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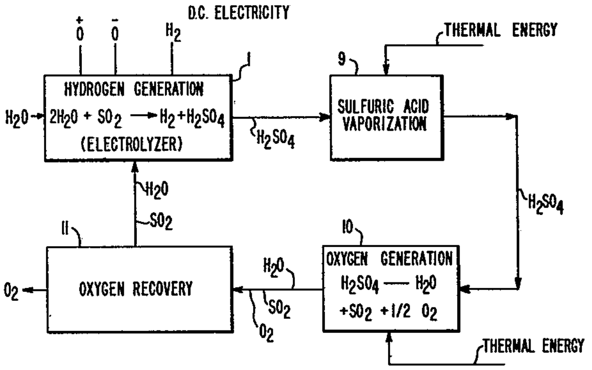
(54) Process for electrode fabrication having a uniformly distributed catalyst layer upon a porous substrate.

(57) Process for preparing electrodes for the oxidation of sulfur dioxide (including the oxidation of sulfur dioxide in a sulfur cycle process for hydrogen generation) in which a platinum group metal containing catalyst material is coated evenly onto a high-surface-area porous substrate. A solution is applied onto the substrate by a vacuum filtration method. A pressure differential of at least 10 mm-Hg is applied across the substrate. The substrate is uniformly heated (preferably by radiant heating).



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PROCESS FOR PREPARING ELECTRODES

This invention relates to a process for preparing electrodes for the anodic oxidation of sulfur dioxide and of the type in which and a platinum group metal-containing catalyst solution is coated onto a high-surface-area porous substrate and dried thus forming a film on the substrate surface.

Of all of the advanced concepts proposed for the large scale production of hydrogen, the process described in U.S. Patent 3,888,750 (Brecher and Wu), appears to be the most economical. That process is a two-step cycle which decomposes water with the hydrogen being generated in an electrolyzer and the oxygen being generated in a separate step in a thermochemical apparatus. Sulfur dioxide is electrochemically oxidized at a relatively low temperature (less than about 150°C) to produce sulfuric acid on the anode while hydrogen gas is simultaneously generated on the cathode. The sulfuric acid is then catalytically reduced at higher temperatures (generally above 870°C) into sulfur dioxide and oxygen. Subsequently, the sulfur dioxide is recycled as a reactant in the first step. The use of sulfur dioxide as an anode depolarizer reduces the thermo-dynamic reversible voltage of an electrolyzer from 1.23 volts (for the conventional electrolysis of water) to only 0.17 volts.

While the sulfur cycle reduces the electric power required in electrolysis, it has been found that conventional electrode coating processes have not resulted in uniform coatings of a catalyst on the porous substrates. Such non-uniformity has resulted in increased electrode voltage at a given production rate and thus a loss of efficiency.

Accordingly the present invention resides in a process for preparing electrodes for the anodic oxidation of sulfur dioxide and of the type in which a platinum group metal containing catalyst solution is coated onto a high-surface-area porous substrate and dried, thus forming a film on the substrate surface, characterized by:

a) applying a solution containing at least one platinum group metal to a first side of said substrate;

b) applying a pressure differential of at least 10 mm-Hg across said substrate with said first side of said substrate being the higher pressure side; and

c) uniformly heating at least one side of said substrate.

Desirably, a pressure differential of 100-100 milli-meters of mercury is applied across the substrate and the latter is radiantly heated.

In order that the invention can be more clearly understood, convenient embodiments thereof will now be described, by way of example, with reference to the accompanying drawings in which:

Figure 1 shows a block diagram illustrating the sulfur cycle hydrogen generation system in which the electrode made by the process of this invention can be used;

Fig. 2 is a diagram of an electrolytic cell (electrolyzer) in which the electrode fabricated by this process can be used;

Fig. 3 is a cross-section of a substrate holder and substrate in which a vacuum is used to produce the pressure differential;

Fig. 4 is a cross-section of a substrate holder and substrate where positive pressure is used to produce the pressure differential;

Fig. 5 shows the appearance of a commercially available platinum-coated carbon electrode;

Fig. 6A shows the general appearance and Figure 6B shows a scanning electron micrograph of a typical carbon substrate prior to coating by the method of this invention; and

Fig. 7A illustrates the general appearance and Figure 6B shows a scanning electron micrograph of a resulting electrode prepared by the process of this invention.

