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(71) Applicant: **GULF RESEARCH & DEVELOPMENT
COMPANY**
P.O. Box 2038
Pittsburgh Pennsylvania 15230(US)

(72) Inventor: **Giannetti, Joseph P.**
4307 Winchester Drive
Allison Park Pennsylvania 15101(US)

(72) Inventor: **Swift, Harold E.**
1410 Woodhill Drive
Gibsonia Pennsylvania 15044(US)

(74) Representative: **Huskisson, Frank Mackie et al,**
48 St. Vincent Street
Glasgow, G2 5TT(GB)

(54) **Novel fuel compositions.**

(57) Novel fuel compositions comprising: (A) a solid and/or semi-solid material formed by a process for upgrading coal which comprises the steps of: (1) subjecting a slurry composed of coal and a solvent containing donatable hydrogen, together with hydrogen, to catalyst-free hydrogenation conditions in a first hydrogenation zone to form an intermediate coal-solvent slurry; (2) deashing said intermediate coal-solvent slurry to form a coal-solvent solution; (3) subjecting said coal-solvent solution to catalytic hydrogenation conditions in a second hydrogenation zone to obtain a product that can be separated at ambient pressure into (a) a first liquid fraction boiling at a temperature in the range of about 100 to 375°C, (b) a second liquid fraction boiling above said first liquid fraction at a temperature in the range of about 200 to about 525°C and (c) said solid and/or semi-solid material; and then (4) recycling at least a portion of said second liquid fraction to said first hydrogenation zone; and (B) a light-boiling hydrocarbon stock boiling at a temperature in the range of about 100 to 375°C at ambient pressure; wherein the weight ratio of said solid and/or semi-solid material to said light-boiling hydrocarbon stock is about 20:1 to about 1.5:1.

NOVEL FUEL COMPOSITIONS

BACKGROUND OF THE INVENTION1. Field of the Invention

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A solvent refined coal product is a solid and/or semi-solid material that cannot be converted readily to a fuel of lower viscosity (ca 220 Saybolt Furol Seconds at 99°C) unless it is blended with a large amount of light-boiling hydrocarbon stock or subjected to hydrogenation. The latter has the

-2-

disadvantage of requiring large amounts of hydrogen. Both these alternatives are costly.

The present invention is directed to novel fuel compositions comprising: (A) a solid and/or semi-solid material formed by a process for upgrading coal which comprises the steps of:

(1) subjecting a slurry composed of coal and a solvent containing donatable hydrogen, together with hydrogen, to catalyst-free hydrogenation conditions in a first hydrogenation zone to form an intermediate coal-solvent slurry; (2) deashing said intermediate coal-solvent slurry to form a coal-solvent solution; (3) subjecting said coal-solvent solution to catalytic hydrogenation conditions in a second hydrogenation zone to obtain a product that can be separated at ambient pressure into (a) a first liquid fraction boiling at a temperature in the range of about 100 to about 375°C, (b) a second liquid fraction boiling above said first liquid fraction at a temperature in the range of about 200 to about 525°C and (c) said solid and/or semi-solid material; and then (4) recycling at least a portion of said second liquid fraction to said first hydrogenation zone; and (B) a light-boiling hydrocarbon stock boiling at a temperature in the range of about 100 to about 375°C at ambient pressure; wherein the weight ratio of said solid and/or semi-solid material to said light-boiling hydrocarbon stock is about 20:1 to about 1.5:1.

2. Description of the Prior Art

Applicant is unaware of any prior art relevant to the invention defined and claimed herein.

