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(54) **Recovery of heavy oil.**

(57) A two stage method for the recovery of heavy crude oil or bitumen associated with a solid inorganic substance and water from an underground deposit comprises chemically conditioning the deposit in situ with an aqueous solution of an alkaline compound and subsequently treating the conditioned deposit to recover the heavy crude oil or bitumen from it.

The method is particularly suitable for recovering bitumen from tar sand.

In situ conditioning increases the yield of product.

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RECOVERY OF HEAVY OIL

This invention relates to a method for the recovery of heavy oil, especially bitumen from tar sands.

As reserves of conventional crude oils (approximately 15° to 30° API) decline, increasing importance will be attached to efficient methods for recovering heavy crude oils (8°-12° API) and the even heavier bitumens (less than 8° API). Most bitumens are associated with minerals such as clays and quartz, and are known as tar sands.

The Alberta tar sands are among the largest deposits of their kind in the world and are estimated to contain about one trillion barrels of bitumen in place. The Athabasca region alone has reserves of 250 billion barrels. About 0.7 million acres of the Athabasca deposit is overlain by 150 ft, or less, of overburden and is potentially capable of being mined from the surface. The remaining 16.6 million acres are at such depths that the bitumen can only be recovered by in-situ methods.

The crude bitumen occurs in beds of sand and clay, usually partly connected together, and in porous carbonate rocks.

In high grade tar sand the pore space is filled with bitumen (typically 15-20% weight) and water.

In low grade tar sands, i.e. containing less than 10% by weight bitumen, clusters of small particles exist within the framework formed by the coarse inorganic grains. These particles, known as fines, are saturated with water. Thus the amount of connate water in the tar sand increases with increasing fines.

The bitumen typically has an API gravity of 7° and is denser than water at room temperature but becomes less dense than water at elevated temperatures.

In the case of deposits near the surface the overburden may be removed and the tar sand recovered by open cast mining.

Mined tar sands are refined by the aforementioned hot water process. A description of this process is given in USP 4 474 616.

In broad summary, this process comprises first conditioning the tar sand, to make it amenable to flotation separation of the bitumen from the solids. Conditioning involves feeding mined tar sands hot water (80°C), an alkaline process aid (usually NaOH), and steam into a rotating horizontal drum wherein the ingredients are agitated together under relatively high shear conditions.

During conditioning, the mined tar sand (in which the bitumen, connate water and solids are tightly bound together) becomes an aqueous slurry of porridge-like consistency, wherein the components are in loose association.

The slurry leaving the drum is screened to remove oversize material and then flooded or diluted with additional hot water.

The bitumen is recovered by primary and secondary froth flotation.

This process suffers from the disadvantages that bitumen/water emulsions are formed and the separated water contains colloidal dispersions of clay, fines and oil which are extremely stable and present serious problems in their disposal.

For deposits at a greater depth, the technique of jet leaching can be employed. Jet leaching is a known technique for the extraction of tar sands which comprises drilling and fixing casing until the pay zone is reached. The ore is then fragmented by directing high velocity jets of water onto it and the bitumen is pumped to the surface, leaving most of the solid particles downhole.

In a conventional single stage jet leaching process alkaline water (pH > 11) at high temperatures (> 80°C) is used to mobilise the bitumen. The water is generally deaerated and stripped of divalent metal ions.

Alternative approaches for deep deposits are the use of cyclic steam stimulation or steam drive to recover the bitumen.

Cyclic steam stimulation is otherwise known as "huff and puff". In this process, steam is injected and the bitumen produced through the same well. The steam is injected down the well for several weeks. On the termination of steam injection, bitumen flows freely up the well for about one week, after which it has to be pumped to the surface. Pumping can usually be continued for several months before more steam must be injected.

In steam drive, the steam acts to heat the deposit and drive the bitumen from an injection well to a production well.

In all these methods, oil recovery is assisted when the sand is water wet and hindered when it is oil wet.

In the case of tar sands, most of the sand is water wet.

It is an object of the present invention to condition chemically the material in situ by injecting an aqueous solution of an alkaline compound into the reservoir.

