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(57) Abstract

There is disclosed a system for separating oil and other immiscible contaminants from a liquid body containing the contaminants such as a water body. The system includes the use of a plurality of microporous hollow fibers which may be arranged in any number of arrangements such as bundles, intersecting arrangements, divergent patterns or in a mat–like arrangement or a combination of the foregoing. The hollow fibers are in communication with a source of pressure in order to force the contaminant via the pores into the fibers for subsequent storage in a suitable container. By incorporating acceptable means of density control, a substantial amount of the hollow fiber surface area may be exposed to the contaminant, thus increasing the extraction efficiency of the contaminant from the water body. The unit optionally may be self–contained. This system provides a substantial advantage over existing arrangements in that extraction efficiency is greatly enhanced in any number of environments. The system and methods are also useful in recovering crude oils, metals or other dissolved components, etc., from the aqueous phase.

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ORGANIC CONTAMINANT RECOVERY ARRANGEMENT AND METHOD OF USING SAME

FIELD OF THE INVENTION

The present invention relates to a contaminant recovery system and method. More particularly, the present invention relates to a self-contained oil contaminant recovery arrangement and method of using same.

BACKGROUND OF THE INVENTION

With the occurrence of oil tankers running aground and spilling their contents into waterways, and with inland fuel spills contaminating acquifers and soils, there has been a significant amount of activity in the oil spill clean-up art. Various methods are known to contain oil once it is spilled in order to prevent damage to aquatic life and of the environment. Chemical additives, porous materials, as well as various sheets and barriers have been proposed. U.S. No. 5,120,598, Robeson et al. teaches a mat product composed of polyvinyl alcohol ultra-fine fibers, which is brought into contact with an oil spill, so that the fibers absorb oil. The Robeson et al. arrangement requires removal from an oil slick once the fiber mate is saturated. In addition, presumably the oil must be removed from the mat before the same can be reused.

Nohmi et al.U.S. No. 4,229,297, teaches a method of separating oil from an oil containing liquid. This reference teaches that the mixture may be separated into distinct phases by forcing the mixture into contact with the inside surface (lumen) of the microporous hydrophobic hollow fibers. (In this regard, the flow is referred to as "down-bore"). This refers to the fact that the two phase mixture is forced down the lumen of the fiber as opposed to being passed into contact with the outside surfaces of the fiber, i.e. shell side feed. United States No. 5,073,261, and Conradi et al. provides a collapsible container having an inlet and an outlet and composed of a water impervious rubber material. The collapsible container is connected to an inlet for charging an oil-water mixture into the container. The container is configured with

baffles, etc., to contain the oil therein, and the container is towed to another location for oil removal.

Coté et al., in U.S. No. 5,248,424, provides a further variation on hollow fiber separation technology, and discloses the use of hollow fibers for separating various compounds. The fibers are essentially unsupported and are disposed in arcuate relationship with one another. This arrangement would not be effective in, e.g. an oil spill on a large body of water. Coté et al. make no provision for fiber dimensional changes which occur when the fibers are in contact with, e.g. oil. In this situation, the arrangement would simply "bundle" or "clump", inherently leading to efficiency limitations.

It is thus clear that the Coté et al. arrangement is not adequate for separation of an organic liquid disposed within an aqueous medium. The Coté et al. arrangement is basically designed for solid particulate removal from an aqueous mixture as opposed to liquid-liquid separation.

Taylor, U.S. No. 4,886,603, teaches a separation method where diesel oil contaminated with water can be apparently dewatered by pumping the mixture through the lumen of microporous polyvinylidene fluoride (PVDF) hollow fiber modules capable of separating the oil as the permeate. The arrangement employed is a two-stage hydrophobic microporous hollow fiber module which relies on forcing a two-phase mixture down the lumen of the hollow fibers in order to apparently achieve separation of the oil from the water. The Taylor reference requires the passage of a retentate into a second chamber equipped with a hydrophillic membrane in order to finalize the treatment and remove free phase water.

Ford, U.S. No. 4,846,976 teaches that oil removal from an oil-water mixture is best conducted if the mixture is forced through the lumens. Ford like Taylor has inherent problems with permeate quality in terms of efficiency of phase separation without contamination.

None of the above citations indicate any physicochemical change in recovered oil properties, other than dehydration.

Funk et al. U.S. 4,617,216, provides a membrane separation of hydrocarbons. In the disclosure, there is taught several different methods for preparation of a membrane for use on various hydrocarbons. The disclosure does not indicate the use of hollow fibers having micropores and further, does not specify the advantages of specific directional feed for treating the hydrocarbons.

Breslau, U.S. No. 4,435,289, discloses a series of ultrafiltration process and apparatus with pressurized permeate. This reference is concerned with separating solutes, suspended matter or colloidal particles from a solution or suspension by ultrafiltration. The Breslau reference does not teach liquid-liquid separation. This is due to the fact that the system will not function in an efficient manner as a liquid separation apparatus. In this manner, the Breslau reference broadly relates to the Nohmi et al. disclosure and would appear to be known to suffer from the same problems that the Nohmi et al. disclosure teaches.

There clearly exists a need in the art for a more advanced system which is capable of removing and recovering the organic material from an aqueous system which is efficient, reliable and results in substantially complete separation of the organic phase from the liquid phase without contamination of one phase within the other. The present invention provides a solution to this problem and satisfies the desirable result of producing discrete and substantially pure phases.

SUMMARY OF THE INVENTION

One object of one embodiment of the present invention is to provide an improved method for oil recovery from an aqueous medium.

A further object of one embodiment of the present invention is to provide a method of separating an immiscible organic compound from an aqueous mixture containing the compound and an aqueous phase, comprising the steps of:

providing a plurality of hollow hydrophobic fibers having micropores therein and opposed ends inaccessible to the mixture, the micropores extending from the outside of each fiber to the hollow interior thereof;

pressurably forcing the mixture through the micropores under sufficient pressure to only permit passage of the immiscible organic compound through the micropores and into the hollow interior, but insufficient for collapse of the fibers and passage of the aqueous phase;

collecting the immiscible organic compound; and

discharging the aqueous phase substantially devoid of the immiscible organic compound.

The hollow fibers may be arranged in an array, a diverging pattern, a parallel pattern, intersecting pattern, bundled into one or more bundles, incorporated into a mat structure or incorporated into a suitable substrate, e.g. a cloth substrate or a polymeric membrane. Many further arrangements will be readily apparent to those skilled in the art.

Suitable polyolefin fibers which achieve the desirable results of the present invention are those fibers made by Mitsubishi Rayon such as the Sterapore™, EHF and KPF as well as those fibers manufactured by Celanese Corporation. Other microporous hydrophobic hollow fiber membranes may also be employed.

It has been found that some types of fibers, when exposed to oil, "swell" or incur dimensional changes. Use of a stabilizing member for maintaining the fibers in a spaced and connected relation substantially alleviates this drawback and prevents kinking or excess distortion of the fibers, particularly when the same are grouped in a bundle. Suitable materials for this purpose may be polyester thread, Teflon thread or any other material which does not substantially swell in the presence of oil. A distinctive advantage with this provision can be realized in that if the bundle of fibers,

mat, etc. is stabilized with respect to dimensional changes, the fibers are maintained in a substantially regular spaced manner therefor allowing the passage of an oil or contaminant containing feed stream to pass therethrough while contacting a maximum number of fibers; this, of course, leads to a more efficient system.

Conveniently, the hydrophobic hollow fibers employed in the present invention do not require any pretreatment in order to achieve the results set forth herein. This is in marked contrast with what has been indicated in the prior art and specifically the Coté et al. reference, supra. In Coté et al. the hydrophobic fibers have to be treated to render them hydrophillic, and accordingly, it is clear that the Coté et al. system has been designed for non-oil based separations.

With respect to fiber selection, these same are preferably microporous with the average pore diameter of the pores typically in a range comprising, for example, 0.03 microns (μm) to about 5 microns (μm). The pore diameter will, of course, vary depending on the intended use for the fibers and therefore may exceed this range.

Suitable conventional material for the hollow fibers can include, for example, polyolefins such as polyethylene, polypropylene, polybutene, polyisobutylene, polypentene, poly(4-methylisopentene) and their halogen-substituted derivatives having at least one fluorine atom: polystyrene and a halogenated polystyrene having at least one fluorine atom: copolymers of ethylenically unsaturated hydrocarbons and/or halogen-substituted ethylenically unsaturated hydrocarbons having at least one fluorine atom, ethylenically unsaturated hydrocarbons and their halogen-substituted derivatives including ethylene, propylene, butene, isobutylene, pentene, hexene, monofluoroethylene, vinylidene fluoride, trifluoroethylene, tetrafluoroethylene, trifluorochloroethylene, hexafluoropropylene and the like; and blend polymers such as a combination of polyethylene with polypropylene, polyvinylidene fluoride, polytetrafluoroethylene or polystyrene; a combination of polypropylene with polyvinylidene fluoride or polytetrafluoroethylene and the like. Preferred examples of materials employable include, as a main component, polyethylene, a halogenated

polyethylene having at least one fluorine atom, polypropylene, a halogenated polypropylene having at least one fluorine atom, or copolymers of two or three kinds of monomers selected from ethylene, propylene and tetrafluoroethylene. It is noted that where a plurality of components having different critical surface tensions are combined, the more the proportion of the component having a lower critical surface tension, the lower the critical surface tension of the entire polymer becomes. Further, membranes which do not themselves yield desired separation characteristics may be modified by, e.g. vacuum deposition to render them capable of the separation. This is indicated in the Nohmi et al. Patent discussed hereinabove.

In terms of apparatus for practising the present invention, an organic storage container and apparatus may be conveniently positioned in any convenient manner with the arrangement of fibers suitably connected to the apparatus. The apparatus may comprise a suitable pump capable of inducing a pressure on the outside of the hollow fibers sufficient in order to force oil therethrough for deposit into the storage container without the collapse of the fiber.

Where it is desirable to have a self-contained unit which is self-propelled, the storage container may incorporate a water discharge outlet which further may include a forcibly exhausted water stream. The forcibly exhausted water stream may be used to propel the floating recovery system through, for example, an oil slick.

The apparatus may additionally include a receiver such that the apparatus is remotely controlled. This may include a radio receiver or other electromagnetic means for detecting a remote signal. The apparatus may also be manually moved by any suitable means, and may include connection fixtures to permit towing. The use of remote controls permits a user access to an oil, chemical or other contaminant spill area even where there are hazardous conditions, e.g. surface fires, toxic fumes, etc. Land-based systems for industrial uses and acquifer fuel spill remediation are also useful.

A further object of one embodiment of the present invention is to provide a method of separating an immiscible organic compound from an aqueous mixture containing the compound and an aqueous phase, comprising the steps of:

providing a plurality of hollow hydrophobic fibers having micropores therein and opposed ends inaccessible to the mixture, the micropores extending from the outside of each fiber to the hollow interior thereof;

creating a pressure differential between the mixture and the hollow fibers such that the mixture is under higher pressure relative to the fibers, the pressure being sufficient to permit passage of the organic compound but insufficient to allow the aqueous phase passage into the micropores and for the hollow fibers to collapse;

contacting the micropores of the fibers with the mixtures;

collecting the immiscible organic compound; and

discharging the aqueous phase substantially devoid of the immiscible organic compound.

The present invention also has the advantage that a host of physicochemical properties can be altered for oil. Examples of the properties that are changed include one or more of liquid viscosity, density, particle size, API rating, pour point temperature, distillation characteristics and combustion efficiency characteristics inter alia. By providing variance in these properties, a more commercially desirable product results and inherently adds value and greater utility to the treated products.

