcting the magnesium content or the
content of said other modifying agent with the aid of
the plateau-temperature time and the equipment parameters
such that this concentration will be sufficient to
35 form compact graphite crystals during the whole of the
pouring time needed in the foundry process.

2. A method according to Claim 1, c h a r a c -
t e r i z e d in that the sample vessel is made of
cement and ballast material or is coated with a layer
containing at least 10% of oxides of silicon, manganese
5 or iron, or at least 0.5% of oxides of potassium and
sodium.

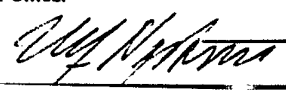
3. A method according to Claim 2, c h a r a c -
t e r i z e d in that the cement and ballast material
10 together contain 10-30% SiO_2 .

4. A method according to Claim 1, c h a r a c -
t e r i z e d in that as temperature responsive means
are used thermocouples.



INTERNATIONAL SEARCH REPORT

International Application No PCT/SE 91/00685

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC5: B 22 D 2/00, C 21 C 1/10, G 01 N 25/04 // B 22 D 46/00 C 22 C 33/08, G 01 N 33/20		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC5	B 22 D; C 21 C; C 22 C; G 01 N	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched ⁸		
SE,DK,FI,NO classes as above		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 4667725 (STIG L. BÄCKERUD) 26 May 1987, see abstract; claims 1-5 --	1
A	US, A, 4765391 (STIG L. BÄCKERUD) 23 August 1988, see abstract; claim 1 --	1
A	EP, A2, 0157308 (FRITZ WINTER, EISENGIESSEREI O.H.G.) 9 October 1985, see page 6, line 24 - line 30; abstract --	1
A	US, A, 4261740 (JACQUES J. PLESSERS) 14 April 1981, see abstract; figures 1-3; claims 1-6 --	1
* Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
15th January 1992	1992 -01- 17	
International Searching Authority	Signature of Authorized Officer	
SWEDISH PATENT OFFICE	Ulf Nyström 	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
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A	US, A, 4059996 (OMER PAUL CURÉ) 29 November 1977, see the whole document --	1
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ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.PCT/SE 91/00685

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the Swedish Patent Office EDP file on 30/11/91
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