(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 417 375 A1**

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **89810674.5**

(51) Int. Cl.5: **H05B 3/30**, H05B 3/18

(22) Date of filing: **12.09.89**

(43) Date of publication of application:
20.03.91 Bulletin 91/12

(84) Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

(71) Applicant: **KRELUS AG**
Hauptstrasse 23
CH-5042 Hirschthal(CH)

(72) Inventor: **Kneubühl, Fritz K.**
Bühlfeldstrasse 7
CH-8968 Mutschellen(CH)
Inventor: **Leupin, Andreas**
Theodor-Brunner-Weg 3
CH-8700 Küsnacht(CH)
Inventor: **Vetsch, Hans**
Kürbergstrasse 20
CH-8049 Zürich(CH)

(74) Representative: **Fischer, Franz Josef et al**
c/o Bovard AG Optingenstrasse 16
CH-3000 Bern 25(CH)

(54) **Resistance heating elements with ceramic coating.**

(57) Electrical resistance heating elements, especially for infrared radiators, comprise a metal sheet or foil and an enamel coating, which in turn comprises either chromium oxide, or nickel oxide, cobalt oxide and manganese oxide, and ceramic binding agents.

EP 0 417 375 A1

RESISTANCE HEATING ELEMENTS WITH CERAMIC COATING

The present invention relates to a resistance heating element especially for infrared radiators. The heating element comprises a metal layer which is coated with a ceramic coating.

The main disadvantage of the foil-type radiators is the damage of the foils caused by corrosive atmospheres. In order to protect the foils, one can combine the advantages of foil-type and ceramic radiators by coating the foils with a thin, protective inert ceramic layer. The thickness of this layer has to be as small as possible to prevent a drastic reduction of the heat transfer between the heating foils and the active radiating area by the additional thermal insulation. Besides, the surface emissivity of the coated foils should be better than or at least comparable to that of the uncoated foils. This second requirement is fulfilled by the admixture of appropriate components into high-temperature ceramic binding agents. Because they resist high temperatures, metal-oxide powders seem to be well suited for this purpose.

It is an object of the invention to provide an electrical resistance heating element comprising a metal sheet or foil protected by a coating against corrosive atmospheres without affecting the properties of the heating element.

After various experiments with commercial and trial ceramic mixtures, suitable ceramic coatings for the application on stainless steel foils, e.g., the foil sold under the trademark "Krelus Infrared" by Krelus AG, Hirschtal, Switzerland, were found. These ceramic coatings comprise chromium oxide or nickel oxide, cobalt oxide and manganese oxide. An enamel according to the invention made of chromium oxide mixed with ceramic binding agents exhibits a distinct green colour in the visible spectrum. A thin layer of this enamel was sprayed onto a foil with a spray gun and subsequently fired at 1533K. Afterwards, the sample was put to the lifetime test by heating it periodically at least to 1233K. The enamel showed no major visible changes after 2500 cycles.

For determining the spectral emissivity of the enamel, preliminary experiments were carried out to determine the spectral emissivitiy of chromium oxide, the most important component of the enamel. The result for wavelengths between 2 and 5 μm was different from the published spectral emissivities between 0.7 and 0.9 of chromium oxide [Sala 1986 b, Touloukian & Dewitt 1972]. The measured emissivities of chromium oxide were not correct due to erroneous surface-temperature measurements with the two-color pyrometer because the emissivity of the chromium oxide is not identical for the two spectral bands of the pyrometer. Consequently, also a reliable determination of temperature and spectral emissivity of the chromium-oxide based enamel could not be obtained.

Therefore, a new ceramic enamel coating which would be grey or black in the visible spectrum was developed which allows reliable temperature measurements with a two-colour pyrometer and, consequently, a reasonable determination of its spectral emissivity.

Preferred embodiments of the invention will now be described in detail with reference to the accompanying drawings, in which:

Fig. 1 is a graph showing the spectral emissivity of enamel according to the invention comprising chromium oxide and ceramic binding agents in wavelengths between 2 and 5 μm;

Fig. 2 is a graph showing the spectral emissivity of nickel oxide, cobalt oxide, manganese oxide and samarium oxide;

Fig. 3 is a graph showing the emissivity of an enamel coated "Krelus Infrared" foil according to Example 2 (curve 2 is an uncoated "Krelus Infrared" control foil);

Figs. 4 and 5 are graphs showing the functional relationship of the angle of deflection and the emissivity of an enamel coated foil according to the invention (the enamel was fired at 1553K and 1473K, respectively); and

Figs. 6 and 7 show the functional relationship of temperature of a black glossy and a grey black dim sample of a foil coated with an enamel comprising oxides of the metals Ni, Co, Mn and Fe (the enamel was fired at 1573K and 1473K, respectively).

For the determination of the emissivity, the emissivity of thin layers of various metal-oxide powders, namely, of nickel oxide, cobalt oxide, manganese oxide and samarium oxide, was determined. In the visible spectrum the nickel and cobalt oxide are grey-black, the manganese oxide brown and the samarium oxide white. With the exception of the cobalt oxide, which was measured directly on a flat part of the original "Krelus Infrared" foil of the test radiator (I), emissivity measurements on the other powders were performed by putting them on a plane silver plate on the test radiator (II). The "Krelus Infrared" foil has the composition, in percent by weight:

0.02 - 0.10 %	C
0.10 %	Mn max.
19.50 %	Cr
about 56 %	Ni
4.25 %	Mo
2.0 %	Fe max.
13.5 %	Co
1.30 %	Al
9.10 %	Cu
0.15 %	Si max.
0.003 - 0.01 %	B
3.00 %	Ti.