A still further object of one embodiment of the present invention is to provide a method of altering the physicochemical properties of crude oil, the properties including at least one of liquid viscosity, density, particle size, API rating, pour point, distillation characteristics and combustion efficiency characteristics, comprising the steps of:

providing a feed containing crude oil;

providing a polymeric matrix having pores therethrough for selectively passing the crude oil;

forming a pressure differential across the matrix such that the pressure is sufficient to permit passage of the oil through the micropores, but insufficient for collapse of the matrix; and

collecting the oil, the oil having at least one altered physicochemical property.

The present technology also has utility in the fragrance industry. To this end, the method may be employed to dewater essential oils.

It will be appreciated by those skilled in the art that although there is discussion of the use of the arrangement for recovering oil, many immiscible organic substances either mixed with or floating on a water body may be recovered using the inventive concept in the present invention.

The apparatus devised herein has numerous possible uses. In addition to self-contained or flotation arrangements using partially land-based equipment, the present invention may be employed in a towing arrangement where the hollow fibers are towed behind a large floating vessel, e.g. a barge or other floating carrier vessel. This has the distinct advantage of removing a supernatant residue as it is discharged from the vessel. In this manner, the arrangement effectively "self-cleans" the surface of the water.

Other arrangements include the use of the fibers for the purpose of treating a contaminated pond. The arrangement may also be totally submersed in a contaminated water body to assist in cleaning, for example, a contaminated river sediment bed, lake bed, etc.

The fibers, when used in a mat arrangement or bundle arrangement may be positioned in an area to be treated in a stacked arrangement of bundles of the fibers, mat arrangements, or woven or non-woven mat arrangements or employing substrates for the purpose of supporting the fibers, or any combination of the above arrangements.

Another advantage of the invention is in removing an organic material from acquifers, soils, etc. containing the organic materials and water, for example, from contaminated acquifers. Through the above methodology, it is possible to utilize a module containing the hollow fibers to remove the organic from the water, while leaving the water in situ. This obviates the need to treat the water according to government or other standards. By using the above methodology the handling requirements for the water can be completely avoided, resulting in time savings and other numerous advantages. In addition effectively removing the organic material, the methodology also facilitates particulate filtration.

Use of the fibers and arrangements herein can be employed in combination with contaminant booms or in combination with any other contaminant clean-up systems. To this end, the outside surface of the hollow fibers in connection with a source of positive pressure can be positioned between conventional oleophilic mats which act to attract the oil thus enhancing the extraction efficiency of the oil from the water body. This would be effective in certain situations and the hollow fiber array would be useful to draw the oil out of the mat preventing saturation of the mats with oil.

In practicing the above methodology it was discovered that if a hydrophobic matrix having pores therethrough were employed in a pressure differential established from the feedside of the matrix to the outlet side, that a crude oil sample underwent significant changes in some physical and chemical properties.

The positive change in pressure may be generated by containment of the higher pressure by liquid head pressure, syphoning, gravity, or enclosing the arrangement within a shell or tank to provide for the pressure.

A further variation, if one desires to exceed the delta P across the fibers such that there would be water breakthrough, could be carried out and the entire breakthrough material, i.e. organic and water, could be then separated by observing the delta P to exclude water breakthrough in a later s.ep. Thus any combination of existing

technology together with the methods of this invention may be combined to effect a certain result.

Having thus generally described the invention, reference will now be made to the accompanying drawings illustrating preferred embodiments.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1A is a graphical representation of the percentage of oil removed from a sample as a function of module length for a given pressure for down-bore feed operation for 50/50 and 94/6 volume percent water/kerosene mixture, illustrating a decrease in removal efficiency at about 95% to about 50%;

Figure 1B depicts similar information as in Figure 1A, but for shell side operation illustrating 100% (organic) kerosene removal;

Figure 2 depicts kerosene recovery rates as a function of the percent kerosene down-bore feed illustrating an asymptotic curve;

Figure 3 is a top plan view of a mat according to a preferred embodiment;

Figure 4 is a cross-sectional view of the mat in Figure 3;

Figure 5 is an enlarged view of a fiber used in the present invention;

Figure 6 shows a magnified view of fiber in illustrating a first microporous morphology;

Figure 7 shows a magnified view of the fiber illustrating a second microporous morphology;

Figure 8 is a cross-sectional view of a further embodiment;

Figure 9A is a perspective view of a still further embodiment;

Figure 9B is an enlarged view of a portion of the embodiment in Figure 9A;

Figure 9C is a top plan view of a system employing a mat of Figure 9A;

Figure 9D is a side elevational view of the embodiment shown in Figure 9C;

Figure 10 is another embodiment of the present invention;

Figure 11 is an alternate embodiment of the present invention;

Figure 12 is a schematic illustration of a network of modules;

Figure 13 is a representation of particle count as a function of particle size for a crude oil sample conventionally dehydrated;

Figure 14 is a representation of a particle count as a function of particle size for the same sample as in Figure 13 but for a treated sample;

Figure 15 is a viscosity temperature chart illustrating kinematic viscosity as a function of temperature for a further example of a conventionally dehydrated crude oil sample;

Figure 16 is a graphical representation of ASTM distillation data indicating temperature as a function of fraction distilled for various fractions in the oil sample of Figure 15 after conventional dehydration;

Figure 17 is a representation of a particle count for the oil sample of Figures 15 and 16 as a function of particle size after conventional dehydration;

Figure 18 is a viscosity temperature chart illustrating kinematic viscosity as a function of temperature for the oil sample set forth with respect to Figures 15 through 17 subsequent to treatment according to the present invention;

Figure 19 is a graphical representation of ASTM distillation data indicating temperature as a function of fraction distilled or fractions in the oil sample of Figures 15 through 18 subsequent to treatment with the present invention;

Figure 20 is a representation of a particle count for the oil sample of Figures 15 through 19 as a function of particle size subsequent to treatment according to the present invention;

Figure 21 is a viscosity temperature chart illustrating kinematic viscosity as a function of temperature for yet another oil sample after conventional dehydration;

Figure 22 is a graphical representation of ASTM distillation data indicating temperature as a function of fraction distilled for various fractions of the sample of Figure 21 after conventional dehydration;

Figure 23 is a representation of a particle count for the oil sample of Figures 21 and 22 as a function of particle size after conventional dehydration;

Figure 24 is a viscosity temperature chart illustrating kinematic viscosity as a function of temperature for the same oil sample of Figures 21 through 23 subsequent to treatment in accordance with the present invention;

Figure 25 a graphical representation of ASTM distillation data indicating temperature as a function of fraction distilled for various fractions of the oil sample of Figures 21 through 24 subsequent to treatment with the present invention;

Figure 26 is a representation of a particle count for the oil sample of Figures 21 through 25 as a function of particle size subsequent to treatment according to the present invention;

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

It has been found that maximum oil-water separation rates may be predicted using Poiseuille's formula. This formula is an expression for the volume of liquid per second (V) which flows through a capillary tube of length L having a radius R, under a pressure P, the viscosity of the liquid being η. P and V are directly proportional, i.e. P = KV where K is fixed for a tube given constant length, radius and liquid viscosity. This puts an absolute upper limit on flow rate per fibre or module before H_20 breakthrough pressure (ΔP_{max}) is reached. By supplying the feedstream to be separated to the outside of the fibers, the pressure drop across the module is much lower, thus, the phases can be readily isolated at much higher water and oil total feedstream rates, which is a distinct advantage over the prior art.

The Figure 1A and 2 graphs show the inherent limitations of prior art as discussed in Example 10. As illustrated, the amount of organic, e.g. kerosene, present in the sample cannot be entirely removed from a sample comprising a mixture of organic in an aqueous medium. This is indicated by the asymptote which is slightly above zero and indicates that regardless of the pressure or length of the fiber or module, 100% pure phase oil removal in one step from the aqueous phase is impractical using the prior art.

In contrast, Figure 1B shows the percentage of oil removed from a sample as a function of module length for the same feed rate as in Figure 1A. It is clear that 100% oil removal, with the present invention is achievable by introduction of a sample on the shell side of the fibers. With the present invention, this significant advance in organic recovery is achievable.

The success of the invention is believed to be the result of a combination of factors, including the use of fluid dynamics as applied to multi-phase flow; the efficiency of the polyolefin microporous hollow fibers; the effect of various physicochemical properties of oil versus, for example, water on microporous polyolefinic fibers; the presence of a positive pressure sufficient to force the organic material from the aqueous mixture into the micropores and subsequently into the lumen, but insufficiently strong to force the water through the micropores unless required as part of a larger process scheme and other similar factors.

Figures 3, 4 and 5, show an apparatus of a first embodiment of the present invention. The mat, numeral 10 (Figure 3), comprises a plurality of individual hollow fibers 12, e.g. hydrophobic having a hollow interior or lumen 13. The fibers 12 further include a plurality of spaced apart parallel micropores 14 (shown in enlarged detail in Figures 6 and 7) extending from the outside of the fiber to the interior of the fiber 12 such that the micropores are in communication with the lumen 13. Generally, the pore sizes of the micropores 14 will vary depending upon the fiber material. As an example, the pore sizes can range from 0.03 microns (μm) to about 5 microns (μm). Broadly, the micropores will be large enough to permit acceptable flux, but small enough to exclude water due to surface tension effects of the hydrophobic fiber.

The fibers may have an internal diameter from about 0.001 cm to about 5 cm, preferably about 0.005 cm to about 1 cm and most desirably about 0.01 cm to 0.1 centimeters (cm) in the case of polypropylene fibers.

Preferably the fibers comprise a hydrophobic material illustrated examples of which may include polyolefins such as: polyethylene, polypropylene, polybutene, polyisobutylene, polypentene, poly(4-methylisopentene) and their halogen-substituted derivatives having at least one fluorine atom; polystyrene and a halogenated polystyrene having at least one fluorine atom; copolymers of ethylenically unsaturated hydrocarbons and/or halogen-substituted ethylenically unsaturated hydrocarbons having at least one fluorine atom, ethylenically unsaturated hydrocarbons and their halogen-substituted derivatives including ethylene, propylene, butene, isobutylene, pentene,

hexene, monofluoroethylene, vinylidene fluoride, trifluoroethylene, tetrafluoroethylene, trifluorochloroethylene, hexafluoropropylene and the like; and blend polymers such as a combination of polyethylene with polypropylene, poly vinylidene fluoride, polytetrafluoroethylene or polystyrene; a combination of polypropylene with poly vinylidene fluoride or polytetrafluoroethylene and the like. Preferred examples of materials employable, as a main component: polyethylene, a halogenated polyethylene having at least one fluorine atom, polypropylene, a halogenated polypropylene having at least one fluorine atom; or copolymers of two or three kinds of monomers selected from ethylene, propylene and tetrafluoroethylene.

As a further option, the membranes may be optionally anisotropic with respect to inside pore structure versus outside pore structure, morphology, porosity, chemical composition, inter alia. Selection of this property will depend on the intended use of the fiber.

In a preferred embodiment each of the fibers 12 includes open ends 16 and 18 (as illustrated in Figure 4) for the embodiment floating on surface S. In this embodiment, ends 16 and 18 are in communication with receptacles or containers 29. The ends 16 and 18 are maintained such that the ends are within the container and not in contact with the fluid, to be treated. This may be achieved by potted seal 32 as shown in Figure 8. Valved discharge ports 30 and 180 are provided.

Conduit 26 extends positive pressure pump 28, which serves as one possible form of introducing pressure into sealed container 29 and thus the fibers 12. In use the containers 29 are sealed and the pressure effect created by pump 28 is experienced by each of the fibers 12 of which the mat structure is made. Conduit 27 draws the organic/aqueous mixture in for pressurized introduction into contact with fibers 12.

In operation, when mat 10 is positioned within a water body for the purpose of removing one or several contaminants, the positive pressure pump 28 is actuated which draws the feed. As the fibers are in communication with the

contaminant e.g. oil to be removed, the oil is forced via containers 29 into contact with fibers 12 via micropores 14 and is eventually collected. The density of the arrangement 10 will be selected to float in the contaminant to be collected in order that maximum possible surface contact of the individual fibers with the contaminant is achieved. The treated water effluent is discharged through port 30 and the contaminant is discharged through ports 180, or stored in receptacles 20 and 22.