SUMMARY OF THE INVENTION

We have discovered novel fuel compositions comprising: (A) a solid and/or semi-solid material formed by a process for upgrading coal which comprises the steps of: (1) subjecting a

-3-

slurry composed of coal and a solvent containing donatable hydrogen, together with hydrogen, to catalyst-free hydrogenation conditions in a first hydrogenation zone to form an intermediate coal-solvent slurry; (2) deashing said intermediate coal-solvent slurry to form a coal-solvent solution; (3) subjecting said coal-solvent solution to catalytic hydrogenation conditions in a second hydrogenation zone to obtain a product that can be separated at ambient pressure into (a) a first liquid fraction boiling at a temperature in the range of about 100 to about 375°C, (b) a second liquid fraction boiling above said first liquid fraction at a temperature in the range of about 200 to about 525°C and (c) said solid and/or semi-solid material; and then (4) recycling at least a portion of said second liquid fraction to said first hydrogenation zone; and (B) a light-boiling hydrocarbon stock boiling at a temperature in the range of about 100 to about 375°C at ambient pressure; wherein the weight ratio of said solid and/or semi-solid material to said light-boiling hydrocarbon stock is about 20:1 to about 1.5:1.

The solid and/or semi-solid component of the novel fuel compositions claimed herein is formed by a process described in our copending application entitled "Improved Solvent Refined Coal Process" (Case A), Serial No. 865,605, filed concurrently herewith. In general, as defined in said application, a slurry composed of coal and a solvent containing donatable hydrogen, together with hydrogen, is subjected to catalyst-free hydrogenation conditions in a first hydrogenation zone under the conditions set forth in Table 1.

Table 1: Catalyst-Free Hydrogenation Conditions

	<u>Broad Range</u>	<u>Preferred Range</u>
Temperature, °C	343 - 510	399 - 482
Pressure, kPa (psig) ¹	3,447 - 34,470 (500 - 5,000)	6,894 - 13,888 (1,000 - 2,000)
5 Solvent/Coal Weight Ratio	0.5/1 - 10/1	1/1 - 4/1
Hydrogen/Coal Feed Weight Ratio	0.01/1 - 0.30/1	0.05/1 - 0.10/1
Hydrogen Gas Purity, mole %	85 - 100	95 - 97
10 Residence Time, hrs	0.1 - 5.0	0.5 - 2.0

¹kilopascals (pounds per square inch gauge)

After subjecting the slurry to catalyst-free hydrogenation conditions, an intermediate coal-solvent slurry is obtained. Ash and/or other insoluble material is separated from the intermediate coal-solvent slurry and a coal-solvent solution is obtained. The coal-solvent solution formed as the result of deashing is subjected to catalytic hydrogenation conditions in a second hydrogenation zone. The catalytic hydrogenation conditions are set forth in Table 2.

Table 2: Catalytic Hydrogenation Conditions

	<u>Broad Range</u>	<u>Preferred Range</u>
Temperature, °C	260 - 538	399 - 454
Pressure, kPa (psig)	3,447 - 68,940 (500 - 10,000)	6,894 - 27,576 (1,000 - 4,000)
25 Liquid Hourly Space Velocity, volume feed/ volume catalyst/hr	0.3 - 10	1.0 - 4
Hydrogen Flow Rate, kmol H ₂ /m ³ feed	25 - 190	60 - 90

Any hydrogenation catalyst suitable for use in coal hydrogenation can be used herein, for example, the catalyst defined and claimed in U. S. Patent No. 3,840,423. The preferred

-5-

catalyst is comprised of a hydrogenation component selected from the group consisting of Group VI and Group VIII metals, their oxides and sulfides, supported on a non-zeolitic carrier, which catalyst is promoted with a Group IV-B metal. Illustrative of particularly preferred catalysts for use in our invention have metal combinations of nickel-titanium-molybdenum, nickel-cobalt-molybdenum, and nickel-tungsten on an alumina carrier.

Catalytic hydrogenation produces a product that can be separated by any conventional method known in the art, especially by distillation at ambient pressure into (a) a first liquid fraction boiling at a temperature in the range of about 100 to about 375°C, preferably about 150 to about 325°C, (b) a second liquid fraction boiling above said first liquid fraction at a temperature in the range of about 200 to about 525°C, preferably about 250 to about 475°C, and (c) a solid and/or semi-solid material. An elemental analysis for a typical solid and/or semi-solid material obtained by the process described in said copending application and which is a necessary component of the novel fuel compositions claimed herein is set forth in Table 3.