Thus according to the present invention there is provided a two stage method for the recovery of

heavy crude oil or bitumen associated with a solid inorganic substance and water from an underground deposit, which method comprises chemically conditioning the deposit in situ with an aqueous solution of an alkaline compound and subsequently treating the conditioned deposit to recover heavy crude oil or bitumen from it.

5 In the first stage the preferred alkaline compound is sodium hydroxide.

This is preferably added to render the pH of the conditioning solution in the range 11 to 12.5.

The alkaline solution is left in a quiescent state so that physico-chemical action (rather than mechanical) detaches the bitumen from the inorganic solid making it more amenable to recovery.

10 In the second stage, a number of options are open to recover the bitumen. These include steam drive, cyclic steam simulation, a modified cyclic steam simulation in which steam and alkali are injected together, cold or hot water drive and jet leaching, preferably the latter, where tar sand is concerned.

It is believed, although applicants do not wish to be bound by this theory, that the presence of the alkali causes the water films surrounding the inorganic grains to swell and thereby promote the separation of bitumen from the tar sand matrix.

15 In all cases, in situ conditioning will increase yields and, in the case of cyclic steam stimulation, will extend the periods between injection of steam.

The invention is illustrated with reference to the following Examples.

20 A medium grade (11.6 wt % bitumen) Athabaskan tar sand sample was used. The tar sand had poor processing characteristics and as such was considered to be suitable for investigating experimental procedures aimed at improving processability.

Example 1

25 Static Tests

A series of experiments were conducted in which samples of tar sand (10 g) were conditioned in a sample jar by contacting with sodium hydroxide solution (10 ml over pH range 9 - 13), initially at a known temperature (20 - 80°C), and allowed to cool naturally for a known time period (0.25 - 24 h).

30 After this conditioning stage, a quantity of deionised water (35 ml) was added to the jar and bitumen removal effected by heat treatment in a water bath (0.5 h at 80°C) followed by inversion of the jar to promote bitumen separation and flotation.

35 Example 2

Dynamic Jet Leaching Tests

40 A series of experiments were carried out in parallel with the static jar tests using a laboratory scale jet leaching test system as described in GB 2176224A.

Samples of tar sand (125 g) were conditioned by contacting with sodium hydroxide solution (50 ml over pH range 9 - 13), initially at a known temperature (20 - 80°C), and allowed to cool naturally over a known time period (0.25 - 24 h).

45 After conditioning, deionised water (1350 ml) was added to the closed jet leaching loop and bitumen recovered by jetting with leachant at known temperature (30 - 80°C), for a constant time period (0.67 h) and jet velocity (ca 3 m s⁻¹).

For both static and jet leaching tests, the extent of bitumen recovery was determined gravimetrically by solvent (toluene) extraction of the cleaned sand following bitumen extraction.

50 Figure 1 illustrates the bitumen recovery from the tar sand for both the static and jet leaching tests, as a function of the initial pH of the sodium hydroxide conditioning agent. For the two different experimental procedures, there is a critical pH (ca 11) below which the conditioning process is less effective. Increasing this pH resulted in tar sand conditioning, characterised by rapid disintegration of the tar sand matrix, the formation of a stable clay dispersion in the supernatant conditioning fluid, and the adoption of a sandy rather than oily tar sand appearance. At higher pH (> ca 12.5) the characteristic physical transformation of the tar sand matrix was not observed. Here the bitumen recovery can be ascribed primarily to emulsification type extraction mechanism, as was evident by the appearance of the leachant following a typical jet leaching experiment. For all conditioned samples subsequent bitumen recoveries in a second stage extraction step were much higher than those observed in a single stage extraction without prior tar sand

conditioning where typically < 5% bitumen was recovered. The apparent limit in bitumen recovery (ca 85%) is thought to arise from the relatively moderate shear conditions (low jet velocity, short jetting times) imposed on the tar sand during a typical experiment.

The concept of a two stage chemical conditioning/extraction type process also resulted in further benefits such as improved quality of both recovered bitumen and leachant, compared to bitumen recovered by a single stage alkali extraction process, as summarised in Table 1.