Figure 8 shows a further alternate embodiment. Access to the fibers is achieved by providing a side port feed inlet 31C for transmitting a mixture of the organic and the aqueous phase and discharge port 31D for discharging the aqueous phase. The collected organic is discharged through ends 16 and 18 and collected in receptacles. The organic material collected via the fibers can be discharged (not shown) by any suitable means. Seals 32 keep the fed and collected organic material separated.

Figures 9A, 9B, 9C and 9D illustrate further embodiments of the present invention. Figure 9A, shows a perspective view of a fiber mat module, indicated by numeral 40. The ends of hollow fibers in the mat arrangement are fixedly sealed by a tube sheet or potting compound to each of the receptacles 20 and 22, the disposition of the individual fibers of mat 40 and the relationship with 20 being shown in Figure 9B. The oil is collected in reservoirs 20 and 22 as indicated by oil 42. This module formation is ideally suited in use, for example, a pressurized container 46 such as that shown in Figure 9D. The feed would be introduced into the container by, e.g. a pump 48. The mats 40 could be set up in a vertically spaced apart manner as indicated in Figure 9D and further, as Figure 9C illustrates juxtaposed arrangements of mats of 40 could also be employed. Collected oil within reservoirs 20 and 22 could be removed by any suitable means.

Figure 10 shows a schematic view of a further embodiment wherein the arrangement may include a nozzle 66 extending inwardly and in communication with vessel 56. Vessel 56 includes an inlet 67 for extractant organic recycle, make-up, or level control. Also, inlet 67 permits access to vessel 56 such that the composition of layer 70 may be selectively altered. The nozzle, in use introduces a

contaminant/water/metal composition into vessel 56 for separation. The result is generally that the materials stratify into layers 70,72 and 74. Layer 70 generally contains the organic phase, layer 72 contains a mixture of phases (water, coalescents, etc.) and layer 74 essentially comprises water. It is known in the art that where the organics, contaminants, etc. have a greater density than water, the order of the stratification will vary in accordance with the difference in density.

Outlet 76 on vessel 56 directly adjacent the mat 10 provides the extraction of the organic layer together with metal compounds. Outlet 78 provides for the discharge of substantially pure water devoid of the metal chelant, coordinated compounds or organics.

As will be appreciated, provision may be made in system design and/or operation for a treatment/phase operation for simultaneous, sequential or selective removal (e.g. for enhancement) of desired components from vessel 56. The apparatus of Figure 10 may alternatively be useful for increasing extraction of ultra fine oil droplets from water by "atomization" of the emulsion, causing coalescence with and/or extraction of oil into organic layer 70.

Figure 11 shows a further embodiment of a solvent extraction system. The arrangement includes a containment vessel, denoted by numeral 80. As shown, the system includes a first mat arrangement 82 composed of fibers 12, which communicate at their terminal ends with a first extractant reservoir 84, adapted to carry a suitable extractant, which may either be forced through the fibers or diffuse naturally. Where the extractant is to be forced through the fibers 12, a suitable positive pressure pump 84A or other suitable means will be employed and connected to line 84B. The second reservoir 86 may be employed to include similar elements 86A and 86B.

As dispersed extractant flows through the body to be treated as indicated by arrow A in Figure 11, the extract may be recovered by the uppermost mat arrangement 82A and collected in reservoirs 20 and 22, the bottom mat arrangement 82 may be substituted with any suitable means for dispersing an extractant, etc. into the

body of material to be treated. Examples include simple perforated tubes or nozzle arrangements. Further still, there may be employed an external source of the extractant, etc. which is delivered to the mat arrangement 82.

In an alternative embodiment, the vessel 80 may include a pump 88 for pressurizing vessel 80, providing the necessary pressure differential across the fibers 12 to effect the separation result.

By providing an outlet 76 and further in view of the fact that the mat arrangement 82 composed of the fibers permits removal of organic contaminants as well as various metals, the invention clearly has utility in the mining art since the arrangement can provide for recovered metal values which would otherwise be lost or irrecoverable.

It will be readily appreciated by those skilled in the art that the present invention is clearly applicable to removing soluble contaminants from a water body containing contaminants dissolved therein. It is clearly within the purview of the present invention to apply suitable treatments, appreciated by those skilled in the art, for the purpose of precipitating an aqueous phase from another phase. In this manner, once the mixed phases are formed, the fiber mat or bundle arrangement or fiber array according to the present invention may be employed for the purpose of separating one phase from the other.

Where the contaminant comprises any other hydrocarbon floating on the surface water body from, e.g., an oil tanker spill, one or several of the mats may be employed for recovering the oil from the surface.

Where temperature increases the viscosity of the oil or the contaminant is of a highly viscous nature, the viscous contaminant may be diluted with a suitable diluent, e.g. a liquid hydrocarbon, or any other suitable viscosity modifier. Further, the viscous contaminant may be heated to reduce its viscosity, if practical. In this manner, units containing the microporous hollow fibers can readily function in a variety of

environments. As discussed the material to be treated contains metals, a suitable pretreatment regime may be employed to add a chelant or other conventional additive, or to coordinate the metal materials and render them soluble in the organic phase and in the instance where the material includes insoluble particulates, e.g. sand, it will be readily understood that the pretreatment regime may include filtering, centrifuging, chelant addition or other chemical treatment, freezing, cooling, or any combination of these. The pretreatment regime will depend on the nature of the material to be treated according to the methodology of the present invention. In applications where water-free fuel or oil is critical (such as that required in the aircraft industry or in emergency generators), a provision is made for the use of any variety of the known dehydration techniques as adjuncts to the invention. Examples of suitable techniques include gravity trapping, absorption, etc.

Sometimes oil-water mixes may require heating prior to contact with the fibers. As oil cools the solubility of water in it may decrease and water droplets may form. Auxiliary dehydration can eliminate this.

Figure 12 schematically illustrates a network of modules as for example of the type illustrated in Figure 8. The overall network 134 includes a master feedstream inlet 136 for feeding oil/water into network 134 for treatment therein. The network includes an oil discharge outlet 138 and a water outlet 140. Optionally, any number of individual modules 120 can be connected in sequence to accommodate a specific apparatus requirement. As a further alternative, outlet 140 may provide a recycling loop for reintroducing substantially organic free water into inlet 136.

Finally, with respect to the choice of material of which the fibers and/or bundles may be composed, it will be appreciated that the fiber composition will depend upon the type of contaminant to be collected. In this manner, the fiber material will be selected such that the contaminant does not deleteriously alter the properties of the fiber with respect to lumen size, internal diameter, external diameter, pore size or surface characteristics such as hydrophobicity of the fiber and/or pore.

It will be understood by those skilled in the art that the process of the invention can be combined with conventional processes.

Having thus described the invention, reference will now be made to examples which set forth the data generated as a result of the use of the methodology set forth herein.

For Examples 1 through 5, and 7, 9 and 10, the apparatus that was employed for the testing is generally illustrated in Figure 8. The fibers employed were EHF 270W, EHF 270FA or EHF 540 all manufactured by the Mitsubishi Rayon Corporation.

In Example 6, a version of the apparatus illustrated in Figure 4 was modified to hang vertically down a 2 inch pipe and remove the kerosene from a kerosene/water mixture.

EXAMPLE 1

REGULAR MODULE FLUX TEST - KEROSENE

% Open Fibers - 67.09%

TEMP (deg.C)	PRESSURE (kPa)	PRESSURE (psi)	FLOW (LPM)	FLOW (LPM/M^2 psi)	AVG FLUX (LPM/M^2 psi)
30	3	0.431	1.227	1.423	0.83
30	11	1.58	2.454	0.776	VISC
30	21	3.017	3.681	0.61	1.97
30	34	4.885	4.908	0.502	Normalized

The test was conducted at 30° C under varying pressure conditions as tabulated. The unit functioned properly.

EXAMPLE 2

REGULAR MODULE FLUX T3XT - DIESEL

% Open Fibers - 67.09%

TEMP (deg.C)	PRESSURE (kPa)	PRESSURE (psi)	FLOW (LPM)	FLOW (LPM/M^2 psi)	AVG FLUX (LPM/M^2 psi)
24	6	0.862	0.603	0.35	0.33
25	12	1.724	1.207	0.35	VISC
25	18	2.586	1.811	0.35	2.67
25	26	3.736	2.415	0.323	Normalized
25	35	5.029	3.019	0.3	0.89

EXAMPLE 3

WATER PRESSURE DROP

Temperature - 14°
Viscosity - 1.1709 centipoise (cP)

PRESSURE (kPa)	PRESSURE (psi)	FLOW (LPM)	BREAKTHROUGH (Y/N)
20	2.8736	4	N
23	3.3046	6	N
26	3.7356	8	N
33	4.7414	10	N
41	5.8908	12	N
45	6.4655	14	N

EXAMPLE 4

LIX-84

TEMP (deg.C)	PRESSURE (kPa)	PRESSURE (psi)	FLOW (LPM)	FLUX ($LPM/m^2/psi$)
17	133	19.109	0.167	0.036
24	95	13.649	0.184	0.055
30	74	10.632	0.201	0.077

EXAMPLE 5

TREATMENT OF SHIPPING CRUDE OIL

ELAPSED TIME (Minutes)	TEMPERATURE IN (deg.C)	PRESSURE (psi)	Oil Received (L)
0	34.5	1	
2	35	1	
4	37	1	0.2
5	37	1	0.28
8	37	5	1.06
9	36	5	1.3
10	39	6	1.53
11	39	6	1.74
12	42	3	2.35
13	43	1	2.95
14	43	1	3.54
15	42	1	4.25
16	42	1	4.85
18	41	1	
22	40	6	7.25
24	40	2	9.92
25	40	2	12.23
26	40	2	14.54
29	41	1	19.27

Example 5 data are illustrated tabulating elapsed time, temperature and the amount of oil received at the outlet of the module. In all instances, the oil received at the outlet did not have any free phase water therein.

EXAMPLE 6
CRUDE/DIESEL/$H_2$0 MIX

ELAPSED TIME (Minutes)	TEMP (deg.C)	PRESSURE (kPa)	ORG. REC'D (mL)	WATER REC'D (mL)
0	22	23	0	0
2	22	24	70	0
4	22	24	160	0
6	22	24	240	0
8	22	25	320	0
10	22	26	400	0
12	22	28	500	0

Viscosity - 4.5 cPs

In Example 6, a mixture of the above-captioned compounds resulted in organic recovery with no free phase water observed therein.

EXAMPLE 7
METAL EXTRACTION/STRIPPING

1. EXTRACTION - A mixture according to the following formulation was tested 900 mm of metal digestate in 150 m of kerosene with 50 ml of LIX 84™ chelant. As a result of the extraction, a dry co-ordinated organic compound was recovered.

ELAPSED TIME (Minutes)	TEMP (deg.C)	PRESSURE (psi)	ORG. REC'D (mL)
0	22	0	0
8	22	7.5	200

Dry "Pregnant" Chelant

2. STRIPPING - 200 mills of chelant in 200 ml H_2SO4. As tabulated, 200 ml of the organic was recovered.

ELAPSED TIME (Minutes)	TEMP (deg.C)	PRESSURE (psi)	ORG. RECD (mL)
0	22	0	0
5	22	7.5	200

Dry "Regenerated" Chelant

Other similar experiments were performed from using a variety of concentrations of LIX84™, LIX984™ as DEHPA chelant dissolved in kerosene to extract/recover a variety of metals from aqueous product solutions, both synthetic and field examples. Metal removals/recoveries range from 40% to 100% per stage; metals evaluated included iron, manganese, copper, nickel and zinc. Organic chelant/metal solutions contain no visible water.