Table 3: Analysis of the Solid and/or Semi-Solid Material

	<u>Broad Range, wt %</u>	<u>Preferred Range, wt %</u>
Carbon	87.0 - 93.0	88.0 - 92.0
Hydrogen	5.5 - 9.5	6.5 - 8.0
Nitrogen	0.3 - 3.0	0.8 - 2.0
Oxygen	0.0 - 1.5	0.1 - 1.0
Sulfur	0.0 - 0.5	0.0 - 0.2

The solid and/or semi-solid material is capable of being blended with a light-boiling hydrocarbon stock boiling at a temperature in the range of about 100 to about 375°C, preferably at about 150 to about 325°C, at ambient pressure. A typical elemental analysis for a light-boiling hydrocarbon stock is set forth in Table 4.

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Table 4: Analysis of Light-Boiling
Hydrocarbon Stock

	Broad Range, wt %	Preferred Range, wt %
Carbon	85.0 - 93.0	88.0 - 91.0
Hydrogen	7.0 - 12.0	8.5 - 11.0
Nitrogen	0.0 - 2.0	0.1 - 0.7
Oxygen	0.0 - 2.0	0.1 - 0.7
Sulfur	0.0 - 3.0	0.0 - 0.3

In general, suitable light-boiling hydrocarbon stocks that can be employed in the invention can include, for example, #2 fuel oil, kerosene, jet fuel, diesel fuel, gasoline, light shale oil fractions and light fractions obtained from coal hydrogenation. A particularly preferred light-boiling hydrocarbon stock is described in said copending application and in the present invention herein as "a first liquid fraction boiling at a temperature in the range of about 100 to about 375°C, preferably about 150 to about 375°C". An elemental analysis of said first liquid fraction is set forth in Table 5 herein.

Table 5: Analysis of the First
Liquid Fraction

	Broad Range, wt %	Preferred Range, wt %
Carbon	87.0 - 93.0	88.0 - 91.0
Hydrogen	7.0 - 12.0	8.5 - 11.0
Nitrogen	0.0 - 2.0	0.1 - 0.7
Oxygen	0.0 - 2.0	0.1 - 0.7
Sulfur	0.0 - 0.5	0.0 - 0.3

The solid and/or semi-solid material is mixed or blended with the light-boiling hydrocarbon stock by means well-known in the art. The ingredients are mixed until a homogeneous product is obtained. The weight ratio of said solid and/or semi-solid material to said light-boiling hydrocarbon stock is about 20:1 to about 1.5:1, preferably about 10:1 to about 2:1.

An elemental analysis of said homogeneous product is set forth in Table 6.

Table 6: Product Analysis

	<u>Broad Range, wt %</u>	<u>Preferred Range, wt %</u>
5 Carbon	87.0 - 93.0	88.0 - 91.5
Hydrogen	5.0 - 11.0	6.0 - 9.0
Nitrogen	0.5 - 2.0	0.8 - 1.5
Oxygen	0.1 - 3.0	0.2 - 1.5
Sulfur	0.0 - 0.5	0.0 - 0.2

10 The product obtained as a result of the invention described herein is useful as a fuel for power generation in place of fuel oil derived from coal and petroleum stocks.

DESCRIPTION OF PREFERRED EMBODIMENTS

15 The invention will be further described with reference to the experimental data.

Example 1

An ash-containing coal from the Pittsburgh and Midway Coal Company Colonial Mine was used in the experimental work. The coal had the following analysis:

20 Table 7: Ash-Containing Coal Analysis
(Dry Basis)

	<u>wt %</u>
Carbon	71.8
Hydrogen	5.0
25 Nitrogen	1.3
Oxygen	7.9
Sulfur	3.7
Ash	10.3

30 The coal was dissolved in a solvent substantially as defined in Table 6 in our said copending application, together with hydrogen, under catalyst-free hydrogenation conditions set forth in Table 8 in a first hydrogenation zone to form an intermediate coal-solvent slurry.