The result of the emissivity measurements at 1073K are presented in Fig. 2. Curve 1 shows the spectral emissivity of nickel oxide which was stabilized with about 3 mass-% of lithium carbonate. This stabilization is necessary to maintain the grey-black appearance of the oxide during its heating in air [Wells 1975]. Without lithium carbonate the nickel oxide would become green. In order to build a homogeneous layer on the silver plate, a suspension of the nickel oxide-lithium carbonate mixture in water was sprayed on the plate with the aid of a spray gun and subsequently fired at approximately the measuring temperature. The resulting layer of the nickel oxide exhibited a uniform emissivity over 0.9 between 1 and 16 µm wavelength.

The spectral emissivity of cobalt oxide at wavelength between 2 and 5 µm plotted in curve 2 corresponds to that of the nickel oxide within 1 to 2 %.

It was not possible to spray a suspension of manganese oxide onto the silver plate because it stopped up the spray gun. Therefore, an aqueous suspension of the powder was painted on the plate. This resulted in a considerably lower quality of the layer and, consequently, of the temperature distribution over the measuring area. Nevertheless, the manganese oxide showed a spectral emissivity close to 0.85 at wavelengths between 1 and 16 µm (curve 3).

For wavelengths longer than 4 µm also the samarium oxide exhibits spectral emissivities (curve 4) between 0.8 and 0.9, although it appears white in the visible spectrum. However, the temperature measurement which underlies the emissivities has an uncertainty of about ±20K, because we had to perform it with a thermocouple within the supporting silver plate instead of the pyrometer pointed directly to the layer surface. Although the spectral emissivities of the powders studied are very high, these powders can be applied in technical radiators only by embedment in a binding ceramic matrix.

The black enamel for coating the foil consists preferably of an admixture of nickel oxide, cobalt oxide, manganese oxide and, additionally, of iron oxide to other ceramic binding agents (Example 2). The resulting enamel layer on the "Krelus Infrared" foils exhibits a black glossy surface if fired at approximately 1553K and a grey-black dim surface for a firing temperature of about 1473K by using test radiator (I) are present in Fig. 3. The curves 1 a and b illustrate the black glossy layer, the curves 2 a and b the grey-black dim one. In order to facilitate comparison, the spectral emissivities of an uncoated "Krelus Infrared" foil is plotted again in curve 3. The curves a and b result from two identical measurements on the same sample performed at an interval of approximately one month. The results demonstrate a good reproducibility of the measurements. The spectral emissivities of the enamel show a slight dependence on its firing temperature. At wavelengths below 6 µm the spectral emissivities of the grey-black dim enamel sample is considerably lower than that of the black glossy one. At wavelengths above 7 µm the emissivities of the grey-black dim sample are higher. However, the spectral emissivities of the enamel and of the original "Krelus Infrared" foils are of the same order of magnitude.

The directional dependences of the spectral emissivities of the above-mentioned enamel comprising oxides of the metals Ni, Co, Mn and Fe are illustrated for several wavelengths in Fig. 4 for the black glossy sample and in Fig. 5 for the grey-black dim sample. Both samples exhibit a small directional dependence at emission angles below 45°. At an angle of 60° a slight decrease of the emissivity is observed. For both samples this decrease is marked for a wavelength of 4 µm.

In Figs. 6 and 7 the measured temperature dependences of the emissivity of the above-mentioned enamel are presented. The results show only small temperature dependences between 1050 and 1180K with the exception at 1 µm wavelength, where the uncertainty due to small errors of the temperature measurement is important. For a temperature of approximately 1000K both samples exhibit a decrease of the emissivity. Because this temperature is near the lower limit of the measuring range of the two-color pyrometer, which leads to larger errors, this effect may nevertheless be caused by a erroneous temperature measurement. Therefore, it should not be overrated.

Finally, the mentioned enamel was investigated with respect to its life time in the atmosphere. For this purpose a sample was examined which was fired at 1553K by the lifetime test at a temperature of approximately 1073K. This resulted after 2500 cycles in a small loss of the surface brilliancy and a minor change of the colour from black to grey-black. The same effect was observed also for the black glossy sample used for spectral measurements. However, no influence of these changes on the spectral emissivities of the sample was measured.

The measurements demonstrated that both examples of ceramic enamels seem to be suited for application to the steel foils with a high Ni content as, e.g., the "Krelus Infrared" foils as protective layers. This permits the operation of the radiators at higher temperatures as well as under aggressive atmospheric conditions.

In the heating elements according to the invention the spectral emissivities are substantially preserved, especially in the cobalt-containing embodiment. For the main component of chromium comprising enamel, the chromium oxide, the literature states a spectral emissivity of approximately 0.8 over the spectral range of interest.

All examples of enamels were applied on original "Krelus Infrared" foils manufactured by the present assignee. Preferably the foil is pretreated by artificial ageing, i.e., oxidation in an athmosphere comprising oxygen . The foil is normally pretreated for a period of few minutes (at strongly elevated temperatures) to a period of several days, e.g., 2 days (at normal room temperature). However, it is obvious to one skilled in the art that other foils of heating elements show similar results.