EXAMPLE 8
CANOLA OIL AND WATER MIXTURE

In this example, 500 mL per minute of a 10 volume % canola oil in water was fed to the module at the shell side inlet 128. The pressure in the shell was adjusted to positive 5 psi. The feed temperature was 25° C. As a result of the test, the canola oil recovered contained no visible water. The canola oil was collected from the fiber lumen at points 126 and 124 as in Figure 13A.

EXAMPLE 9
COMPARATIVE EXAMPLES

In this example, 426 mL min^{-1} of water at 25° C was fed to the module set forth in Example 8 at 126, i.e. the feed was introduced down bore. The result of this was that approximately 30 ml min^{-1} of water entered the shell through the fiber walls exiting at the inlet and outlet 128 and 130 respectively as indicated in Figure 13A. Accordingly, there was water breakthrough in the unit.

TABLE 1

CRUDE OIL: SUMMARY OF DATA FROM EXAMPLES 10 THROUGH 14

CRUDE OIL FIELD TRIAL EXAMPLES

Example	Feed Data		"Dry" Oil Data								Distillation Initial Boiling Point °C		Kinematic Viscosity (40°C, mm^2s^{-1})	
	% Water		Density, kgm^{-3}			API * @ 15.6°C			Pour Point, °C					
	Inlet	Outlet	Inlet	Outlet	Δ	Inlet	Outlet	Δ	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
10	20.8	< 0.01	849.6	848.1	- 1.5	35.0	35.3	+ 0.3	- 15	- 12	67	58	6.113	5.907
11	31.4	< 0.01	849.9	848.3	- 1.6	34.9	35.2	+ 0.3	- 18	0	-	-	6.022	5.938
12	16.0	< 0.01	850.7	848.9	- 1.8	34.7	35.1	+ 0.4	- 15	- 18	63	54	6.369	5.736
13	8.9	< 0.01	874.4	865.7	- 8.7	30.2	31.8	+ 1.6	- 39	-39	67	51	7.690	6.164
14	0.5	< 0.01	849.5	847.0	- 2.5	35.0	35.5	+ 0.5	12	9	54	53	5.964	5.920

* API = American Petroleum Institute

These examples clearly illustrate the effectiveness of the present invention. In Example 8, the water flow rate of 450 ml per minute did not result in any water breakthrough while, in contrast, the flow rate of 426 ml min^{-1} down bore caused water breakthrough in Example 9. Clearly, by providing a shell side feed in accordance with the present methodology, water breakthrough is not a concern as in down bore feeding.

As tabulated in Table 1, significant changes were noted in very desirable physical and chemical properties of crude oil feeds demonstrated for on-site pilot tests at a variety of sites. By exposing the crude oil feed to the hollow fiber arrangements and by observing a methodology of the present invention, some or all of physicochemical changes in the properties of crude oils subsequent to treatment were observed:

1. the oil was substantially anhydrous;
2. decrease in oil density was observed;
3. a lower distillation temperature range was observed;
4. at least a reduction in the wax-out or tar deposition in the product;
5. a reduction in liquid viscosity in substantially all of the examples;
6. a change in particle size (for some oils, the change appeared to be a reduction in size);
7. an increase in API;
8. a decrease in some pour point temperatures and substantial changes in the combustion efficiency of the product was expected and other chemical properties of the liquids are also expected (these vary with particle size); and
9. effluent water from crude oil pilot runs were suitable for reinjection back into the wells.

As known in the art, enhancing or reducing suitable properties of a crude oil becomes more valuable and it is possible to employ the product in a broader scope of applications, not known in the prior art.

Examples 1, 2 and 4, show flux data for different organic liquids. Example 3 shows module pressure drops/volume H_20 feed rate data further demonstrating a zero breakthrough of water to the organic collection side of the apparatus. Example 5 shows laboratory data on a crude oil site dehydration run. Example 6 demonstrates that dry organic product can be recovered from a vertically hanging arrangement of less than about 2 inches about diameter tubing; this is useful for down hole or in-situ oil recovery. Example 7 shows utility in separation of metal chelant/organic/aqueous mixtures; this is useful to the end of achieving solvent extraction.

Table 1 tabulates the data from Examples 10 through 14 with respect to various parameters as measured prior to treatment (inlet data) and subsequent to treatment (outlet data) for percentage of water in the sample, density, API gravity, pour point, distillation and kinematic viscosity.

Generally, the protocol observed involved feeding the sample at desired rates and conditions to the shellside of the fibers. In the table, the terminology "inlet" refers to the percentage of water in the feed or the properties of dehydrated oil. "Outlet" refers to permeated oil.

In all instances, the effluent aqueous phase was substantially oil free and was suitable for reinjection back into the formation from which it came.

Figures 13 through 26 graphically illustrate data from Table 1, and in particular particle counts for an oil sample prior to treatment and subsequent to treatment, viscosity temperature charts indicating kinematic viscosity as a function of temperature for pretreatment and post-treatment of the sample and ASTM distillation data indicating temperature as a function of the fraction

distilled for various fractions in the oil prior to treatment and subsequent to treatment according to the methodology of the present invention.

Figure 13 illustrates particle distribution for a crude oil sample containing oil and water prior to treatment with the hollow fiber methodology as set forth herein. It is clear that the particle size distribution varies from approximately 1 micron (μm) to approximately 9 microns (μm).

Figure 14 illustrates the particle size distribution after the sample has been treated with the fibers. It is clear that a significant particle size distribution shift occurred subsequent to the treatment with the particle size generally between .01 microns (μm) to .1 microns (μm). This phenomenon has been demonstrated in the past when oils have been subjected to a strong magnetic field. This exposure resulted in permanent particle distribution shift.

The value of crude oil may be determined by an industry equalization scale, the value being a function of the API. The scale classifies oil in distinct API ranges. Depending on the requirements for the oil, the ranges in API designation differ. Having regard to this difference, even a small increase in API may be sufficient to enhance the value of an oil to a higher category.

Figures 15 through 17 show a viscosity temperature chart indicating the kinematic viscosity of a crude oil sample as a function of temperature, an ASTM distillation summary illustrating temperature data as a function of the fraction distilled from the sample and a particle size and distribution graph for Example 10 and specifically at the "inlet" of a module. Similar graphical representations are set forth in Figures 21, 22 and 23 illustrating the same information, respectively but for the "outlet" information. In the case of the percentage of water present in the sample subsequent to treatment, the same went from 20.8% to less than 0.01%, a significant decrease in the density was also -3. There was an API gravity change of 0.3 as measured at 15.6° C and the pour point subsequent to treatment increased 3° C. Of further significance, is the distillation

and kinematic viscosity data, where the boiling point in Example 10 dropped 9° C subsequent to treatment with the methodology of the present invention. A significant decrease in the kinematic viscosity was also noted, the inlet having an viscosity of 6.113 mm^2s^{-1} compared to the outlet value of 5.907 mm^2s^{-1}.

WE CLAIM:

1. A method of separating an immiscible organic compound from an aqueous mixture containing said compound and an aqueous phase characterized in that said method comprises the steps of:

providing a plurality of hollow hydrophobic fibers having micropores therein and opposed ends inaccessible to said mixture, said micropores extending from the outside of each fiber to the hollow interior thereof;

pressurably forcing said mixture into contact with said micropores under sufficient pressure to only permit passage of said immiscible organic compound through said micropores and into said hollow interior, but insufficient for collapse of said fibers and passage of said aqueous phase;

collecting said immiscible organic compound; and

discharging said aqueous phase substantially devoid of said immiscible organic compound.

2. The method as set forth in claim 1, characterized in that said fibers are isotropic fibers.

3. The method as set forth in claim 1, characterized in that said fibers are anisotropic fibers.

4. The method as set forth in claim 1, characterized in that said method further includes the step of recirculating said aqueous phase in the system.

5. The method as set forth in claim 1, characterized in that said method further includes the step of pretreating, in a pretreating step, said mixture prior to contact with said fibers.

6. The method as set forth in claim 5, characterized in that said pretreating step includes at least one of heating, filtration, centrifuging, cooling,

freezing, dilution, precipitation or addition of chemical reagents and/or solvents or any combination of these for pretreatment of said mixture.

7. The method as set forth in claim 1, characterized in that said aqueous phase contains soil or sediment.

8. The method as set forth in claim 7, characterized in that said method further includes the step of percolating a solvent through said soil or sediment to dilute said organic compound and entrain said organic compound in said solvent.

9. The method as set forth in claim 5, characterized in that said method further includes the step of forcibly injecting into said soil or sediment, a solvent to entrain organic material in said solvent.

10. The method as set forth in claim 1, characterized in that said immiscible organic compound comprises an edible oil or an essential oil.

11. The method has set forth in claim 1, characterized in that said method is conducted in a pressurized container or pressurizing said mixture.

12. A method of separating an immiscible organic compound from an aqueous mixture containing said compound and an aqueous phase, characterized in that said method comprises the steps of:

providing a plurality of hollow hydrophobic fibers having micropores therein and said fiber ends inaccessible to said mixture, said micropores extending from the outside of each fiber to the hollow interior thereof;

creating a pressure differential between said mixture and said hollow fibers such that said mixture is under higher pressure relative to said fibers, said pressure being sufficient to permit passage of said organic compound but insufficient to allow said aqueous phase passage into said micropores and for said hollow fibers to collapse;

contacting said micropores of said fibers with said mixtures;

collecting said immiscible organic compound; and

discharging said aqueous phase substantially devoid of said immiscible organic compound.

13. The method as set forth in claim 12, characterized in that said organic compound comprises crude oil.

14. The method as set forth in claim 12, characterized in that said organic compound comprises oil and organometallic complex(es) to be recovered.

15. The method as set forth in claim 12, characterized in that said organic compound comprises edible oil or fixed oil.

16. The method as set forth in claim 12, characterized in that said hollow fibers comprise anisotropic fibers or isotropic fibers.

17. A method of altering the physicochemical properties of crude oil, said properties including at least one of liquid viscosity, density, particle size, API rating, pour point, distillation characteristics and combustion efficiency characteristics, characterized in that said method comprises the steps of:

providing a feed containing crude oil;

providing a polymeric matrix having pores therethrough for passing said crude oil;

forming a pressure differential across said matrix such that said pressure is sufficient to permit passage of said oil through said micropores, but insufficient for collapse of said matrix;

collecting said oil, said oil having at least one altered physicochemical property.

18. The method as set forth in claim 17, characterized in that said matrix comprises a matrix with a high oil flux.

19. The method as set forth in claim 17, characterized in that said method further includes the step of removing any free water phase present in said crude oil prior to passage through said matrix.

20. The method as set forth in claim 17, characterized in that said matrix includes micropores having a diameter from about 0.03 microns (μm) to about 5 microns (μm).

21. The method as set forth in claim 20, characterized in that said matrix comprises isotropic hollow fibers or anisotropic hollow fibers.

22. The method as set forth in claim 17, characterized in that said matrix comprises a hydrophobic matrix or a hydrophilic matrix.