The sulfur cycle hydrogen generation system of Fig. 1 is a typical use of the sulfur dioxide oxidation electrode of this invention. In Figs. 1 and 2, an electrolyzer 1 contains an aqueous solution of sulfuric acid 2 which is saturated with SO_2. Direct current is applied to the solution through an anode 3 (made by the process described herein) and a cathode 4. Sulfuric acid and hydrogen gas are generated at the anode 3 and the cathode 4, respectively. Inlets 5 and 6 are provided for the addition of more dilute sulfuric acid and additional sulfur dioxide. The hydrogen product leaves by outlet 7 where it separates from the sulfuric acid. Unconsumed sulfur dioxide leaves by outlet 8 with the more concentrated sulfuric acid solution, and both are recycled. A portion of the sulfuric acid from outlet 8 passes to vaporizer 9 where water is evaporated and its concentration is increased. The concentrated sulfuric acid then passes to oxygen generator 10 where the sulfuric acid is heated over a catalyst, for example, of platinum or vanadium pentoxide, to decompose it into water, sulfur dioxide, and oxygen which pass to oxygen recovery unit 11. In oxygen recovery unit 11, the sulfur dioxide is separated from the oxygen by lowering the temperature to condense the sulfur dioxide into a liquid. The sulfur dioxide and the water are then returned to inlet 6 of the electrolytic cell 1, thus completing the cycle. A hydrogen-ion-permeable membrane 12 separates the fluid around the anode 3 from the fluid around the cathode 4.

Cyclic voltammetric studies have revealed that the anodic oxidation of sulfur dioxide is highly irreversible. The overvoltage on the anode contributes a significant proportion to the overall potential of an electrolyzer, and thus is one of the major sources of efficiency loss in the cell. Methods to reduce the anode overvoltage include the use of appropriate electrode catalyst and the maximization of active surface areas of the electrode. To maximize the surface area, are electro-catalysts supported on highly porous substrates (electrodes made completely of a palladium, for example, rather than as a palladium coating on a substrate would, of course, be extremely expensive). Carbon substrates formed from extremely fine carbon powder provides a porous substrate with a very high surface area (a specific surface area of at least 200 and typically about 450 square meters per gram). The appearance and microstructures of a typical carbon (plate) substrate are illustrated in Fig. 6. These inexpensive carbon substrates provide good porosity, electrical conductivity and mechanical strength. While anodes of carbon (graphite) catalyzed with fine platinum particles have been used for preparation of sulfuric acid from sulfur dioxide, commercially available platinum-coated carbon electrodes have been found to have an extremely non-uniform coating of platinum. All such electrodes had, as shown in Fig. 5, areas which were clearly uncoated.

Early experiments to improve the uniformity of catalyzed carbon plate electrodes which, like the commercially available electrodes, when visually inspected, had little or no catalyst in the center. When these electrodes were disected, there was also little or no catalysts on interior surfaces. In this early work, the aqueous solution of noble metal compound (such as dihydrogen hexachloroplatinate or palladium acetate) was applied to the surface of a porous carbon substrate by painting. The substrate doped with catalyst was slowly dried in a furnace at about 50°C. The resultant non-uniform coatings may have been caused by the pressure of the water vapor in the pores increasing during the evaporation process and gradually repealing the solution out of the pores (the aqueous solution also apparently migrated toward low temperature regions at the edges).

In order to avoid the problems of those early techniques, a new method was developed in which a pressure differential across the substrate was used to push solution through the substrate and radiant heating of one side of the substrate was used to heat the substrate uniformly (note that uniformity on the surface and on planes parallel to the surface is a critical but that temperature differences through the thickness of the material - e.g. between planes parallel to the surface - can be tolerated).

The invention will now be illustrated with reference to the following Example:

EXAMPLE

A. A five by five centimeter porous carbon substrate (mean pore size approximately nine microns) was activated by oxidation in a concentrated nitric acid (13.5 normal at 80°C).

B. 0.255 grams of palladium acetate was dissolved in 30 milliliter of distilled water and the solution was then heated at 80°C for 30 minutes.

C. The oxidized carbon substrate 13 was mounted (as shown in Fig. 3) in a lucite holder 14 using a seal around the perimeter of the substrate. The substrate was then positioned in a horizontal plane with its underside exposed to a cavity 18 that was connected to a vacuum pump.