Example 1

Composition of a chromium-containing enamel. The mixture was ground for 70 hours in a jar mill with porcelain balls. The composition of the mixture is indicated in Table 1.

Table 1

Component	Quantity
Chromium(III) oxide	100 g
Titanium dioxide	20 g
Zinc oxide	20 g
Calcium carbonate	50 g
Silicon dioxide K50	100 g
Feldspar	50 g
Phonolite	50 g
Potassium carbonate	20 g
Water, distilled	250 ml
Ethanol	250 ml
Abrasion of mill	3.5 g/70 h

Example 2

<Composition of enamel comprising nickel cobalt and manganese. The mixture was ground during 70 hours in a jar mill with porcelain balls. The composition of the mixture is indicated in Table 2.

Table 2

Component	Quantity
Nickel oxide	15 g
Tricobalt tetroxide	15 g
Manganese dioxide	10 g
Iron(III) oxide	20 g
Titanium dioxide	10 g
China clay	100 g
Potassium feldspar	80 g
Lithium feldspar	40 g
Talcum	20 g
Dolomite	10 g
Barium carbonate	10 g
Zinc borate	10 g
Calcium carbonate	80 g
Water, distilled	300 ml
Abrasion of mill	2.5 g/70 h

Claims

1. Electrical resistance heating elements, especially for infrared radiators, comprising a metal sheet or foil and an enamel coating, characterized in that the enamel coating comprises
   a) chromium oxide, or
   b) nickel oxide, cobalt oxide and manganese oxide, and ceramic binding agents.

2. Heating elements according to claim 1 wherein the metal sheet or foil is less than 0.1 mm thick.

3. Heating elements according to claim 1 or 2 wherein the enamel coating comprises
80 - 120 parts by weight chromium(III) oxide
16 - 24 parts by weight titanium dioxide
16 - 24 parts by weight zinc oxide
40 - 60 parts by weight calcium carbonate
80 - 120 parts by weight silicon dioxide
40 - 60 parts by weight feldspar
40 - 60 parts by weight phonolite
16 - 24 parts by weight potassium carbonate.

4. Heating elements according to claim 1 or 2 wherein the enamel coating comprises
12 - 18 parts by weight nickel oxide
12 - 18 parts by weight tricobalt tetroxide
8 - 12 parts by weight manganese dioxide
16 - 24 parts by weight iron(III) oxide
8 - 12 parts by weight titanium dioxide
80 - 120 parts by weight china clay
64 - 96 parts by weight potassium feldspar
32 - 48 parts by weight lithium feldspar
16 - 24 parts by weight talcum
8 - 12 parts by weight dolomite
8 - 12 parts by weight barium carbonate
8 - 12 parts by weight calcium carbonate.

5. Heating elements according to claim 3, characterized in that the enamel coating comprises
100 parts by weight chromium(III) oxide
20 parts by weight titanium dioxide
20 parts by weight zinc oxide
50 parts by weight calcium carbonate
100 parts by weight silicon dioxide

50 parts by weight feldspar
50 parts by weight phonolite
20 parts by weight potassium carbonate.

6. Heating elements according to claim 4, characterized in that the enamel coating comprises
15 parts by weight nickel oxide
15 parts by weight tricobalt tetroxide
10 parts by weight manganese dioxide
20 parts by weight iron(III) oxide
10 parts by weight titanium oxide
100 parts by weight china clay
80 parts by weight potassium feldspar
40 parts by weight lithium feldspar
20 parts by weight talcum
10 parts by weight dolomite
10 parts by weight barium carbonate
10 parts by weight zinc borate
80 parts by weight calcium carbonate.

7. Heating elements according to one of the claims 1-6, characterized in that the metal sheet or foil has a chemical composition in percent by weight as follows:

0.02 - 0.10%	C
0.10%	Mn max.
19.50%	Cr
about 56%	Ni
4.25%	Mo
2.0%	Fe max.
13.5%	Co
1.30%	Al
9.10%	Cu
0.15%	Si max.
0.003 - 0.01%	B
3.00%	Ti

8. A process for preparing an electrical resistance heating element according to claim 1, characterized in that
a) chromium oxide or
b) nickel oxide, cobalt oxide and manganese oxide are mixed with the components of a ceramic binding agent and ground for 50 to 100 h in presence of water, the obtained suspension is coated on a metal sheet or foil and the coated sheet or foil is fired.

9. A process according to claim 8 for preparing a heating element according to claim 3 or 5 characterized in that the following components are mixed in a jar mill with porcelain balls for about 70 h to obtain a coating composition:
80 - 120, preferably 100 parts by weight chromium oxide
16 - 24, preferably 20 parts by weight titanium oxide
16 - 24, preferably 20 parts by weight zinc oxide
40 - 60, preferably 50 parts by weight calcium carbonate
80 - 120, preferably 100 parts by weight silicon dioxide
40 - 60, preferably 50 parts by weight feldspar
40 - 60, preferably 50 parts by weight phonolite
16 - 24, preferably 20 parts by weight potassium carbonate
200 - 300, preferably 250 parts by weight water
200 - 300, preferably 250 parts by weight ethanol.