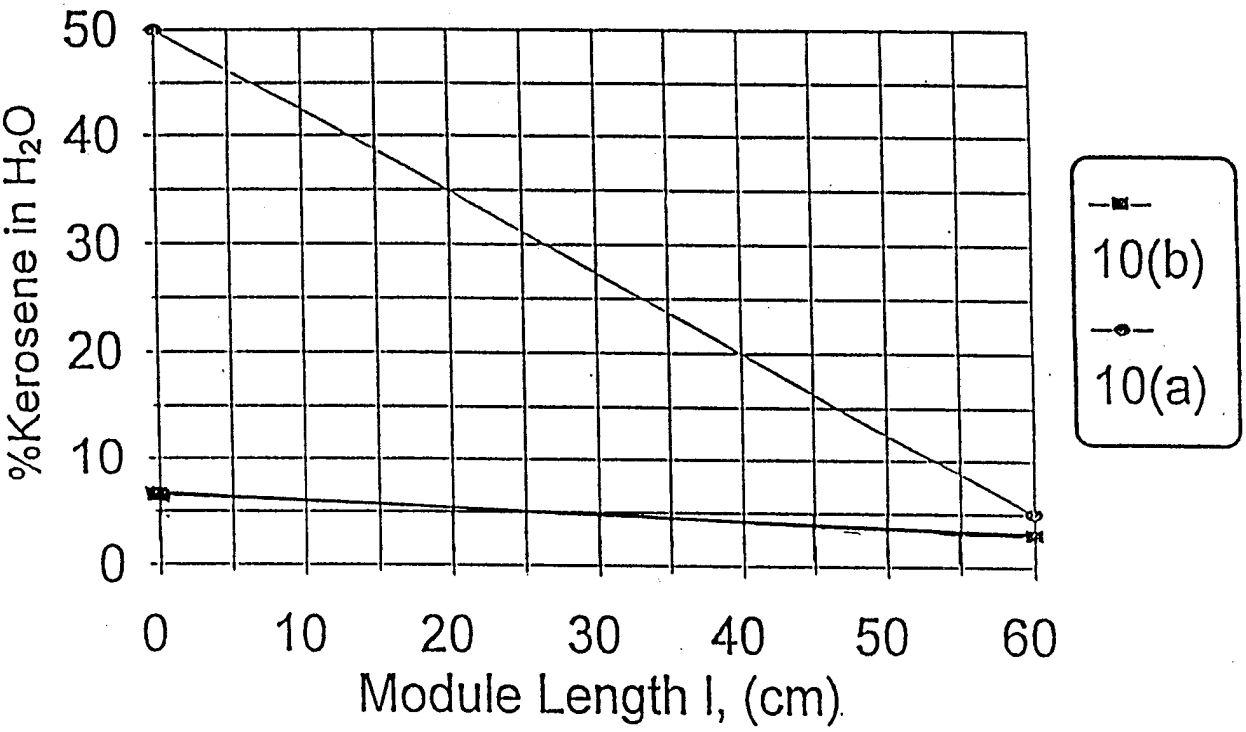
23. The method as set forth in claim 22, characterized in that passage of said crude oil through said hydrophobic matrix produces an organic mixture having altered physicochemical properties and a separate and discrete aqueous phase substantially devoid of said crude oil.

24. The method as set forth in claim 17, characterized in that said polymeric matrix comprises an oleophilic polymer.

25. The method as set forth in claim 17, characterized in that said matrix having pores therethrough for selectively passing said crude oil.

Fig. 1A

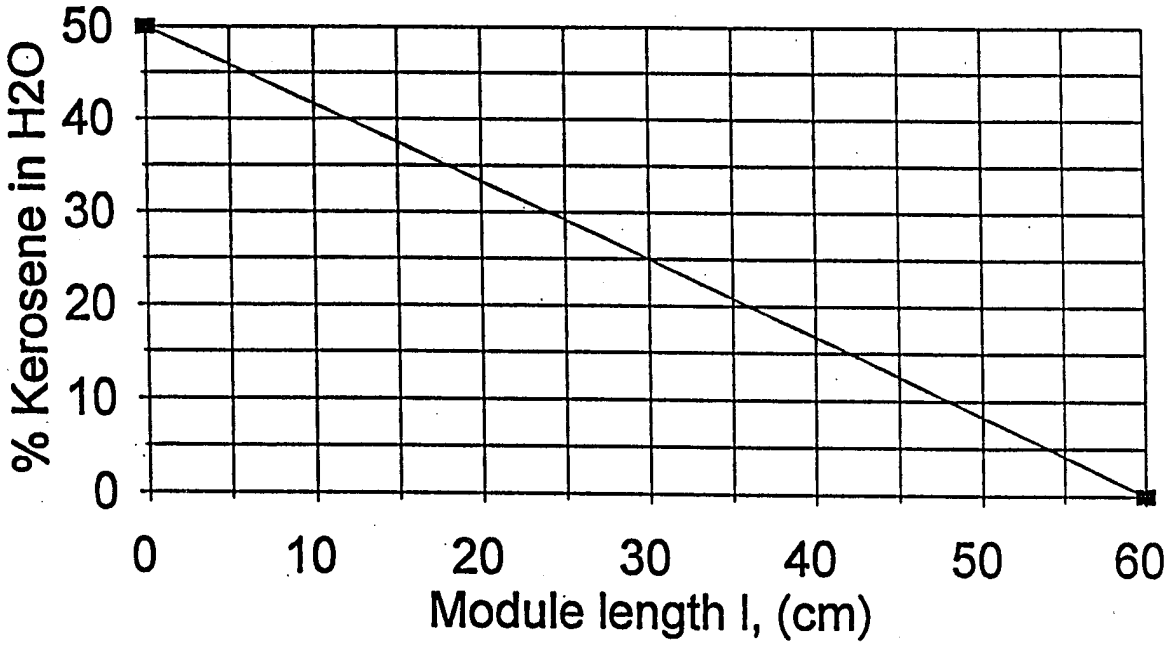
LUMEN FEED-KEROSENE REMOVAL RATES *



*influent and effluent concentrations only

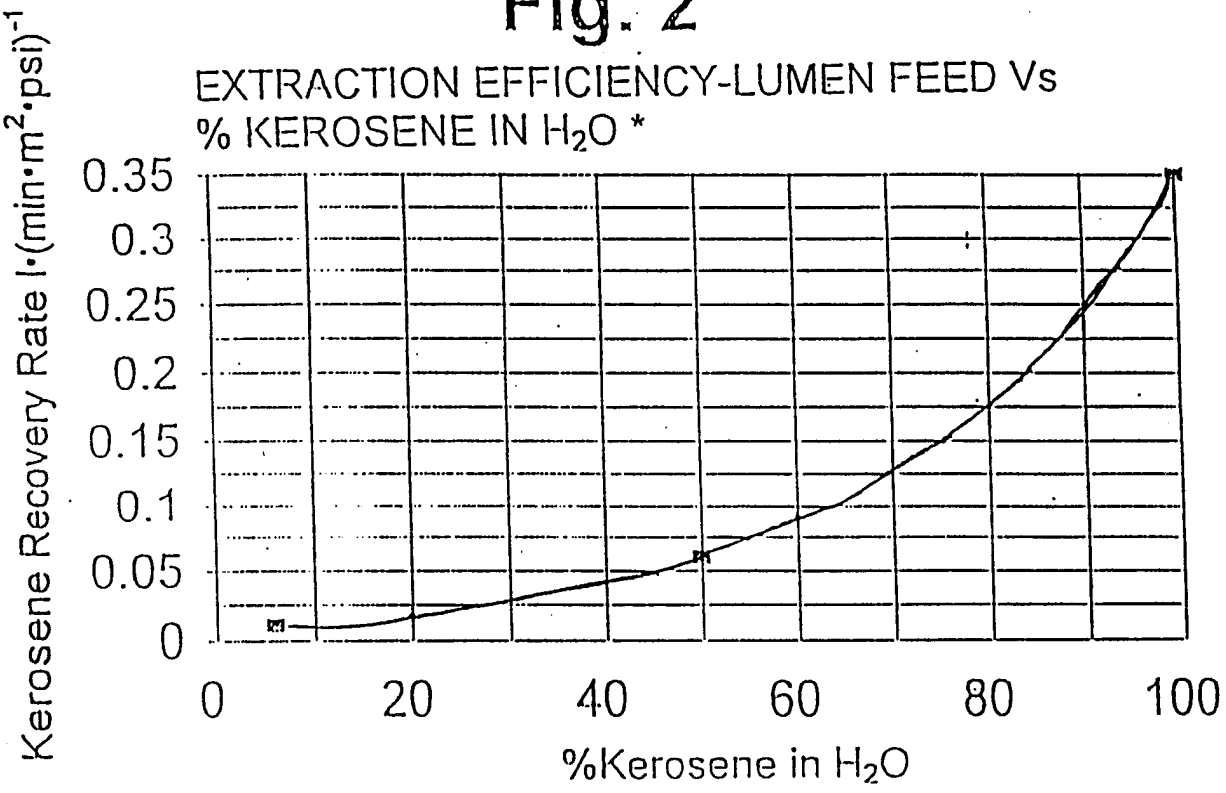
Fig. 1B

KEROSENE REMOVAL RATES FOR SHELL SIDE FEED*



*influent and effluent only

Fig. 2



*data graphed is the data from Figure 1A **(6 and 50%)** and a similar run using 100% Kerosene