Effect of Contact Time/Temperature

These aspects are illustrated in Figure 2 in which bitumen recovery is seen to increase with increasing contact time and conditioning temperature, approaching a plateau in recovery at around 24 h contact time. At low contact times, the effect of varying the temperature of the conditioning agent is more important, whereas for longer times (> 24 h), the bitumen recovery is independent of the initial conditioning temperature. For example, tar sand conditioned at 20°C for 24 hours results in an equivalent bitumen recovery to that conditioned initially at 80°C for 24 hours. This suggests that the predominant mechanism in the conditioning process and, in particular, the migration of bitumen within the tar sand matrix is chemically rather than temperature controlled.

Effect of Leachant Temperature Following Conditioning

Figure 3 shows the effect of varying the temperature of the leachant in the extraction step following the conditioning process. After tar sand conditioning at 20°C (24 h), a leachant temperature of only 45°C results in high (ca 80%) bitumen recovery. Higher leachant temperature only marginally improves the extent of recovery, although the kinetics or rate of bitumen recovery is observed to increase significantly.

Such a profile is in sharp contrast to the strong temperature dependence exhibited for an unconditioned single stage bitumen extraction process in which a higher total concentration of sodium hydroxide than for the two stage process of conditioning and recovery (5.6×10^{-3} moles NaOH cf to 7.9×10^{-4} moles) was present in the leachant.

The data in Table 1 reveal that the total alkali consumption in both the two stage process (conditioning + recovery) and the single stage alkali extraction procedure are similar, although the mode of operation of the sodium hydroxide differs greatly.

In the two stage process the alkali serves to reject un-wanted clay particles from the tar sand matrix and causes migration of bitumen droplets away from sand grains in readiness for detachment. Reduction of pH in the second stage extraction step (to ca pH 9) promotes clay settling and discourages bitumen emulsification. By comparison, in the single stage alkali process, a similar chemical driving force is not present to the same extent, such that bitumen removal is more dependent on a viscosity reduction mechanism with the requirement of high leachant temperatures. Furthermore, the relatively high final alkalinity of the leachant (ca pH 11.2) promotes stabilisation of the clay dispersion and emulsification of the bitumen.

Thus a two stage process (chemical conditioning followed by jet leaching) not only improves the degree of bitumen recovery but also produces a higher quality bitumen with lower solids and water content. A further advantage is gained in that stable fines suspensions are not produced thereby reducing the need for effluent treatment and water processing prior to recycling.

TABLE 1
Comparison of Bitumen and Leachant Quality from Conditioned
and Un-conditioned Tar Sand

	CONDITIONED		UNCONDITIONED
	pH 12.2, 80°C, 4.5 h (jet 80°C, 0.67 h)	pH 12.2, 80°C, 19.5h (jet 80°C, 0.67 h)	jet with leachant at pH 11.6, 80°C, 0.67 h
Bitumen Recovery (%)	78.7	79.7	67.1
Solids Content of 1 Bitumen (wt %)	7.4	4.3	44.5
Water Content of 2 Bitumen (wt %)	0	0	0.4
Leachant Quality	Good	Good	Poor
NaOH uptake (moles/g tar sand)	1.5-2.5 x 10 ⁻⁵		2.7 x 10 ⁻⁵

Note 1. Determined gravimetrically after solvent extraction
2. Determined by Karl Fischer analysis

Claims

1. A two stage method for the recovery of heavy crude oil or bitumen associated with a solid inorganic substance and water from an underground deposit by treatment with an alkaline compound characterised
5 by the fact that the method comprises chemically conditioning the deposit in situ with an aqueous solution of the alkaline compound and subsequently treating the conditioned deposit to recover heavy crude oil or bitumen from it.
2. A method according to claim 1 wherein the deposit is a tar sand deposit.
3. A method according to either of the preceding claims wherein the alkaline compound is sodium
10 hydroxide.
4. A method according to any of the preceding claims wherein the alkaline compound is added in amount sufficient to render the pH of the conditioning solution in the range 11 to 12.5.
5. A method according to any of the preceding claims wherein the conditioned deposit is treated by steam drive, cyclic steam simulation, modified cyclic steam stimulation, or cold or hot water drive.
- 15 6. A method according to any of claims 1-4 wherein the conditioned deposit is treated by jet leaching.

