



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/SE79/00209 <b>(22) International Filing Date:</b> 19 October 1979 (19.10.79)  <b>(31) Priority Application Number:</b> 7810976-6 <b>(32) Priority Date:</b> 20 October 1978 (20.10.78) <b>(33) Priority Country:</b> SE  <b>(71) Applicants; and</b> <b>(72) Inventors:</b> KUBAT, Josef [SE/SE]; Solparksvägen 3, S-171 35 Solna (SE). RIGDAHL, Hans, Mikael [SE/SE]; Klostersgöngen 7, S-413 18 Göteborg (SE). DJURNER, Jan Krister [SE/SE]; Viktoriagatan 8, S-411 25 Göteborg (SE).  <b>(74) Agents:</b> HALLDIN, Bo, et al.; Dr. Ludwig Brann Patentbyrå AB, Kungsgatan 3, S-103 92 Stockholm (SE).		<b>(81) Designated States:</b> AT (European patent), BR, CH (European patent), DE (European patent), DK, FR (European patent), GB (European patent), JP, LU (European patent), NL (European patent), SU, US.  <b>Published</b> <i>With international search report</i>
<b>(54) Title:</b> INJECTION MOULDING OF HIGH MOLECULAR POLYETHYLENE USING ELEVATED MOULD TEMPERATURE  <b>(57) Abstract</b>  Process for producing injection moulded articles having highly improved mechanical properties of polyethylene having very high molecular weight and high density with the use of elevated pressure exceeding 250 MPa which process is characterized in that the injection moulding is carried out with the simultaneous use of an elevated mould temperature between 40 and 125°C.		

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INJECTION MOULDING OF HIGH MOLECULAR POLYETHYLENE USING  
ELEVATED MOULD TEMPERATURE

The present invention relates to a process for preparing injection moulded articles of HD-polyethylene (polyethylene of high density type) having a high molecular weight by injection moulding with injection and holding pressures  
5 exceeding 250 MPa with the use of an elevated mould cavity temperature between 40 and 125°C, suitably between 50 and 120°C. The articles prepared by means of the process are characterized by extremely improved mechanical strength properties such as very high values for tensile strength  
10 at rupture and modulus of elasticity.

From the Swedish Patent Specification 401,129 it is known that an essential increase of the pressure in the mould cavity in processing of thermoplastics by injection moulding results in a number of property improvements  
15 of the injection moulded part while simultaneously certain technical process advantages can be obtained. Said Swedish Patent Specification thus discloses an injection moulding process wherein the pressure in connection with the injection of the melt and the subsequent  
20 solidification exceeds 250 MPa. Said pressure range shall be compared with the pressure range of 50 to 150 MPa which is the normal pressure range in injection moulding.

Among the improvements of the properties of the moulded part which are provided with a processing pressure exceeding 250  
25 MPa there is to be noted a general increase of the level as regards the stiffness (modulus of elasticity) and strength parameters such as have been obtained in experiments with polyethylene of varying density and polypropylene. Furthermore, in measurements on both crystalline and amorphous  
30 polymers a marked decrease in the mould shrinkage has been observed. In certain cases said change was so large that the mould shrinkage assumed negative values.



An additional property improvement which has been observed in experiments of this type has been a marked decrease of the internal stress level. As is well known internal stresses are a defect of normal injection moulded products ; they  
5 i.a. can result in warpage, undesirable crazing and cracking, etc. Their reduction, in some cases complete elimination, can be traced back to an increase of the melting and softening point respectively of the plastic with the pressure. Thus, pressures within the above specified range have been shown  
10 to increase these critical temperatures so that a practically momentary solidification of the melted plastic material injected in the mould cavity is obtained. This prevents the formation of an internal stress structure which, as is well known, is due to a gradual solidification of the melt and  
15 to the forces which the already solidified and the still liquid parts of the detail exert on each other.

As regards the improvement of the property profile of the detail, especially as regards the mechanical parameters, the effects obtained with an increase of the process pressure  
20 are dependent on the structure of the plastic used. Thus, the largest changes have been observed for crystalline plastics, especially polyethylene, wherein they could be related to changes in the structure of the crystalline phase. In the crystallization of a polyethylene melt under pressure  
25 exceeding about 300 MPa a crystal modification is obtained wherein the folded lamellar structure present at normal pressures to an extent increasing with the pressure is converted to a structure consisting of straight chains. The presence of this new structure explains the improved property profile.  
30 Thus, the new modification with straight chains i.a. gives a more organized package of the molecules in the space.