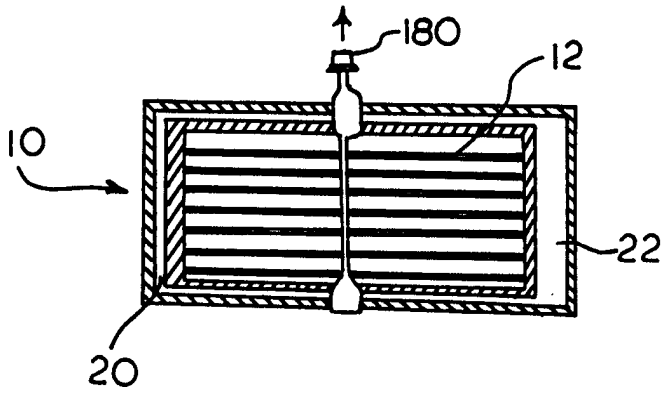


FIGURE 3

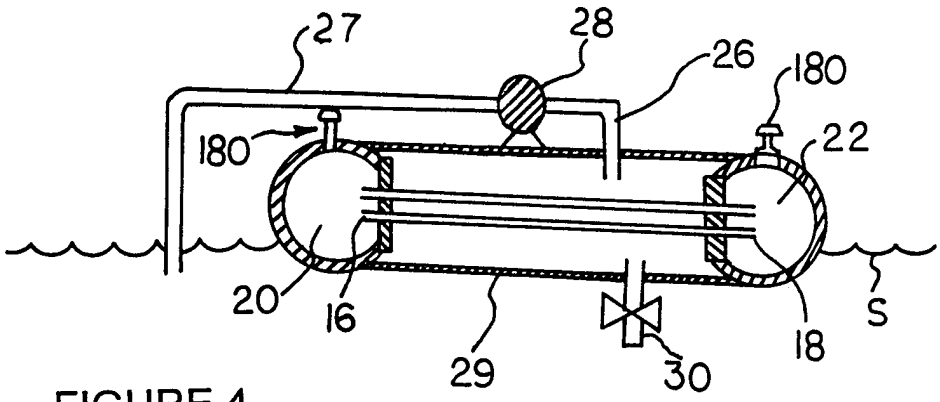


FIGURE 4

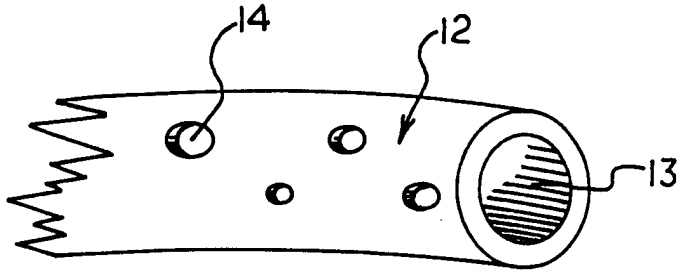


FIGURE 5

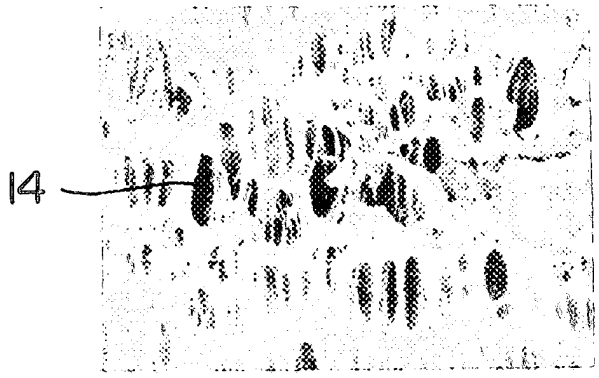


FIG. 6

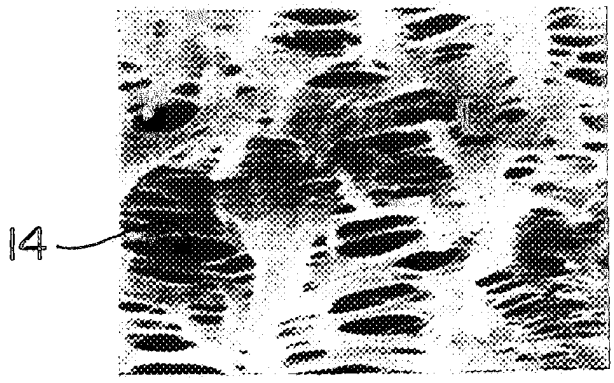


FIG. 7

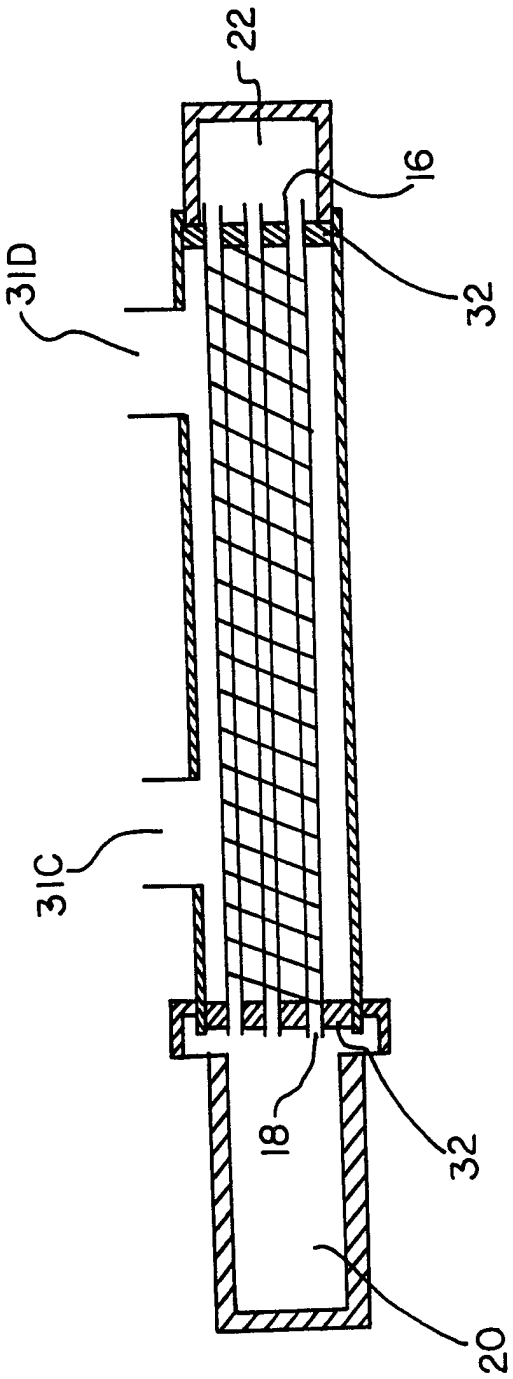


FIGURE 8

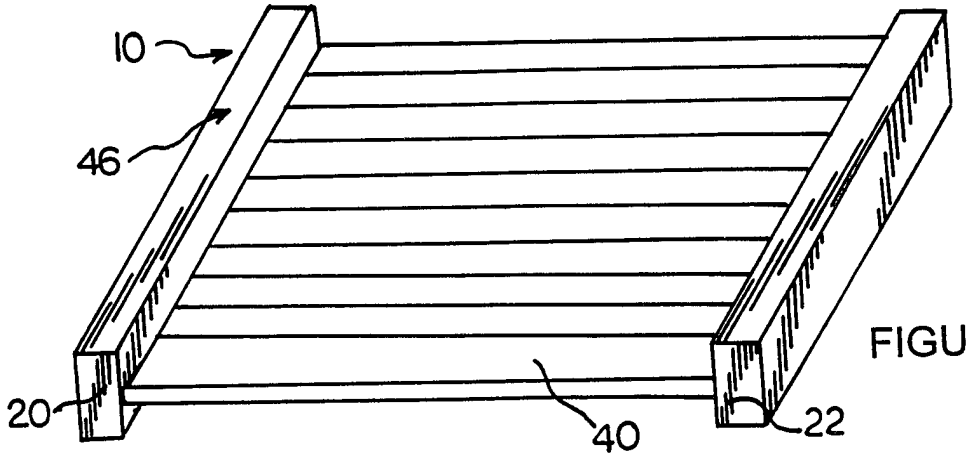


FIGURE 9A

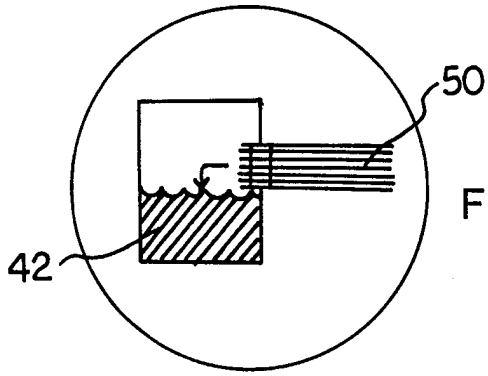


FIGURE 9B

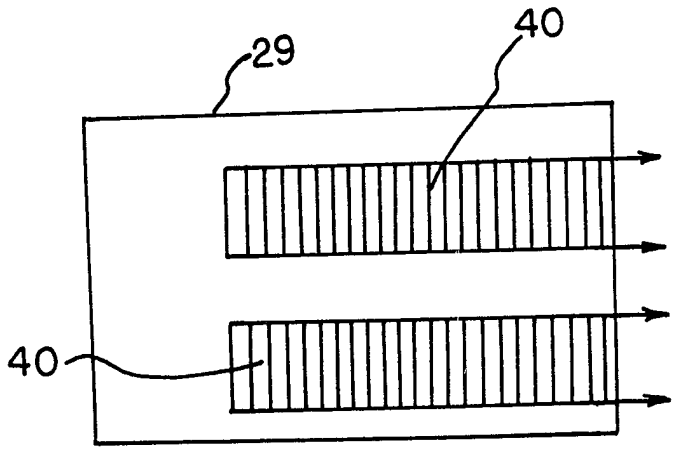