10. A process according to claim 8 for preparing a heating element according to claim 4 or 6, characterized in that the following components are mixed in a jar mill with porcelain balls during for 70 h for obtaining a coating composition:
12 - 18, preferably 15 parts by weight nickel oxide

12 - 18, preferably 15 parts by weight cobalt oxide
8 - 12, preferably 10 parts by weight manganese oxide
16 - 24, preferably 20 parts by weight iron oxide
8 - 12, preferably 10 parts by weight titanium oxide
80 - 120, preferably 100 parts by weight china clay
64 - 96, preferably 80 parts by weight potassium feldspar
32 - 48, preferably 40 parts by weight lithium feldspar
16 - 24, preferably 20 parts by weight talcum
8 - 12, preferably 10 parts by weight dolomite
8 - 12, preferably 10 parts by weight barium carbonate
8 - 12, preferably 10 parts by weight calcium carbonate
200 - 400, preferably 300 parts by weight water.

11. A process according to one of the claims 8 - 10, characterized in that the coated metal sheet or foil is fired at a temperature of 1100 - 1600 K, preferably at 1400K.

12. A process according to one of the claims 8 - 11, characterized in that the metal sheet or foil has the composition as indicated in claim 6.

13. A process according to one of the claims 8 - 12, characterized in that the metal sheet or foil is coated by spraying the suspension on the metal sheet or fcil.

14. A process according to one of the claims 8 - 13, characterized in that the metal sheet or foil has a thickness of less than 0,1 mm.

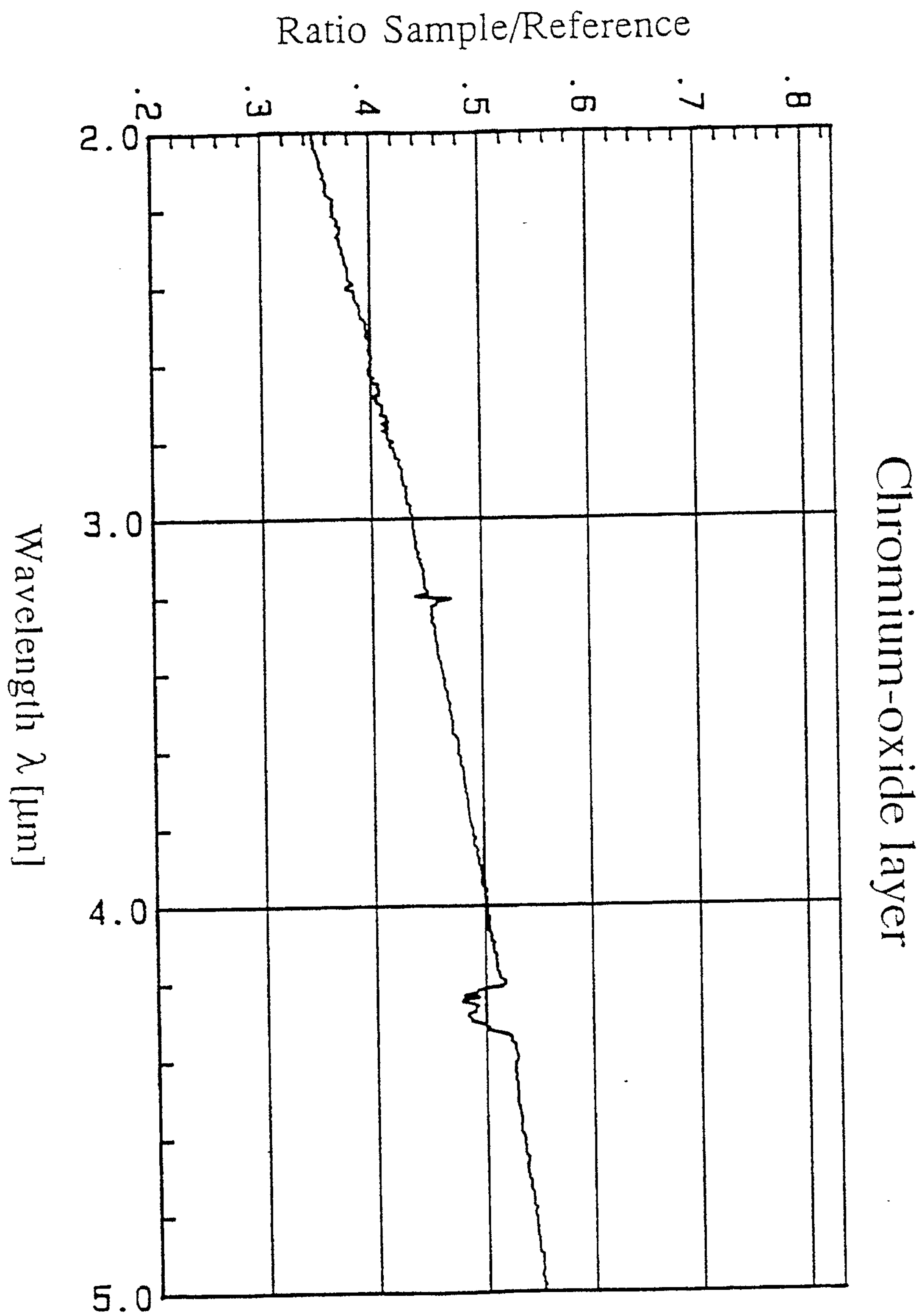
Ratio Sample/Reference
.2
.3
.4
.5
.6
.7
.8
2.0
3.0
4.0
5.0
Wavelength λ [μm]
Chromium-oxide layer