Especially striking results are obtained with HD-polyethylene having high molecular weight, which means polyethylene having a molecular weight of from 200.000 up to  
35 1.5 millions and higher (or corresponding to a melt index of less than 1 g/10 minutes at 190°C/2 kg load) hereinafter

designated HMWHDPE. As compared to the improvement of modulus and strength obtained with this and similar qualities the corresponding values obtained with HDPE of normal molecular weight were relatively small. As an  
 5 illustration of the extremely remarkable increase of the property level with an increase of the pressure reference is made to the values stated in the following table I.

TABLE I

	E GPa	$\sigma_B$ MPa
10 HMWHDPE	3.4	130
HDPE	0.6	25

Process conditions: Injection pressure 500 MPa  
 Mould temperature 30°C

E = modulus of elasticity

15  $\sigma_B$  = tensile strength at rupture

According to the present invention it has been found that an additional surprising improvement of the properties of details of HMWHDPE injection moulded at pressures exceeding 250 MPa, preferably from 300 MPa and upwards can be obtained  
 20 by means of a suitable selection of the mould temperature. Thus, according to the present invention it has been found that very manifest improvements of the properties of the detail are obtained if the mould temperature is increased to e.g. 100°C, which increase especially gives rise to an  
 25 increase of the modulus and the tensile strength. Thus, it has been found that the increased pressure per se is not sufficient for producing details with optimum mechanical properties; an optimum property profile in this respect rather is obtained by a simultaneous increase of both the  
 30 pressure in the mould cavity and the mould temperature.



Without wishing to restrict the invention to a certain theory a probable explanation to the results obtained seems to reside in a more complete transformation of the crystalline phase to the extended chain modification. This  
5 transformation takes place via a crystalline transition (hexagonal  $\rightarrow$  orthorhombic) which is facilitated when the temperature increases.

In the drawings enclosed

Figure 1 shows tensile strength at rupture and modulus of  
10 elasticity of injected moulded articles of HMWHDPE plotted against the mould temperature.

Figure 2 shows elongation at rupture of injection moulded articles of HMWHDPE plotted against the injection pressure  
15 for two different mould temperatures;

Figure 3 shows tensile strength at rupture and modulus of elasticity of injection moulded articles of HMWHDPE plotted against the injection pressure for two different mould temperatures.

20 It has also been found, as is described more closely in our copending Swedish Patent Application No. 7810977-4 with the title "Injection moulding process with the use of polymer blends containing high molecular HD-polyethylene" that in injection moulding at high injection moulding pressures  
25 exceeding 250 MPa, preferably from 300 MPa and upwards, of blends of HMWHDPE with polymeric materials with which HMWHDPE has a limited compatibility (solubility) HMWHDPE forms a fibrous phase in a matrix of the other polymeric material. In this manner a reinforced composite material is  
30 obtained as a final product. By increasing the mould temperature beyond the mould temperature normally used as in accordance with a process according to the present



invention it also has been found that composite materials with still more improved mechanical properties can be obtained as compared to the same composite materials injection moulded at the usual low mould temperature of 30°C.

- 5 Suitable matrix materials together with which HMWHDPE can be injection moulded in the process according to the present invention are such polymeric materials with which HMWHDPE has limited compatibility. Such polymeric materials include polyethylene of HD-, MD- and LD-types of normal molecular
- 10 weight which means such material which normally is used in injection moulding or extrusion. Other suitable materials are e.g. polyolefines, such as polypropylene ; polystyrene, polyvinylchloride, polyacetal, polyamides, copolymers of these and others.
- 15 The invention is illustrated by means of the following specific examples which describe embodiments of the invention but which are not intended to limit the invention in any respect.

#### Example 1

- 20 Test bars of high molecular polyethylene having high density were injection moulded with an injection pressure of 500 MPa and with the use of varying mould temperatures from 30°C up to 100°C. The polyethylene material used was DMDS2215 obtained from Unifos Kemi AB and which had a density of
- 25 0.953 g/cm<sup>3</sup> and a melt index of 0.1 g/10 minutes.

- In figure 1 the values obtained for tensile strength at rupture,  $\sigma_B$ , and modulus of elasticity, E, of the test bars produced have been plotted against the mould temperature. From the figure it can be seen that improved values for said
- 30 properties are obtained when the mould cavity temperature is increased. From the results obtained it can be seen that the absolute values for modulus of elasticity and tensile strength at rupture are very high and vastly exceed those normally obtained for HDPE and furthermore also exceed the
- 35 corresponding values of e.g. glass fiber reinforced engineering plastics.