D. A small amount of solution was poured onto the upper side of the substrate and the vacuum was applied to maintain a pressure differential of approximately 10 millimeters of mercury across the substrate 13. The substrate 13 was heated *in situ* to 40-60°C using an overhead infrared lamp 20 (palladium acetate was thus uniformly deposited over the electrode 13 as the solution filtered through the pores). This treatment (adding solution, applying pressure differential, and reheating) can be repeated to increase the thickness of compound applied.

E. After the deposition of palladium acetate was completed, the thermal decomposition process was performed in a nitrogen or hydrogen atmosphere at 600°C for 2 hours, which resulted in the formation of a thin layer of palladium completely covering the electrode surface (as shown in Fig. 7, the density of palladium particles is high and the distribution is uniform).

When a palladium-oxide electrode is to be used, the palladium-covered carbon substrate prepared as above is further treated, for example, at a temperature of 400-500°C in a stream of helium gas containing 5% oxygen.

While the electrode is preferably heated from above (as apparently the solution being applied tends to migrate towards lower temperature regions), the substrate could be heated from below, as shown in Fig. 4. Fig. 4 also illustrates the use of a positive pressure cavity 22 (as opposed to the vacuum cavity of Fig. 3) as a means for applying the pressure differential across the substrate 13. Whether heated from above as in Fig. 3, or below as in Fig. 4 (or both as can be done by sticking a radiant heating source in either the vacuum cavity 18 of Fig. 3 or the pressure cavity 22 of Fig. 4) or whether the pressure differential is applied by a positive pressure or by a vacuum (or both), it is critical that one uses a pressure differential to uniformly move the solution through the substrate.

Experiments in which uniform heating alone was used (a variation of the above process without a pressure differential), failed to produce uniform coatings. When a pressure differential was used with non-uniform heating, poor results were obtained. Only by using both the uniform heating and the pressure differential were even coatings obtained. Although uniform heating in an oven was accomplished experimentally, oven heating tended to be non-uniform unless extreme care was taken and radiant heating is preferred.

Again with reference to Fig. 4, it should be noted that the pressure could be applied by a pump directly to the coating solution (thus the pressure chamber 22 would be completely filled with fluid) or by using sufficient depth of solution to provide the pressure hydrostatically. Neither of these techniques, however, lend themselves to radiant heating from the side to which the solution is applied and thus the arrangement of Fig. 3 is preferred.

It has been found that at least ten millimeter of mercury's differential pressure is required to move the fluid through the substrate at a practical rate and that the differential pressure should be less than about 100 millimeters of mercury if carbon substrates are used to avoid damage to the substrate. Preferably a differential pressure of 10-30 millimeters of mercury is used with carbon substrates. Other types of substrates (e.g. a substrate sintered from finely divided titanium powder) can also be used and the upper limit of the pressure differential is determined by the strength of the substrate. As described in the aforementioned copending application, the palladium or palladium oxide catalyst is preferred (although other platinum group of metals can also be uniformly deposited by the techniques described herein) and palladium is preferably deposited using radiant heating to 40-60°C.

In U.S. Patent Application S.N. 084,494 entitled "Palladium Electrode For Use In Sulfur Cycle Hydrogen Operation Process", filed October 15, 1979, there is described a palladium electrode for use in the anodic oxidation of sulfur dioxide. The use of a palladium catalyst rather than the platinum provides for a significant voltage reduction and therefore a greatly increased electrolyzer efficiency. The process of the present invention can be used to fabricate the palladium electrode of this copending application.

What we claim is:

1. A process for preparing electrodes for the anodic oxidation of sulfur dioxide and of the type in which a platinum group metal containing catalyst solution is coated onto a high-surface-area porous substrate and dried, thus forming a film on the substrate surface, characterized by:

a) applying a solution containing at least one platinum group metal to a first side of said substrate;

b) applying a pressure differential of at least 10 mm-Hg across said substrate with said first side of said substrate being the higher pressure side; and

c) uniformly heating at least one side of said substrate.

2. A process according to claim 1, characterized in that the differential pressure across the substrate is 10-100 mm-Hg.

3. A process according to claim 2, characterized in that the differential pressure is 10-30 mm-Hg.

4. A process according to claim 3, characterized in that the substrate is radiantly heated.

5. A process according to claim 4, characterized in that the platinum group metal is palladium and the substrate is radiantly heated to 40-60°C.