FIG. 1

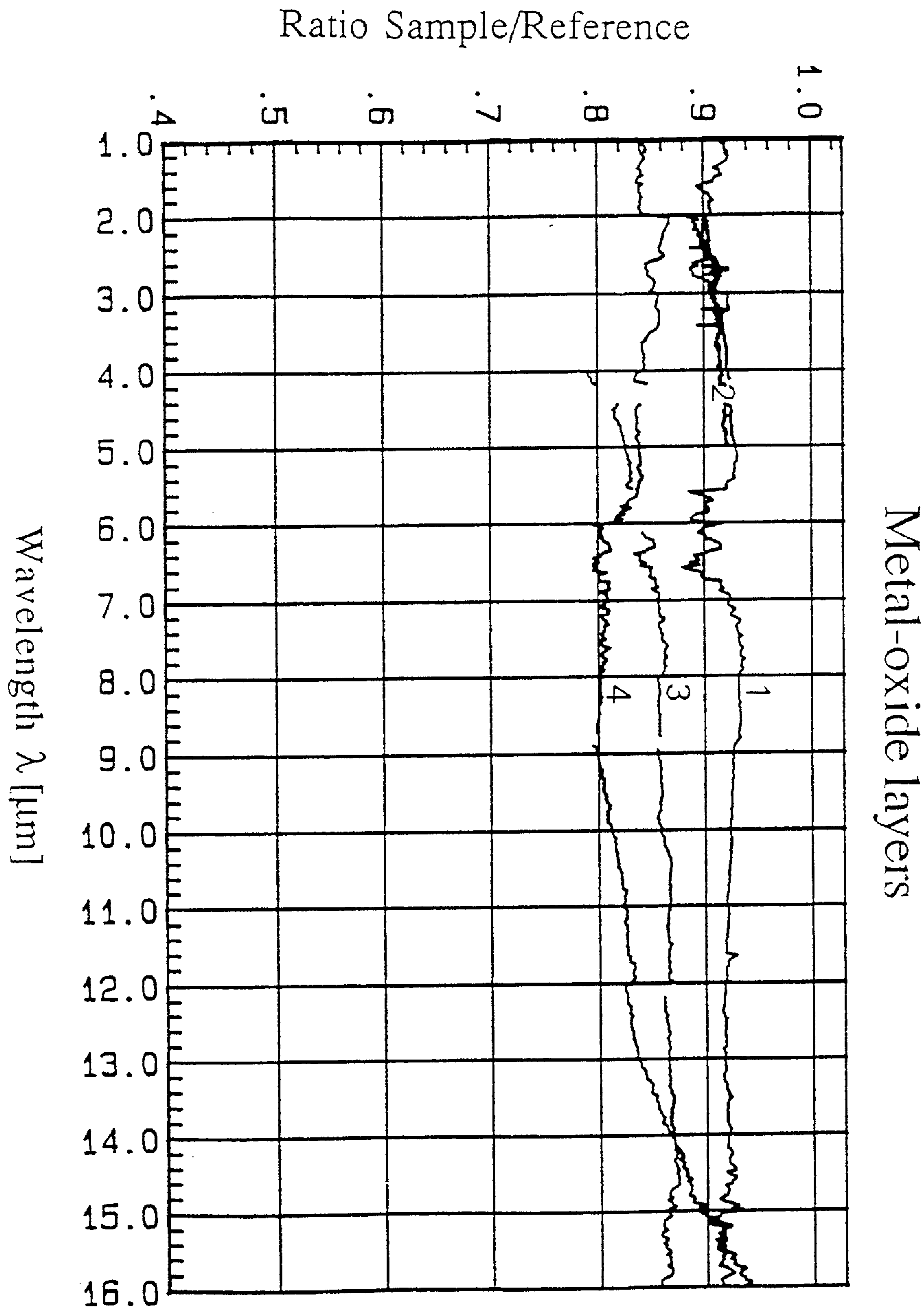
Ratio Sample/Reference
.4
.5
.6
.7
.8
.9
1.0
Metal-oxide layers
Wavelength λ [μm]
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
1
2
3
4