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-8-

Table 8: Catalyst-Free Conditions

5	Temperature, °C	450
	Pressure, kPa (psig)	10,755 (1560)
	Solvent/Coal Weight Ratio	2.14/1
	Hydrogen/Coal Feed Weight Ratio	0.08/1
	Residence Time, hrs	1

Ash and/or other insolubles were separated from the coal-solvent slurry by filtration under the conditions set forth in Table 9 to form a coal-solvent solution. An analysis of the coal-solvent solution is set forth in Table 10.

Table 9: Filtration Conditions

15	Filter Temperature, °C	229
	Filter Pressure, kPa (psig)	1206 (175)
	Pressure Drop, kPa (psig)	207 (30)
	Knife Advance, mil/min	1
	Drum Speed, min/revolution	1.0 - 1.5
	Basecoat	Fibra F10-11C and Celite 545
	Precoat	Celite 535

Table 10: Coal-Solvent Solution Analysis

25		wt %
	Carbon	89.3
	Hydrogen	6.3
	Nitrogen	1.2
	Oxygen	2.5
	Sulfur	0.7
	Ash	0.04

The coal-solvent solution was subjected to catalytic hydrogenation by passing the solution over a specific catalyst under specific reaction conditions set forth in Table 11 to form a product.



Table 11: Catalyst Composition and
Reaction Conditions

5	Catalyst ¹	0.5 wt % nickel 1.0 wt % cobalt 8.0 wt % molybdenum
	Temperature, °C	427
10	Pressure, kPa (psig)	20,700 (3,000)
	Liquid Hourly Space Velocity, ml feed/ml catalyst/hr	2.0
	Hydrogen Flow Rate, kmol H ₂ /m ³ feed	75.2

¹The metals were deposited on alumina having a surface area of 185 m²/g, a pore diameter of 188 Å and a pore volume of 0.66 cc/gm.

15 The product was subjected to separation by distillation after catalytic hydrogenation into (a) a first liquid fraction which boiled between about 191 to about 288°C, (b) a second liquid fraction that boiled between about 288 to about 396°C and (c) a solid and/or semi-solid material. An analysis of each of these

20 is set forth in Table 12.

Table 12: Liquid Fractions and Solid
and/or Semi-Solid Analyses

			<u>wt %</u>
25	First Liquid Fraction (191 to 288°C)	Carbon	89.3
		Hydrogen	9.8
		Nitrogen	0.4
		Oxygen	0.4
		Sulfur	0.06
30	Second Liquid Fraction (288 to 403°C)	Carbon	<u>wt %</u> 90.6
		Hydrogen	8.1
		Nitrogen	0.5
		Oxygen	0.4
		Sulfur	0.1
35	Solid and/or Semi-Solid Material	Carbon	<u>wt %</u> 89.3
		Hydrogen	7.0
		Nitrogen	1.3
		Oxygen	0.8
		Sulfur	0.1
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The solid and/or semi-solid material defined in Table 12 was blended with a light-boiling hydrocarbon stock which has been defined as the first liquid fraction in Table 12. The blends had the characteristics set forth in Table 13.

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Table 13: Blends of Solid and/or Semi-Solid Material and First Liquid Fraction

	<u>Blend No. 1</u>	<u>Blend No. 2</u>
Solid and/or Semi-Solid Material: wt % (A)	82	75
10 First Liquid: wt % Fraction (B)	18	25
Ratio A/B	4.6	3.0
Viscosity: Saybolt Furol Seconds at 99°C	180	58
	<u>wt %</u>	<u>wt %</u>
15 Carbon	89.3	89.3
Hydrogen	7.5	8.2
Nitrogen	1.1	1.1
Oxygen	0.7	0.7
Sulfur	0.1	0.1

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Example 2

This example is identical to Example 1 except that the catalytic hydrogenation conditions were as follows:

	Temperature, °C	427
	Pressure, kPa (psig)	10,300 (1,500)
25	Liquid Hourly Space Velocity, ml feed/ml catalyst/hr	2
	Hydrogen Flow Rate, kmol H ₂ /m ³ feed	75.2

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and the weight ratio of solid and/or semi-solid material (boiling above 454°C) to the light-boiling hydrocarbon stock was 2.7:1. The final product obtained had the characteristics set forth in Table 14.