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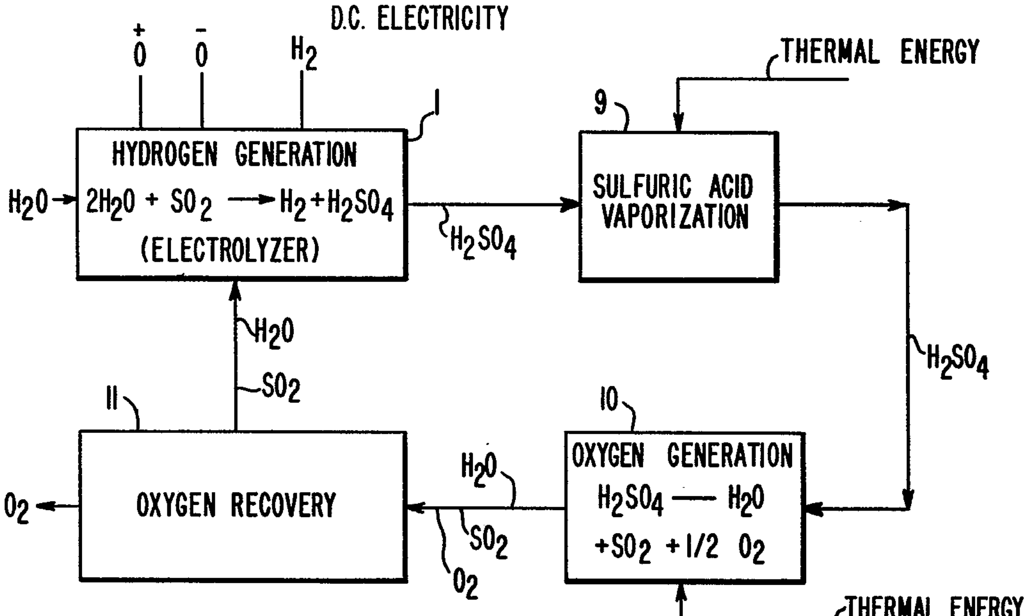
D.C. ELECTRICITY
+ 0
- 0
H_2
THERMAL ENERGY
9
1
HYDROGEN GENERATION
H_2O
$2H_2O + SO_2 \rightarrow H_2 + H_2SO_4$
(ELECTROLYZER)
H_2SO_4
SULFURIC ACID VAPORIZATION
H_2SO_4
H_2O
SO_2
11
10
OXYGEN GENERATION
$H_2SO_4 — H_2O + SO_2 + 1/2\ O_2$
O_2
OXYGEN RECOVERY
H_2O
SO_2
O_2
THERMAL ENERGY

FIG. 1

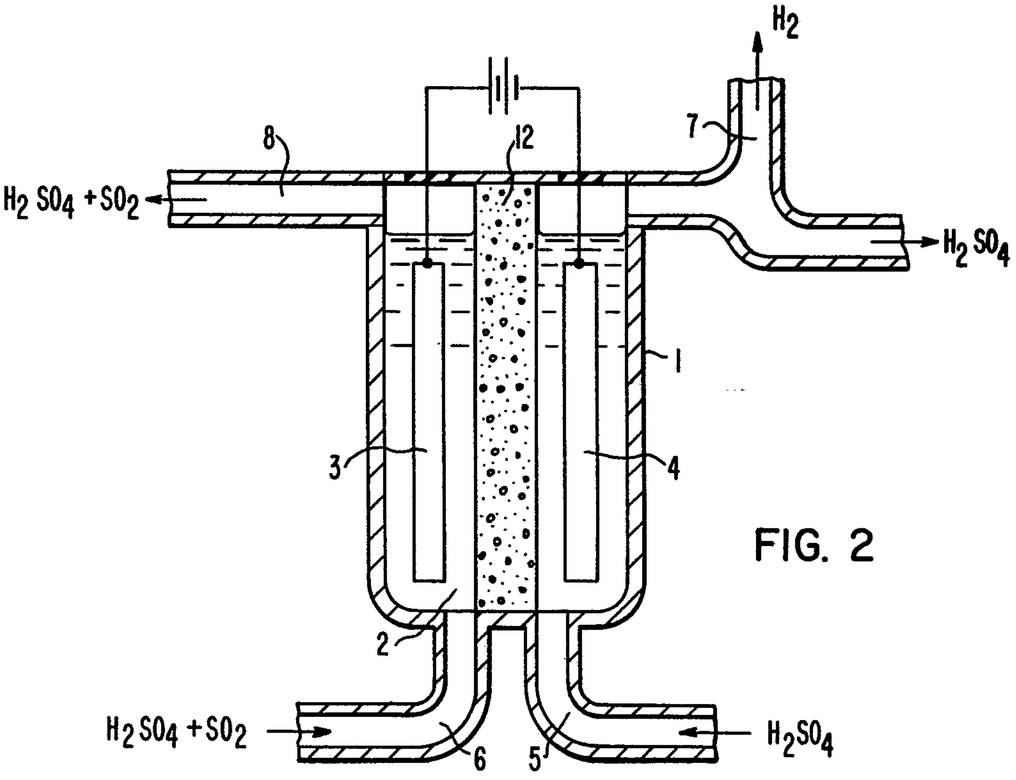
H_2
12
7
8
$H_2SO_4 + SO_2$
H_2SO_4
1
3
4
2
$H_2SO_4 + SO_2$
6
5
H_2SO_4