FIG. 2

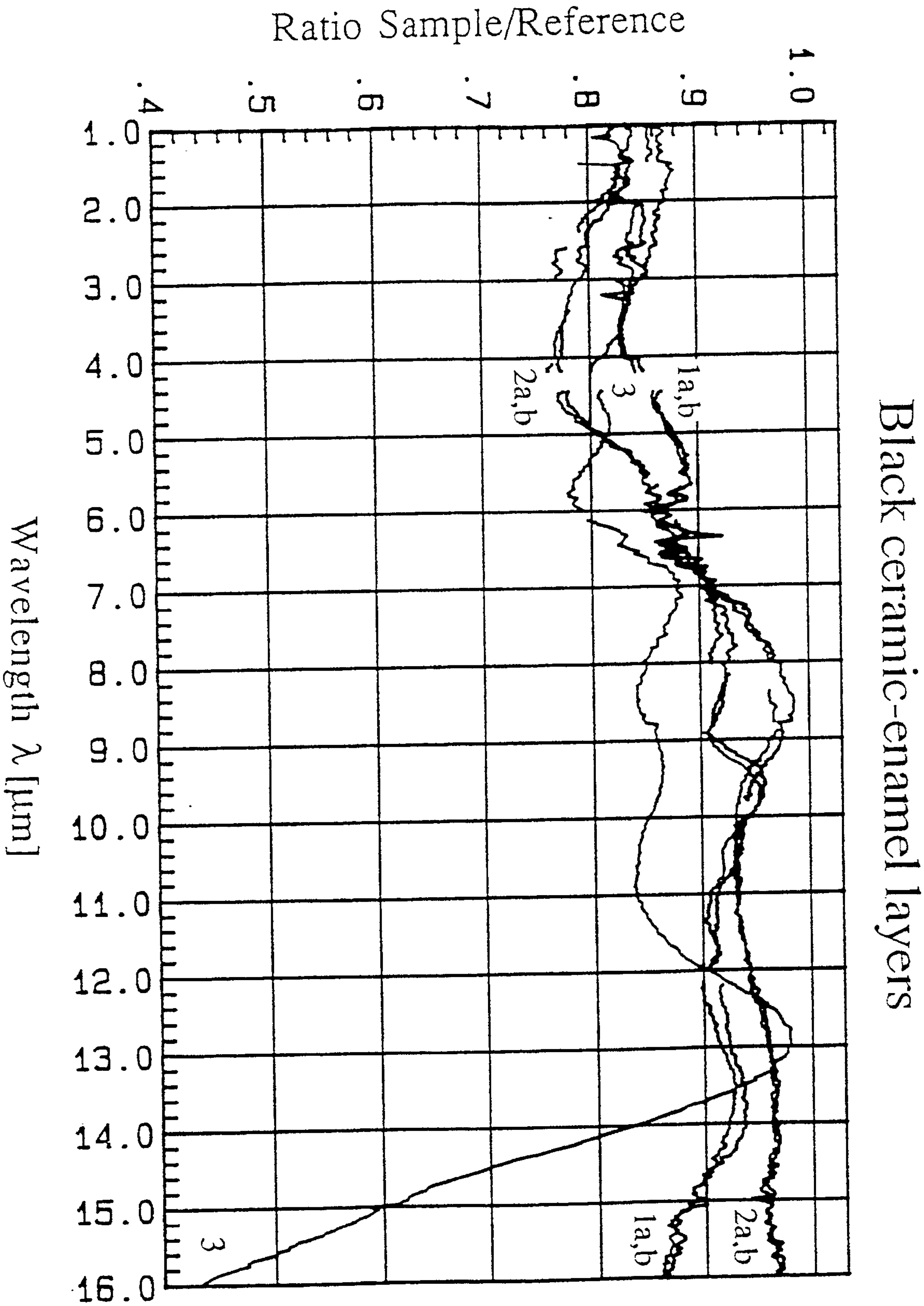
Ratio Sample/Reference
.4
.5
.6
.7
.8
.9
1.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
Wavelength λ [µm]
Black ceramic-enamel layers
1a,b
2a,b
3
1a,b
2a,b
3

FIG. 3

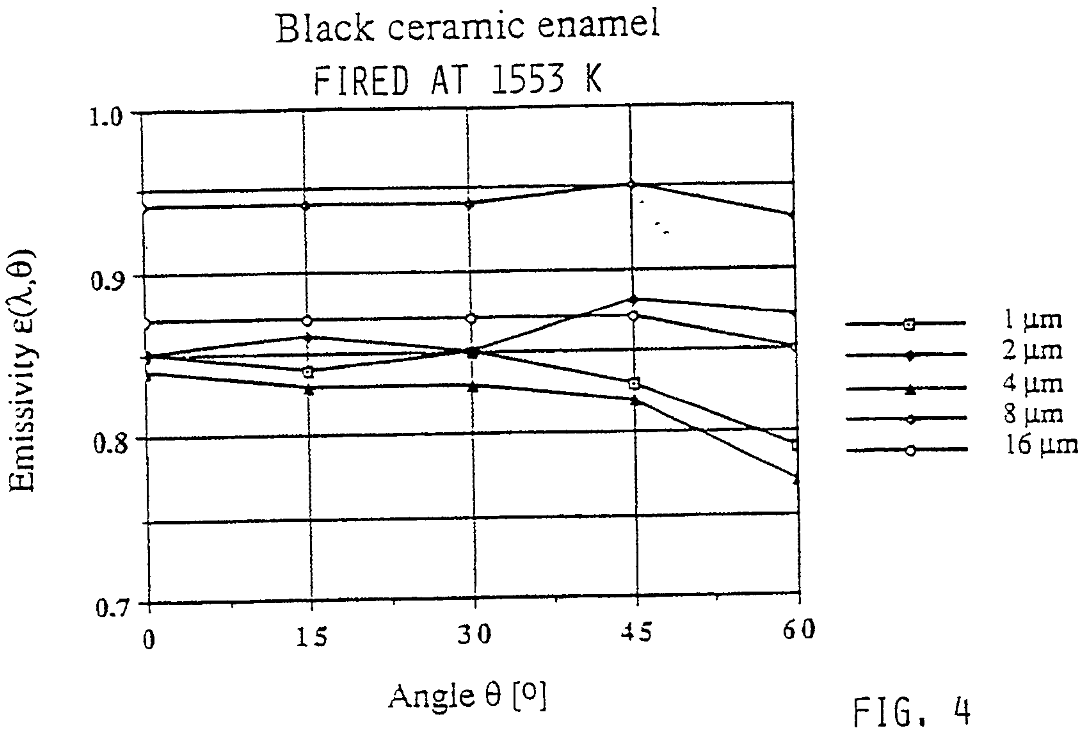
Black ceramic enamel
FIRED AT 1553 K
1.0
0.9
0.8
0.7
Emissivity ε(λ,θ)
0
15
30
45
60
Angle θ [°]
1 µm
2 µm
4 µm
8 µm
16 µm