FIGURE 9C

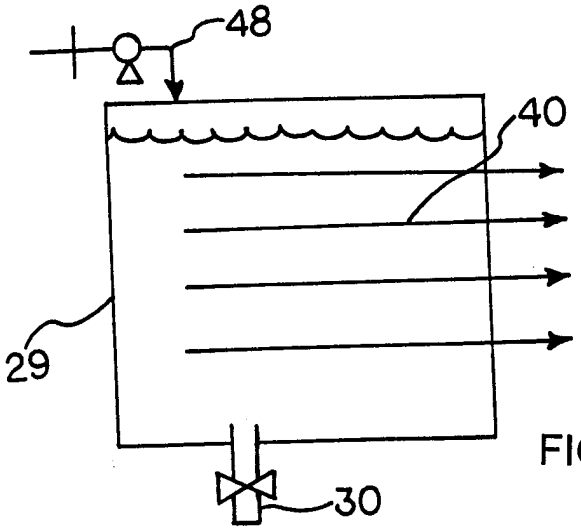


FIGURE 9D

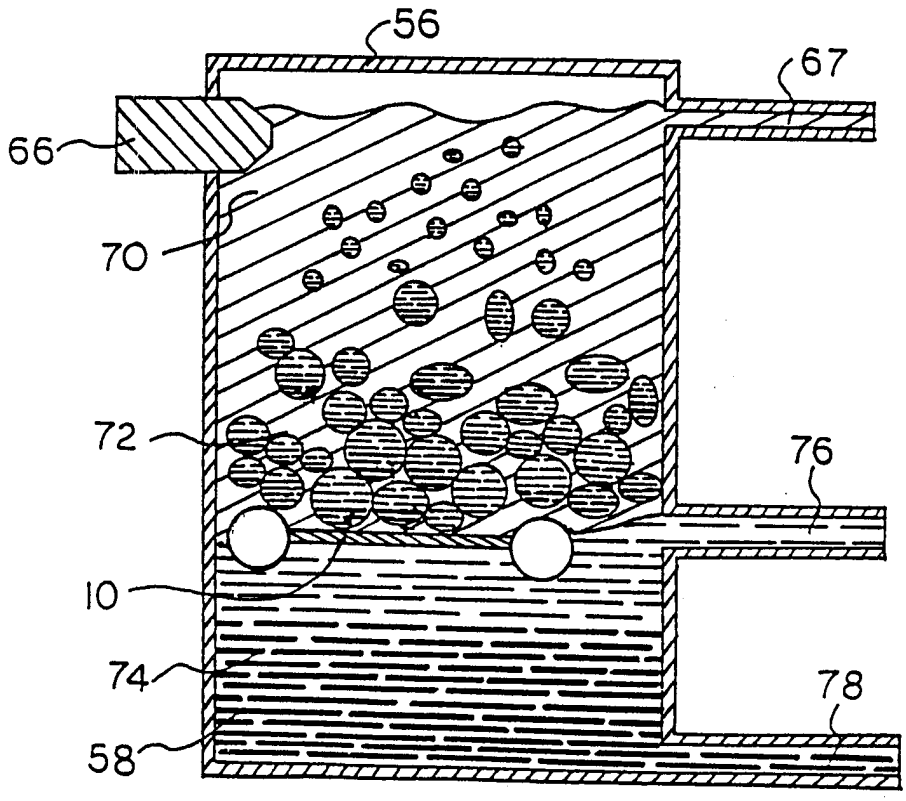


FIGURE 10

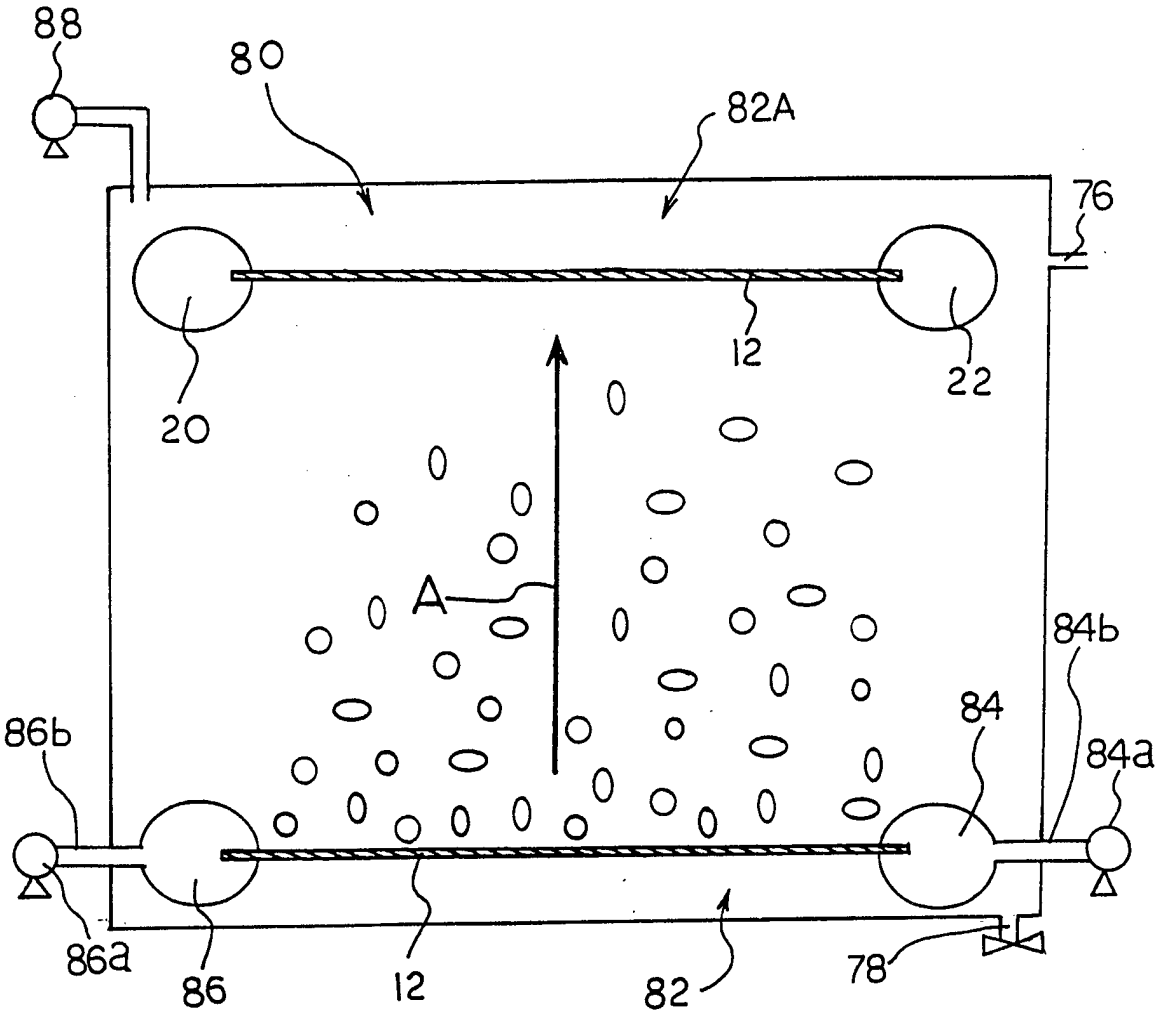
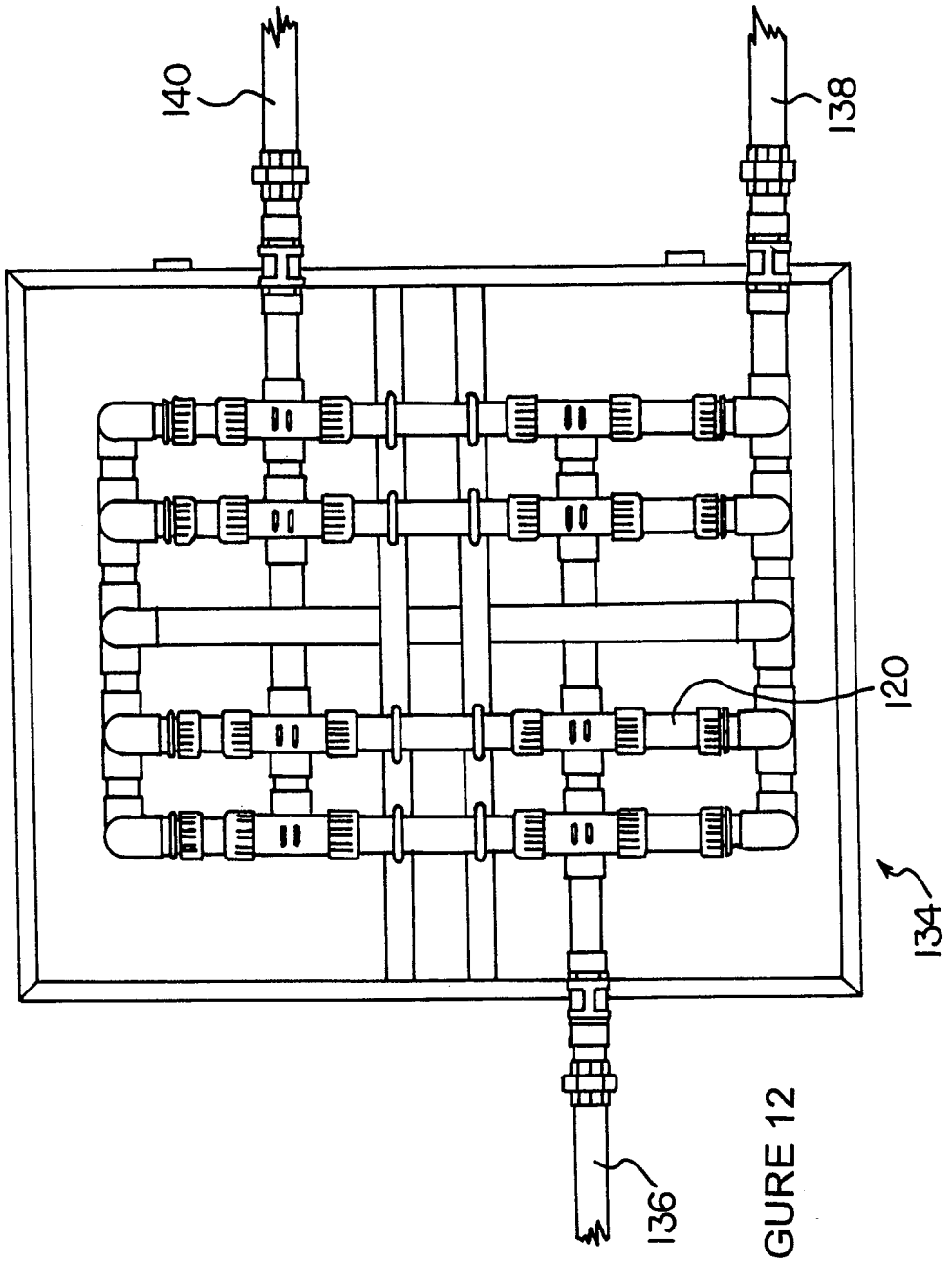


FIGURE 11



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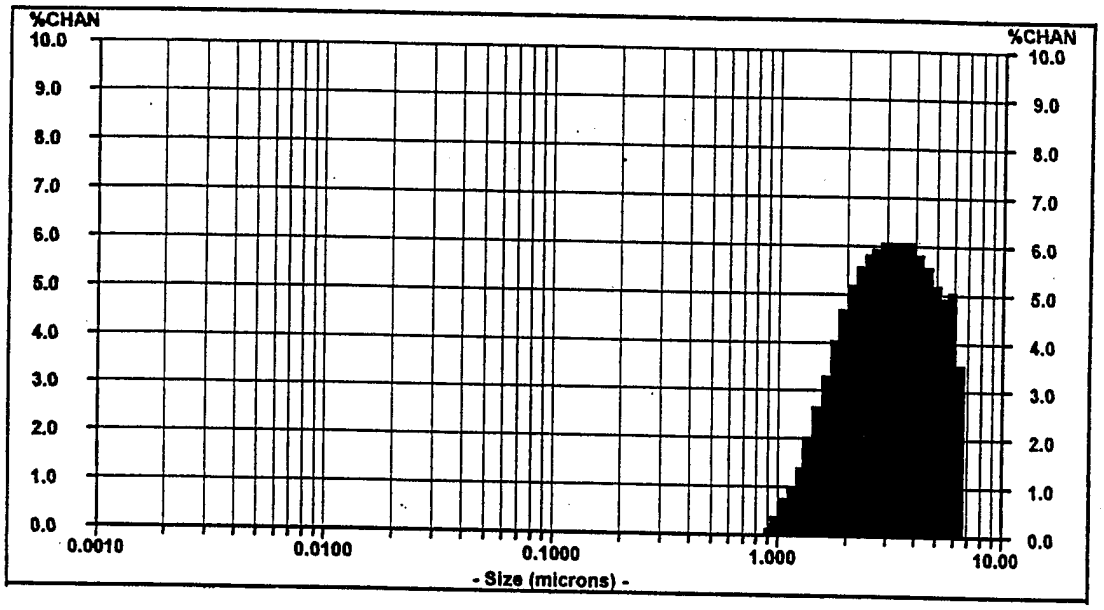
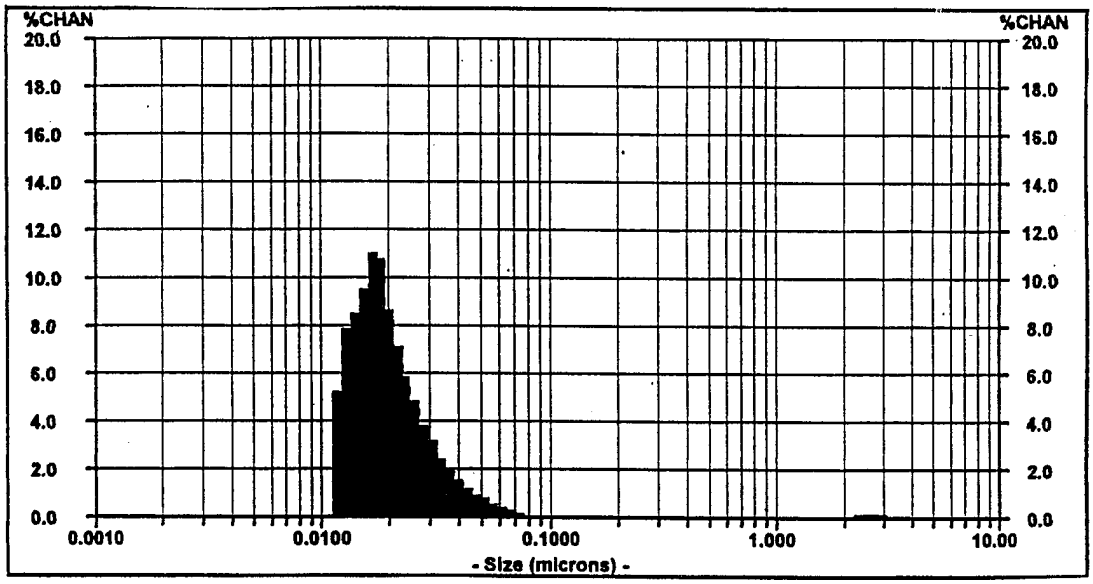


FIGURE 13



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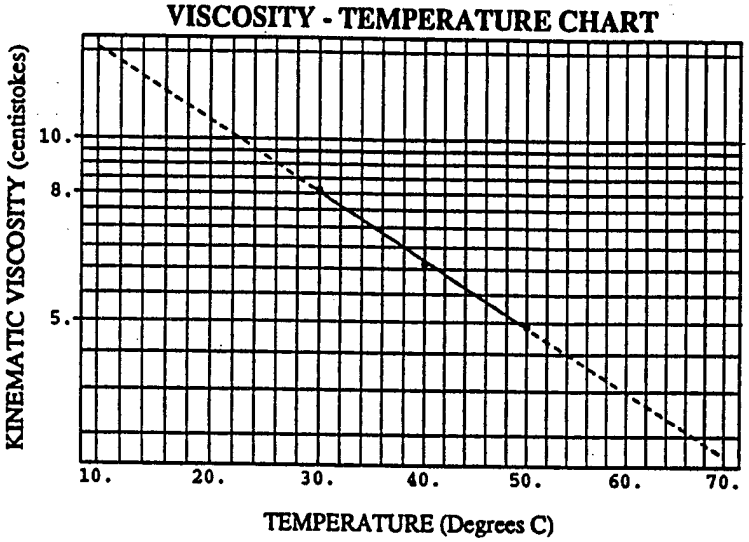