-11-

Table 14: Blend of Solid and/or Semi-Solid
Material and First Liquid Fraction

		Blend No. 3
5	Solid and/or Semi-Solid Material, wt % (A)	73
	First Liquid Fraction, wt % (B)	27
	Viscosity: Saybolt Furol Seconds at 99°C	75
		wt %
	Carbon	90.8
	Hydrogen	7.1
10	Oxygen	1.3
	Nitrogen	1.3
	Sulfur	0.1

Example 3

This example is identical to Example 1 except that the
15 catalytic hydrogenation conditions were as follows:

20	Temperature, °C	427
	Pressure, kPa (psig)	20,700 (3,000)
	Liquid Hourly Space Velocity, ml feed/ml catalyst/hr	1
	Hydrogen Flow Rate, kmol H ₂ /m ³ feed	75.2

The solid and/or semi-solid material (boiling above 389°C) was
blended with the first liquid fraction. The blends had the charac-
teristics set forth in Table 15.

25 Table 15: Blend of Solid and/or Semi-Solid
Material and First Liquid Fraction

		Blend No. 4	Blend No. 5	Blend No. 6
30	Solid and/or Semi-Solid Material, wt % (A)	89	87	82
	First Liquid Fraction, wt% (B)	11	13	18
	Ratio A/B	8.1	6.7	4.6
35	Viscosity, Saybolt Furol Seconds at 99°C	180	70	30
		wt %	wt %	wt %
	Carbon	89.6	89.6	89.6
	Hydrogen	7.6	7.6	7.8
	Nitrogen	1.2	1.2	1.1
	Oxygen	0.4	0.4	0.4
40	Sulfur	<0.04	<0.04	<0.04



-12-

Obviously, many modifications and variations of the invention, as hereinabove set forth, can be made without departing from the spirit and scope thereof, and, therefore, only such limitations should be imposed as are indicated in the appended claims.

Claims

1. Novel fuel compositions comprising:

(A) a solid and/or semi-solid material formed by a process for upgrading coal which comprises the steps of:

- 5 (1) subjecting a slurry composed of coal and a solvent containing donatable hydrogen, together with hydrogen, to catalyst-free hydrogenation conditions in a first hydrogenation zone to form an intermediate
- 10 coal-solvent slurry;
- (2) deashing said intermediate coal-solvent slurry to form a coal-solvent solution;
- (3) subjecting said coal-solvent solution to catalytic hydrogenation conditions in a
- 15 second hydrogenation zone to obtain a product that can be separated at ambient pressure into (a) a first liquid fraction boiling at a temperature in the range of about 100 to about 375°C, (b) a second
- 20 liquid fraction boiling above said first liquid fraction at a temperature in the range of about 200 to about 525°C and (c) said solid and/or semi-solid material; and then
- 25 (4) recycling at least a portion of said second liquid fraction to said first hydrogenation zone; and
- (B) a light-boiling hydrocarbon stock boiling at a temperature in the range of about 100 to about

- 14 -

375°C at ambient pressure.

2. Novel fuel composition according to claim 1 wherein a weight ratio of said solid and/or semi-solid material to said light-boiling hydrocarbon stock is about 20:1 to about 1.5:1.

3. Novel fuel compositions according to claim 1 wherein a weight ratio of said solid and/or semi-solid material to said light-boiling hydrocarbon stock is about 10:1 to about 2:1.

4. Novel fuel compositions according to claim 1 wherein said first liquid fraction boils at a temperature in the range of about 150 to about 325°C; and said second fraction boiling above said first liquid fraction boils at a temperature in the range of about 250 to about 475°C.

5. Novel fuel compositions according to claim 1 wherein said first hydrogenation zone has a temperature ranging from about 343 to about 510°C; a pressure ranging from about 500 to about 5,000 psig; a solvent/coal weight ratio ranging from about 0.5/1 to about 10/1; a hydrogen/coal feed weight ratio ranging from about 0.01/1 to about 0.30/1; a hydrogen gas purity ranging from about 85 to about 100 mole percent; and a residence time of about 0.1 to about 5.0 hours.