FIG. 4

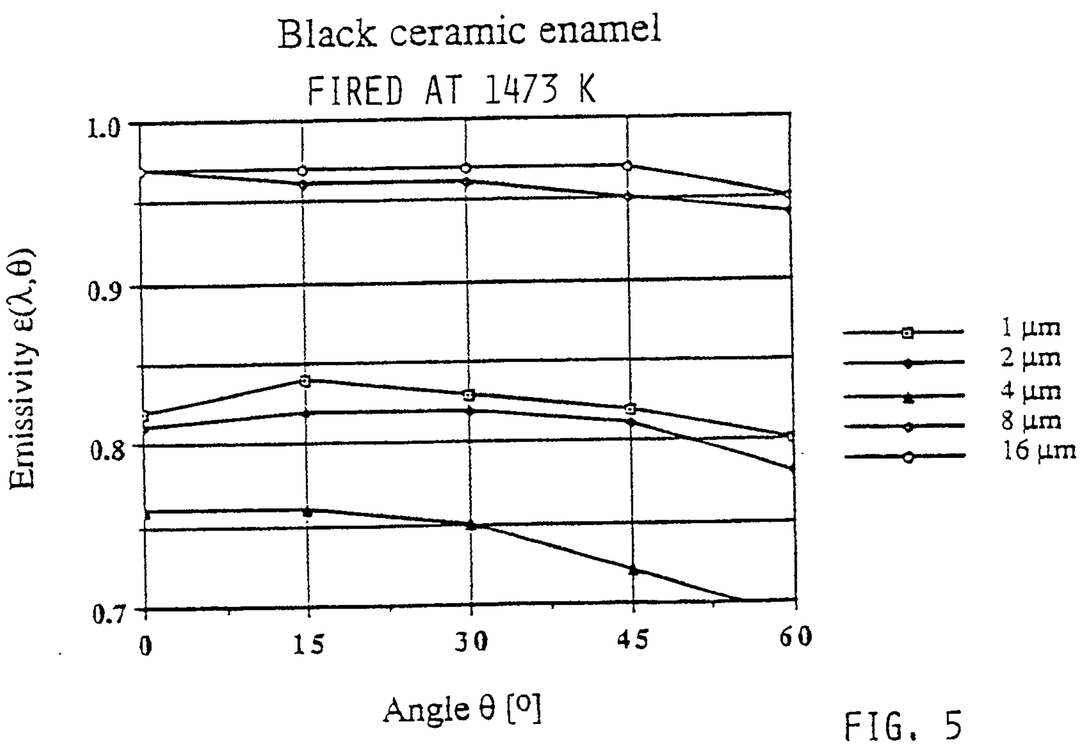
Black ceramic enamel
FIRED AT 1473 K
1.0
0.9
0.8
0.7
Emissivity ε(λ,θ)
0
15
30
45
60
Angle θ [°]
1 µm
2 µm
4 µm
8 µm
16 µm

FIG. 5

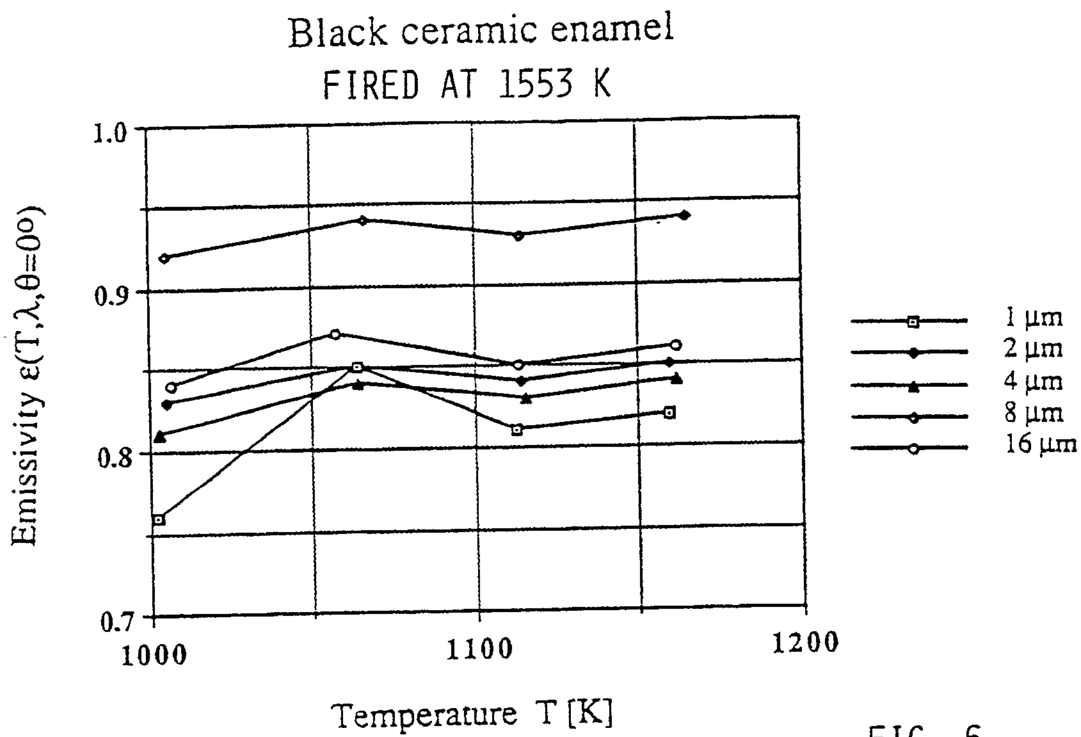
Black ceramic enamel
FIRED AT 1553 K
1.0
0.9
0.8
0.7
1000
1100
1200
Emissivity ε(T,λ,θ=0°)
Temperature T [K]
1 µm
2 µm
4 µm
8 µm
16 µm