Example 2

A set of test bars of the same material as used in example 1 were injection moulded at injection pressures varying between 100 and 500 MPa and with the use of two different  
5 mould cavity temperatures, 30°C and 70°C respectively.

Figures 2 and 3 show the results of measurements concerning the mechanical properties of the products obtained. From figure 2 it can be seen that the elongation at rupture is lower when using the higher mould cavity temperature while  
10 figure 3 shows that both the modulus of elasticity and the tensile strength at rupture increase when the higher mould cavity temperature is used.





CLAIMS

1. A process for producing injection moulded articles having highly improved mechanical properties of polyethylene of very high molecular weight and high density with the use of elevated pressure exceeding 250 MPa
- 5 characterized in that the injection moulding is carried out with a simultaneous use of an elevated mould temperature between 40°C and 125°C.
2. A process according to claim 1 characterized in that the mould temperature is between 50 and 120°C.
- 10 3. A process according to claim 2 characterized in that the polyethylene having very high molecular weight and high density is blended with a polymeric material with which said polyethylene has a limited compatibility.



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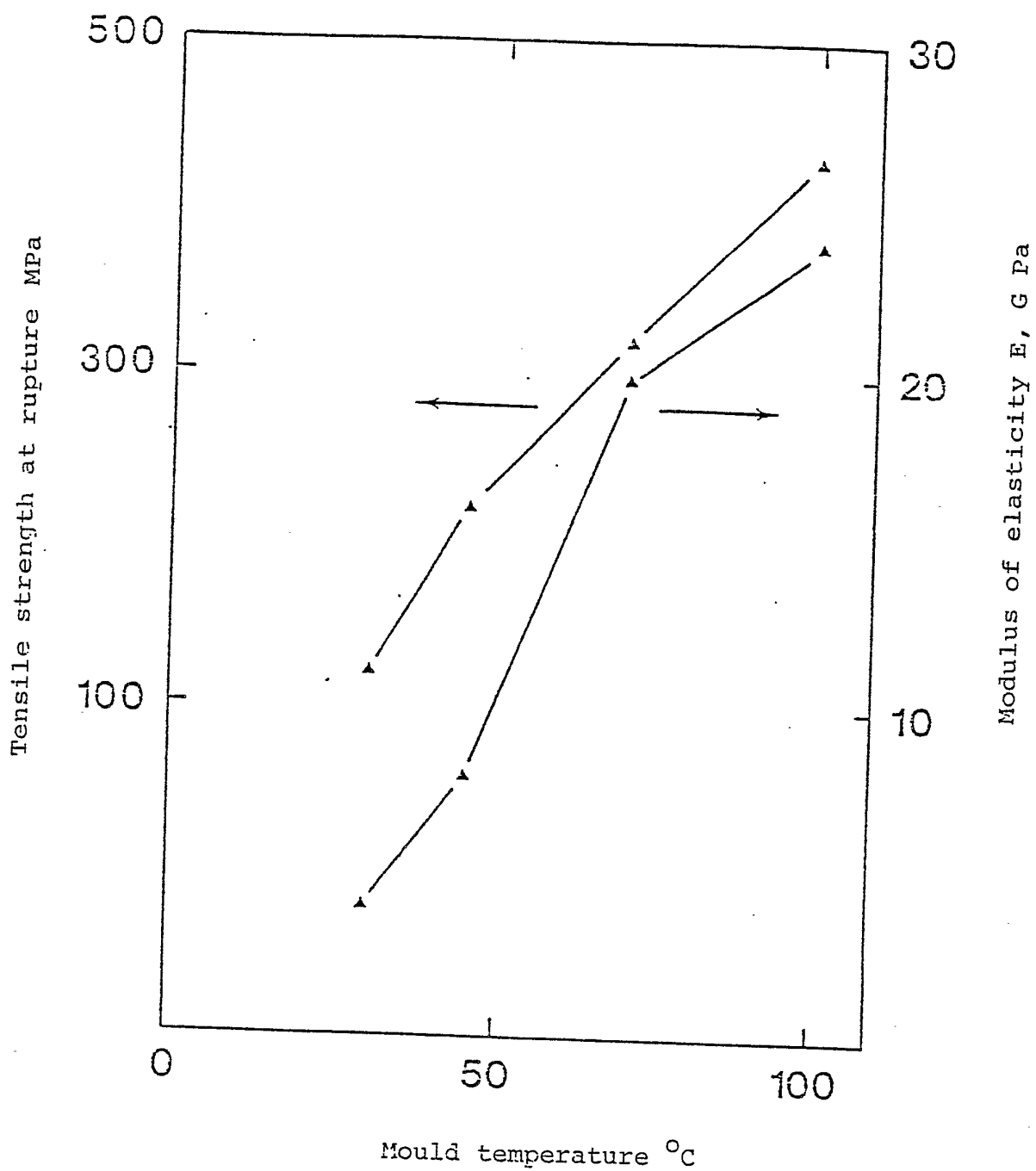