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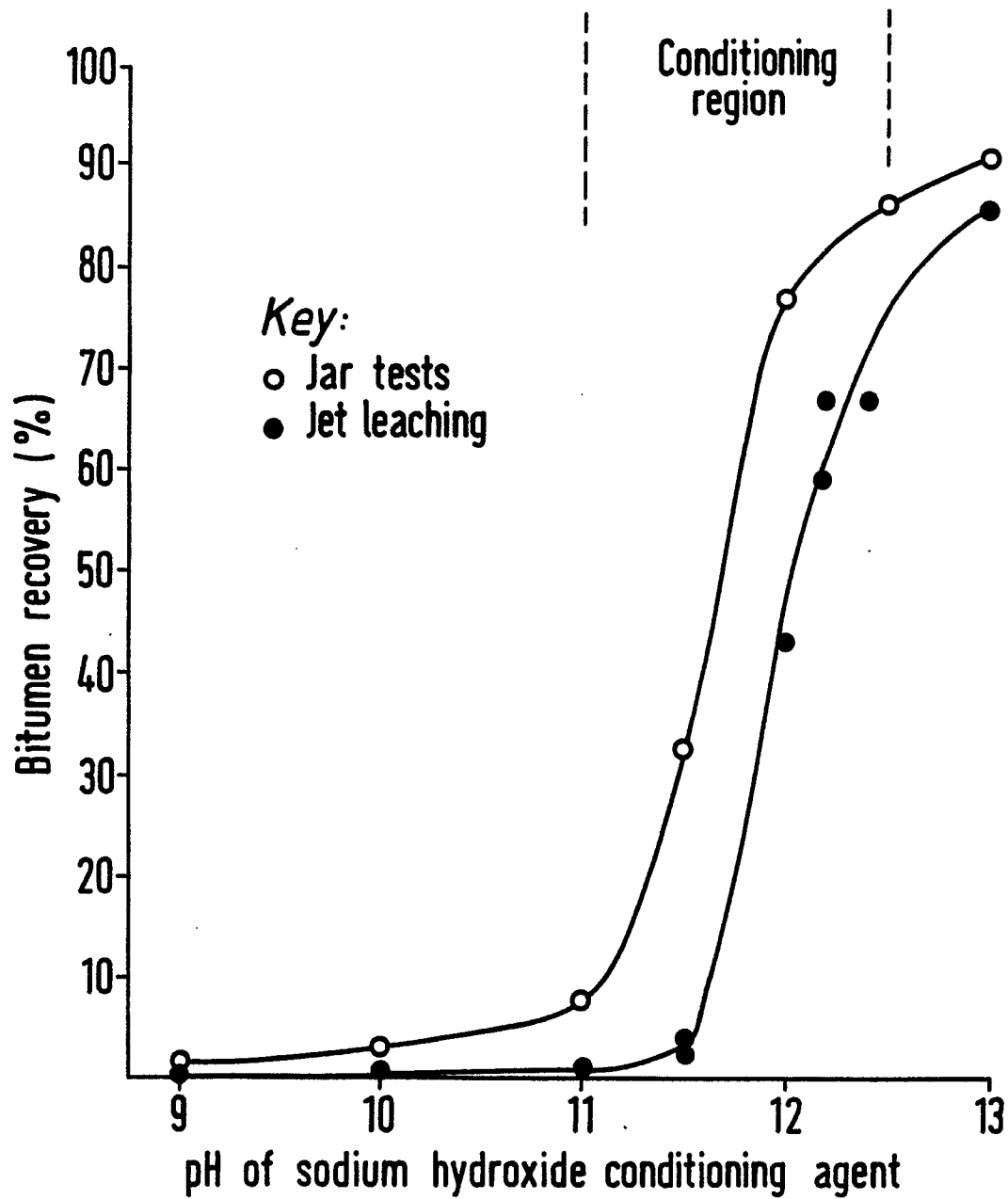
FIG.1