FIG. 6

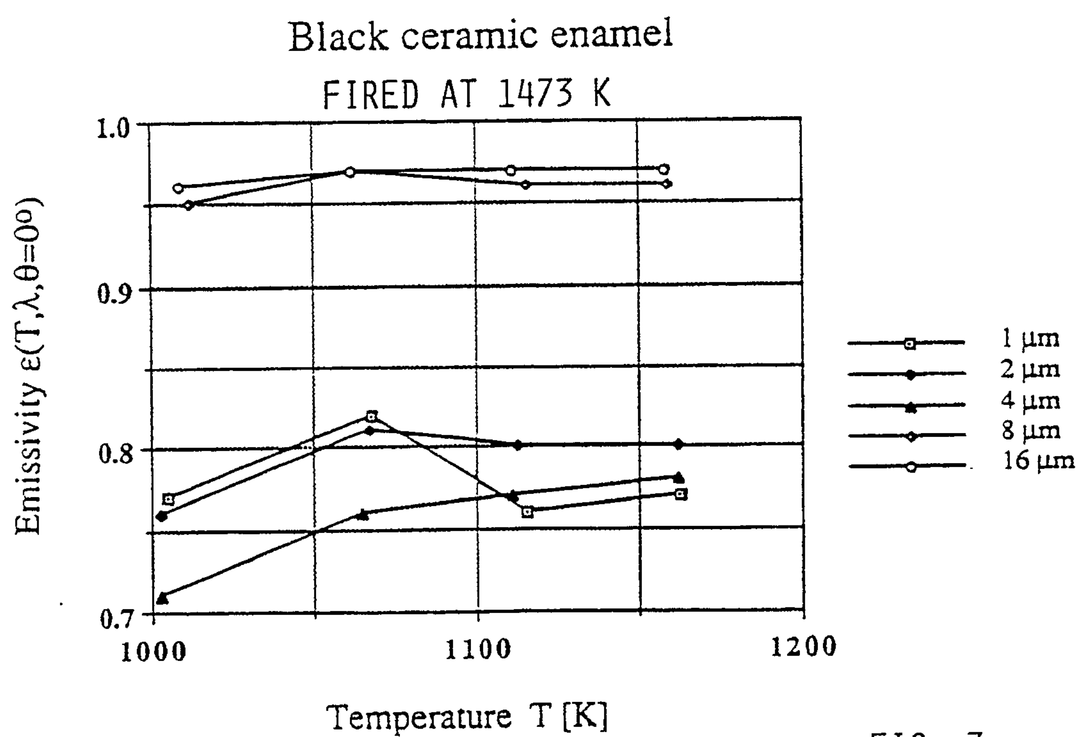
Black ceramic enamel
FIRED AT 1473 K
1.0
0.9
0.8
0.7
1000
1100
1200
Emissivity ε(T,λ,θ=0°)
Temperature T [K]
1 µm
2 µm
4 µm
8 µm
16 µm

FIG. 7

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 81 0674

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)
X	EP-A-112922 (MISHINO) * page 3, line 4 - page 3, line 15 * * page 11, line 1 - page 11, line 8 *	1	H05B3/30 H05B3/18
A	* page 7, line 12 - page 7, line 23 * * page 11, line 17 - page 12, line 8 * * page 8 * * page 4, line 6 - page 5, line 19 * * figure 1 * ---	2 3-6 8, 11, 13, 14	
A	DE-A-1496482 (EAGLE-PICHER) * page 3, line 14 - page 3, line 20 * * page 7, line 21 - page 8, line 18 * ---	1, 4, 6, 8, 10, 11, 13	
A	FR-A-2091493 (RADIATION LIMITED) * page 5, line 20 - page 7, line 6 * * claim 3 * ---	1, 4, 6, 8, 10, 11	
A	FR-A-2140344 (FERRO) * page 8, line 1 - page 8, line 21 * * page 13 * ---	3-6	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	ADVANCED MATERIALS & PROCESSES. February 1981, METALS PARK, OHIO US pages 84 - 85; "Materials & processing databook 81" ---	7	H05B
A	EP-A-222162 (BAYER) * page 1, line 15 - page 3, line 34 * -----	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17 MAY 1990	SPEISER P.

CATEGORY OF CITED DOCUMENTS

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

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