6. Novel fuel compositions according to claim 1 wherein said first hydrogenation zone has a temperature ranging from about 399 to about 482°C; a pressure ranging from about 1,000 to about 2,000 psig; a solvent/coal weight ratio ranging from about 1/1 to about 4/1; a hydrogen/coal feed weight ratio ranging from about 0.05/1 to about 0.01/1; a hydrogen gas purity ranging from about 95 to about 97 mole percent; and a residence time of about 0.5 to about 2.0 hours.

7. Novel fuel compositions according to claim 1 wherein said deashing is by filtration.

- 15 -

8. Novel fuel compositions according to claim 1 wherein said second hydrogenation zone has a temperature ranging from about 260 to about 538°C; a pressure ranging from about 500 to about 10,000 psig; a liquid hourly space velocity of about 0.3 to about 10 volume feed/volume catalyst/hr; and a hydrogen flow rate of about 25 to about 190 kmol H₂/m³ feed.

9. Novel fuel compositions according to claim 1 wherein said second hydrogenation zone has a temperature ranging from about 399 to about 454°C; a pressure ranging from about 1,000 to about 4,000 psig; a liquid hourly space velocity of about 1.0 to about 4 volume feed/volume catalyst/hr; and a hydrogen flow rate of about 60 to about 90 kmol H₂/m³ feed.

10. Novel fuel compositions according to claim 1 wherein said second hydrogenation zone contains a catalyst comprised of a hydrogenation component selected from the group consisting of Group VI and VIII metals, their oxides and sulfides, and combinations thereof; and wherein said catalyst is supported on a non-zeolite carrier and promoted with a Group IV-B metal.

11. Novel fuel compositions according to claim 1 wherein said second hydrogenation zone contains a catalyst comprised of nickel-titanium-molybdenum metals, oxides and/or sulfides dispersed on alumina.

12. Novel fuel compositions according to claim 1 wherein said second hydrogenation zone contains a catalyst comprised of nickel-cobalt-molybdenum metals, oxides and/or sulfides dispersed on alumina.

13. Novel fuel compositions according to claim 1 wherein said second hydrogenation zone contains a catalyst comprised of nickel-tungsten metals, oxides and/or sulfides dispersed on alumina.



-16-

14. Novel fuel compositions according to claim 1 wherein said liquid product is separated by distillation.

15. Novel fuel compositions according to claim 1 wherein a portion of ash obtained from said intermediate coal solvent slurry in step 2 is recycled to said first hydrogenation zone.

16. Novel fuel compositions according to claim 1 wherein said light-boiling hydrocarbon stock boils at a temperature in a range of about 150 to about 325°C at ambient pressure.

17. Novel fuel compositions according to claim 1 wherein said light-boiling hydrocarbon stock is selected from the group consisting of #2 fuel oil, kerosene, jet fuel, diesel fuel, heavy gasoline, light shale oil fractions and light fractions obtained from coal hydrogenation.

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18. Novel fuel compositions according to claim 1 wherein said light-boiling hydrocarbon stock is a first liquid fraction boiling at a temperature ranging from about 100 to about 375°C.

19. Novel fuel compositions according to claim 1 wherein said light-boiling hydrocarbon stock is a first liquid fraction boiling at a temperature ranging from about 150 to about 375°C.



DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	NAVY TECHNICAL DISCLOSURE BULLETIN, 1 vol. 3, no. 4, April 1978, pages 41-44 Arlington, Virginia, U.S.A. G.H. FIELDING: "Coal/Liquid Hydro- carbon Hybrid Fuel" * Entire article * --		C 10 L 1/32 C 10 G 1/00 C 10 L 9/00
A	<u>GB - A - 1 251 336</u> (CONSOLIDATION COAL CO.)		
A	<u>DE - A - 2 728 569</u> (GULF)		TECHNICAL FIELDS SEARCHED (Int.Cl. ³)
A	<u>US - A - 3 997 425</u> (GATSIIS et al.)		C 10 L 1/32 C 10 G 1/00 1/04 1/08 C 10 L 9/00

			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
☒ The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
The Hague	22-04-1980	DE HERDT	