FIG. 2

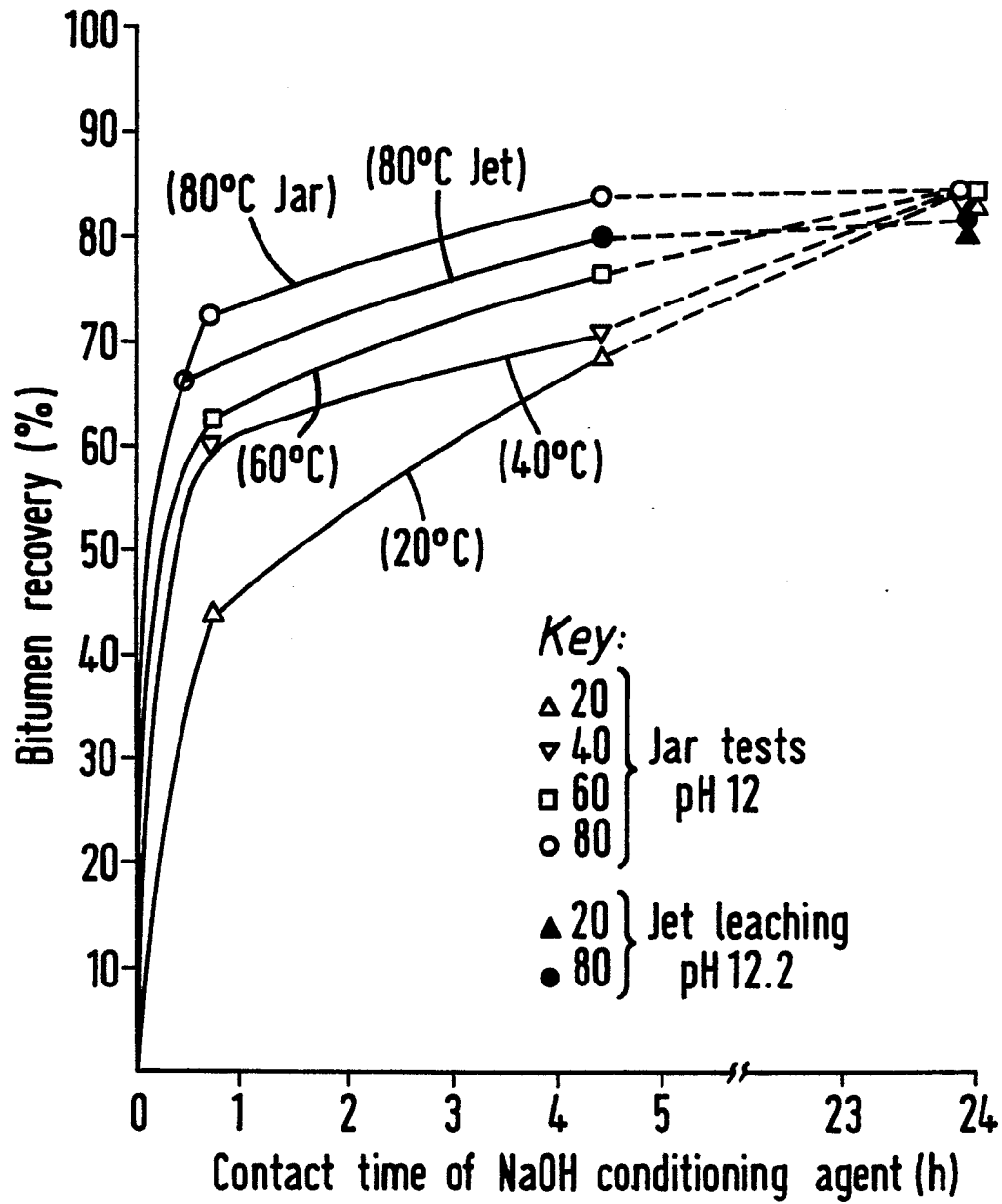
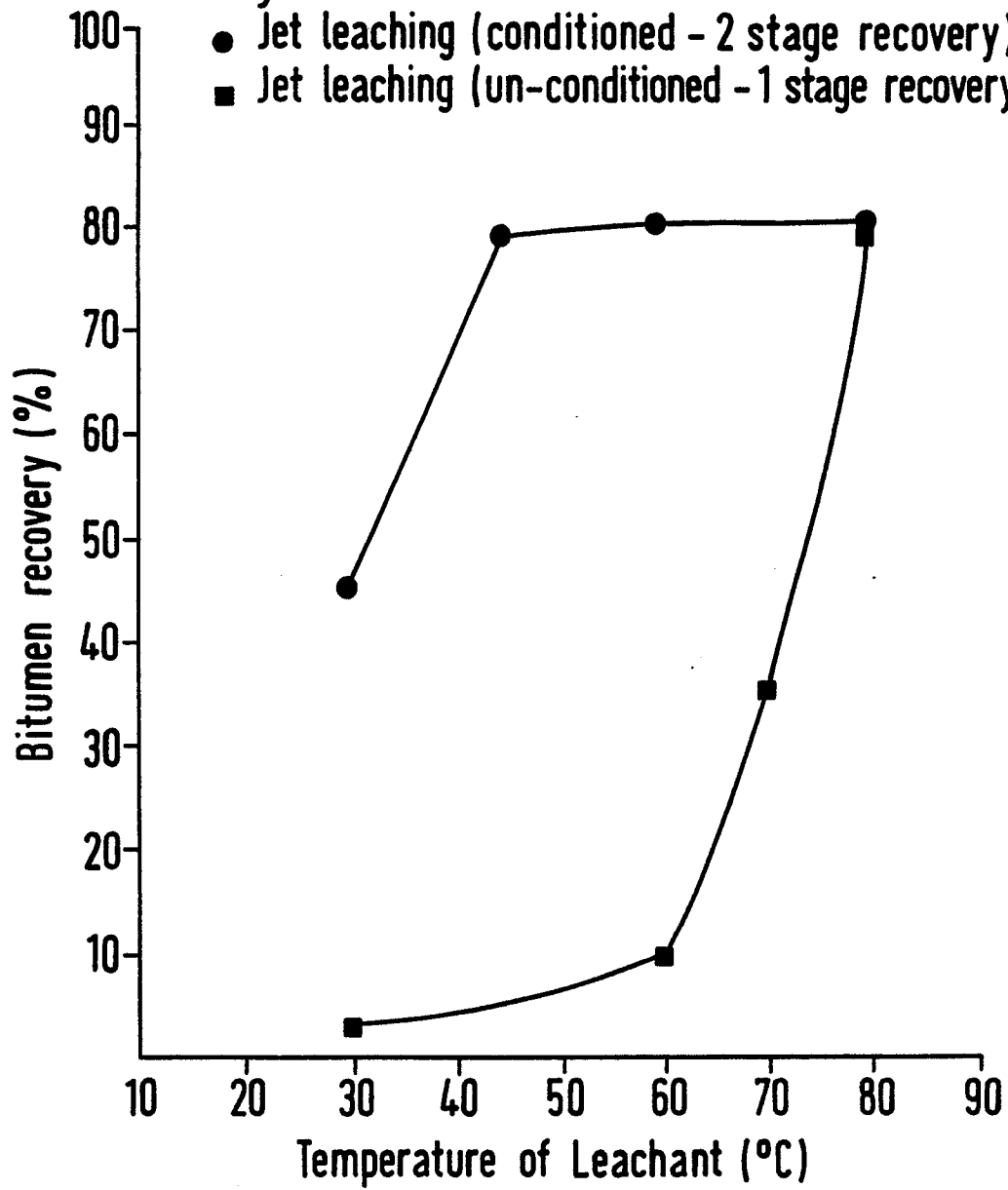


FIG.3**Key:**

- Jet leaching (conditioned - 2 stage recovery)
- Jet leaching (un-conditioned - 1 stage recovery)





DOCUMENTS CONSIDERED TO BE RELEVANT			EP 87308937.0
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	<u>US - A - 4 409 091 (KESSICK)</u> * Claims * --	1,3,4	C 10 G 1/04 C 10 C 3/08
A	<u>US - A - 4 549 935 (TCHERNYAK)</u> * Claims; column 1 * ----	1-5	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 10 G 1/00 C 10 C
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 12-02-1988	Examiner PAMMINGER
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	