FIG. 2

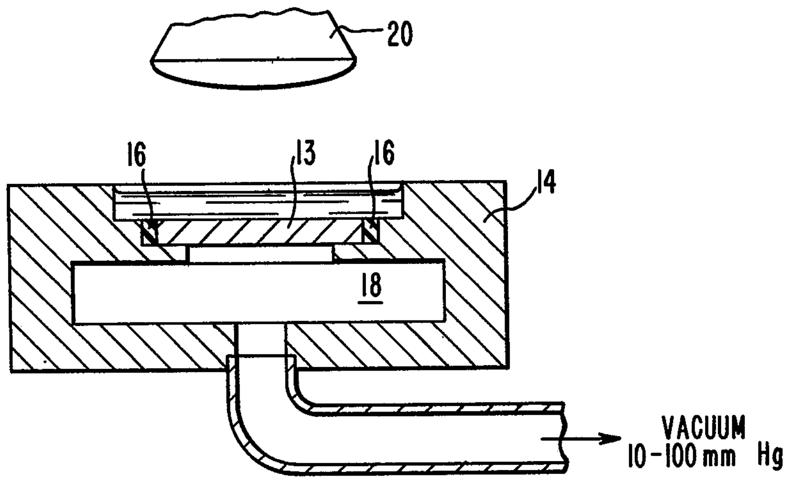

FIG. 3

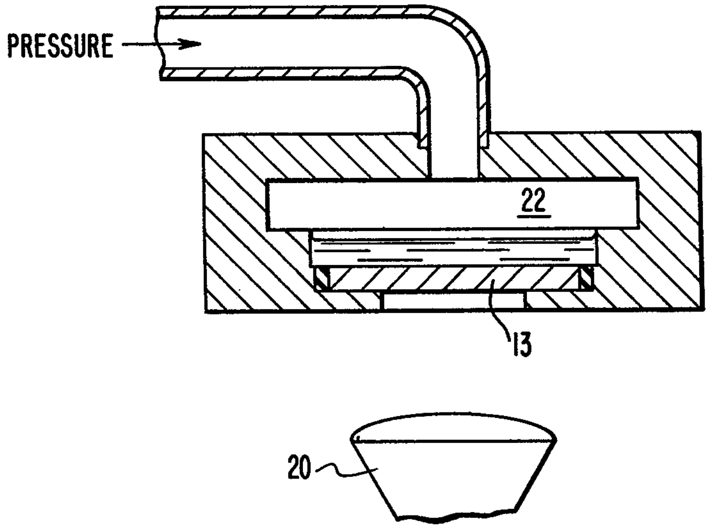

FIG. 4

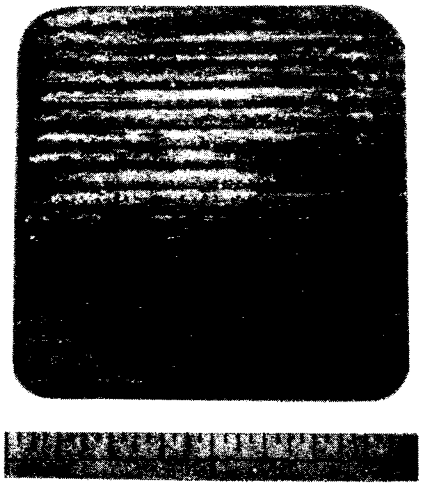

FIG. 5

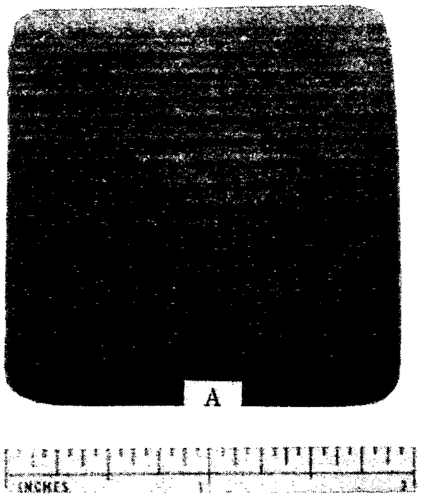

FIG. 6A

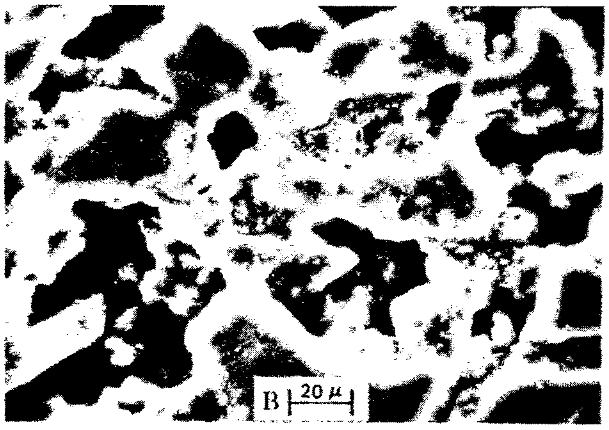

FIG. 6B

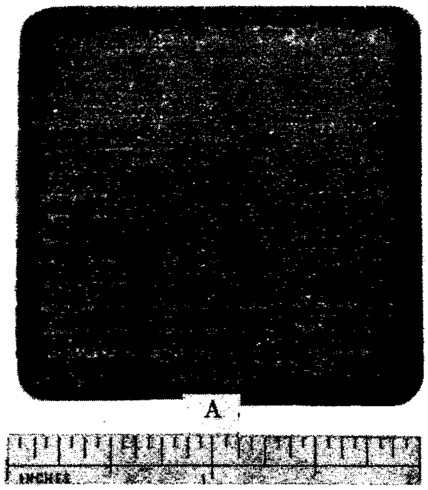

FIG. 7A

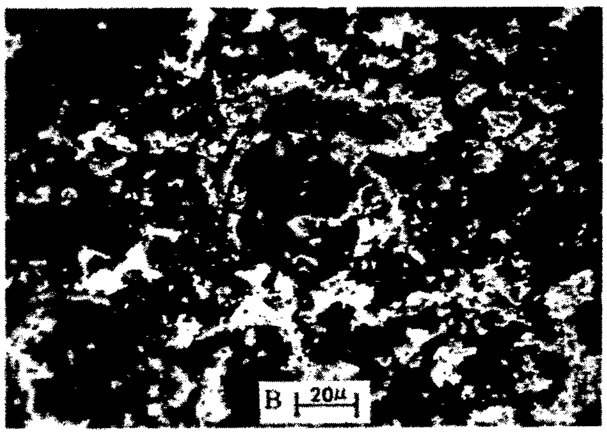

FIG. 7B

European Patent Office

EUROPEAN SEARCH REPORT

0040897

Application number

EP 81300306.8

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.3)
	DE - B - 2 002 298 (BARTHEL) * Column 6, lines 44-60 * --	1	C 25 B 11/06 C 25 B 11/14 C 25 B 1/04
A	GB - A - 1 329 153 (SOLVAY) * Totality * --	1	
A	US - A - 4 164 457 (H. BARNERT, M. PEREC, B.D. STRUCK) * Abstract; column 1, lines 57-68; column 2, lines 1-34 * --	1	
	US - A - 3 778 307 (H.B. BEER) * Column 7, lines 54-66 * ----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.3)

C 25 B

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	21-07-1981	PILLERSTORFF