Figure 1

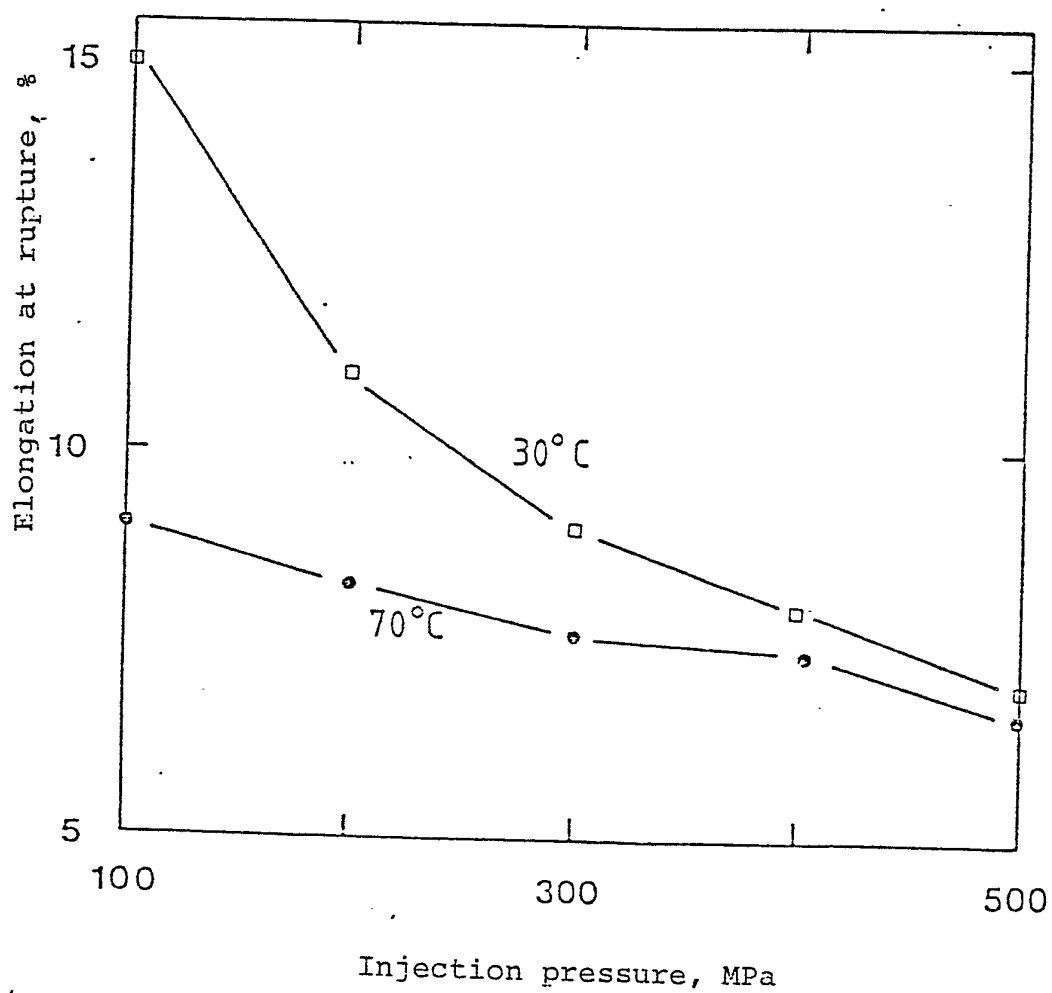


Figure 2

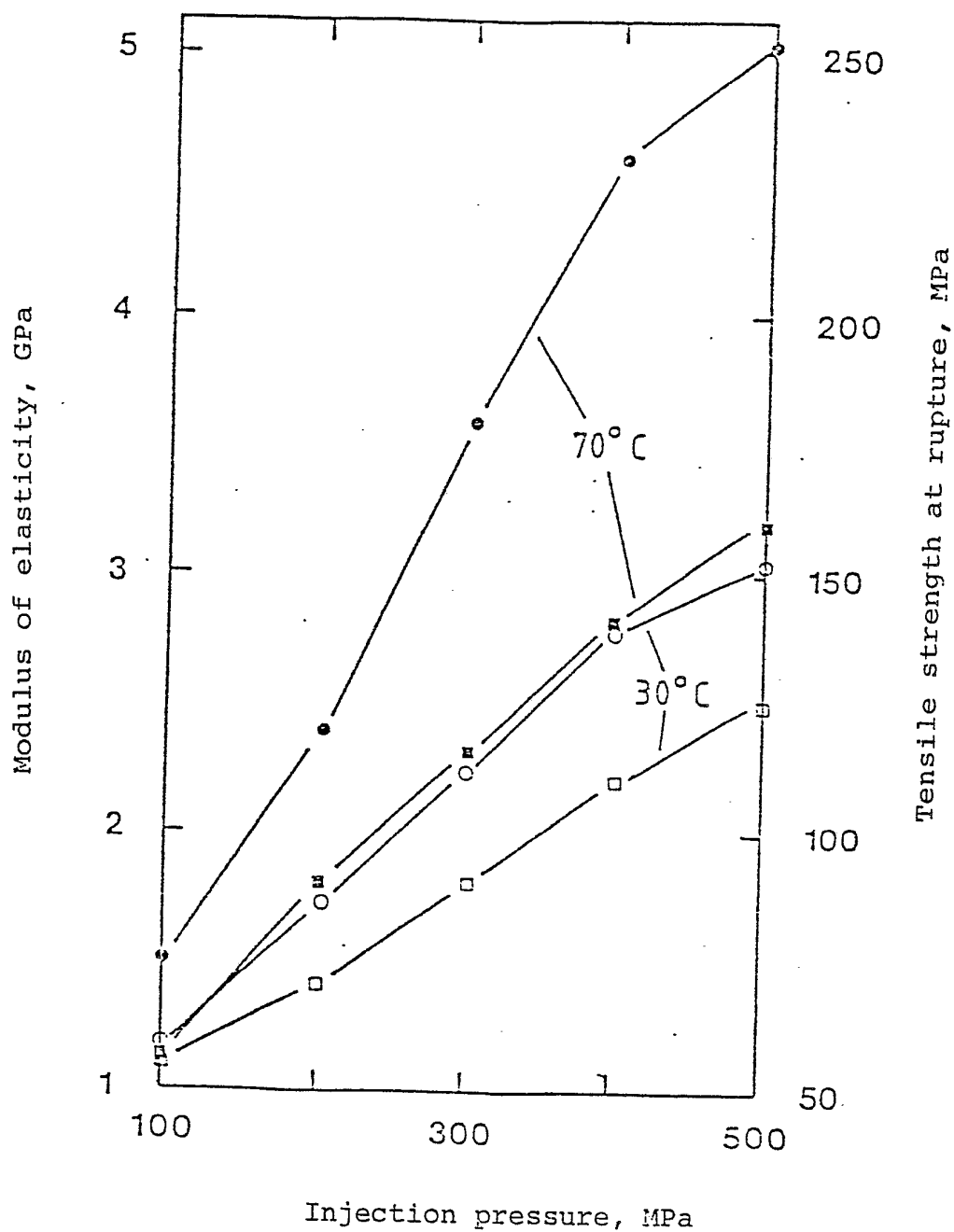


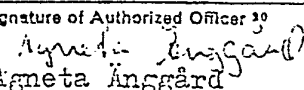
Figure 3

- ○ E-modulus
- □  $\sigma_p$  Tensile strength at rupture



# INTERNATIONAL SEARCH REPORT

International Application No PCT/SE79/00209

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>3</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
B 29 F 1/00		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>4</sup>		
Classification System	Classification Symbols	
IPC <sup>1</sup>	B 29 f 1/00	
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Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>5</sup>		
SE, NO, DK, FI classes as above		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>		
Category <sup>*</sup>	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
A	GB 1 273 839	
A	Chemical Abstracts 83:132788	
A	Chemical Abstracts 83:116107	
A	Chemical Abstracts 84:60665	
<p><sup>*</sup> Special categories of cited documents: <sup>15</sup></p> <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the International filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> </div> <div style="width: 45%;"> <p>"P" document published prior to the International filing date but on or after the priority date claimed</p> <p>"T" later document published on or 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</p> <p>"X" document of particular relevance</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search <sup>3</sup>	Date of Mailing of this International Search Report <sup>3</sup>	
1980-01-22	1980-02-04	
International Searching Authority <sup>1</sup>	Signature of Authorized Officer <sup>20</sup>	
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