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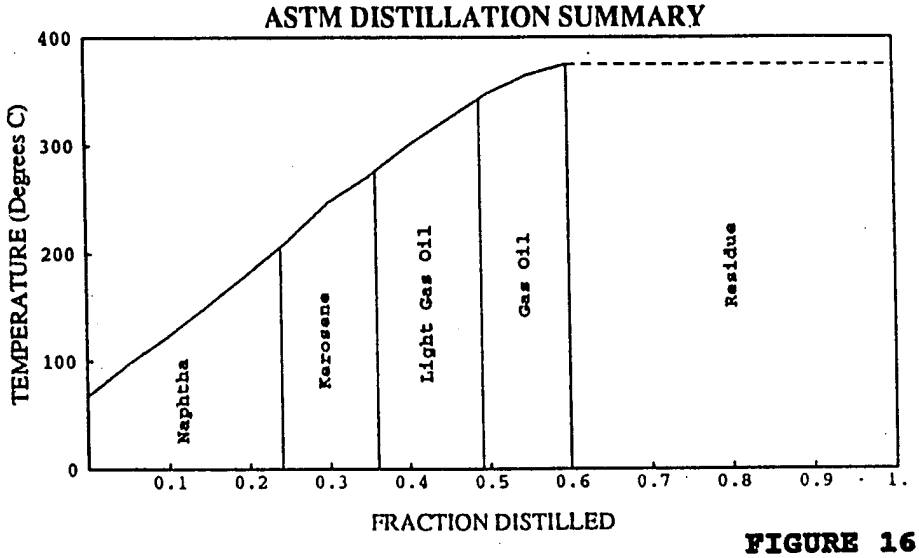


FIGURE 16

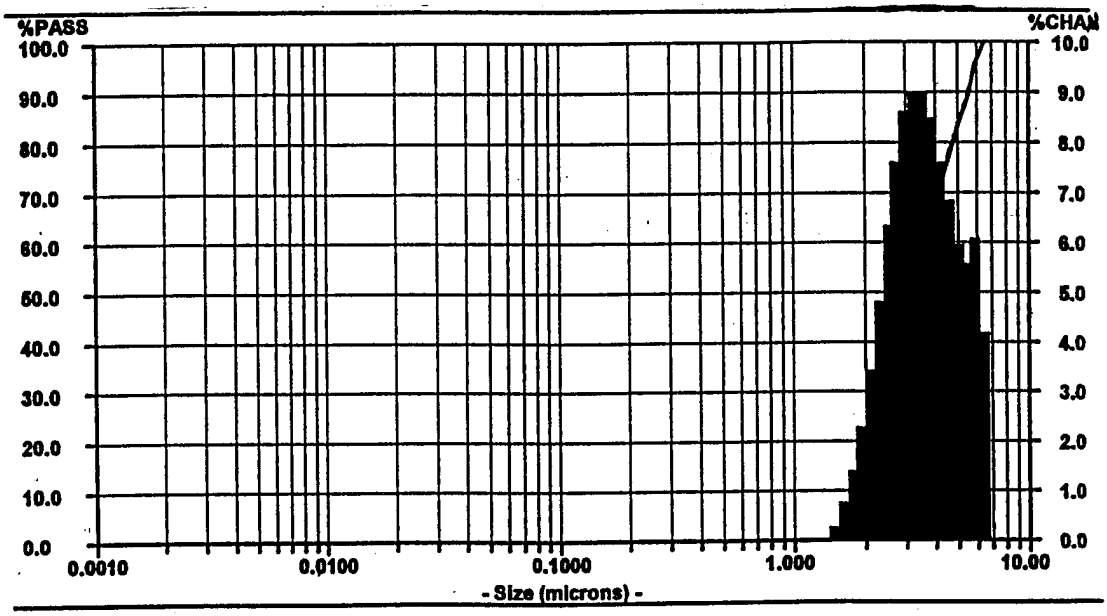
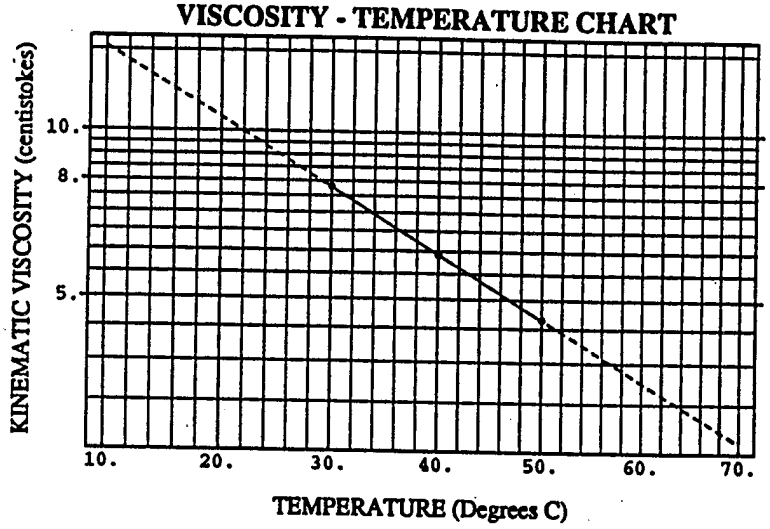


FIGURE 17



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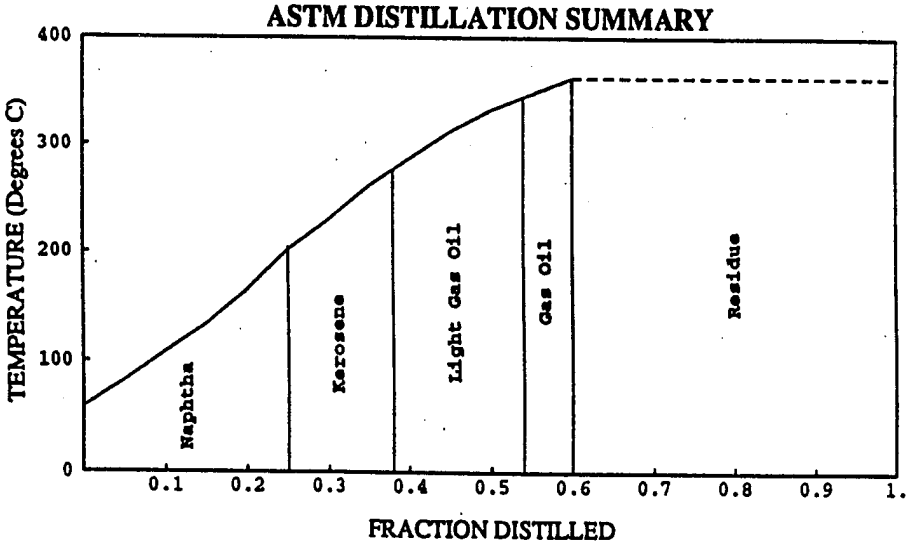

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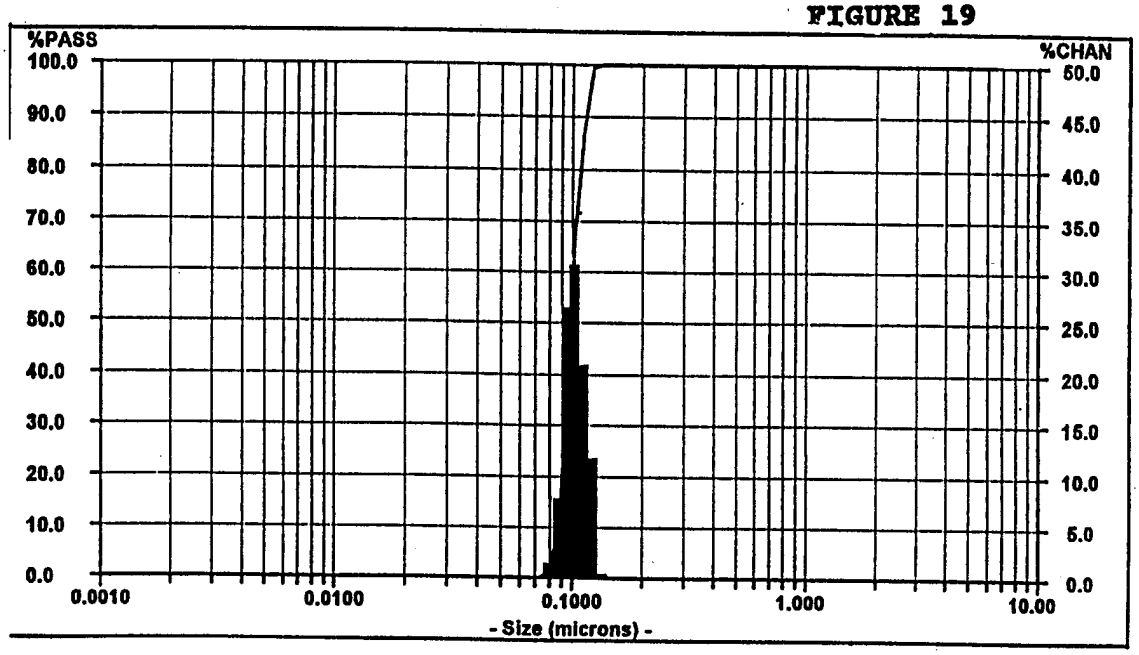

FIGURE 20

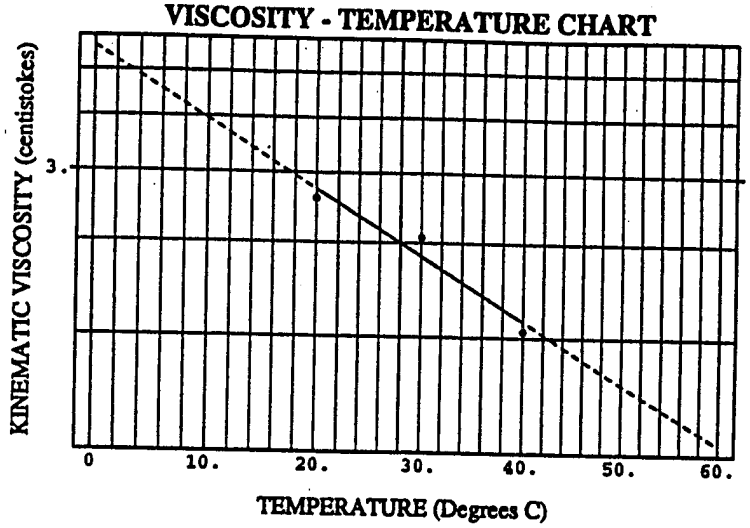

FIGURE 21

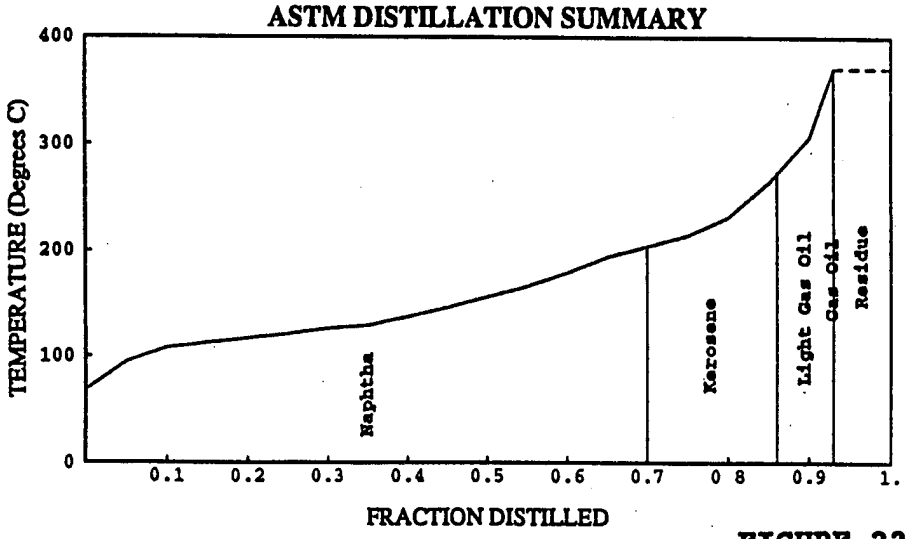

FIGURE 22

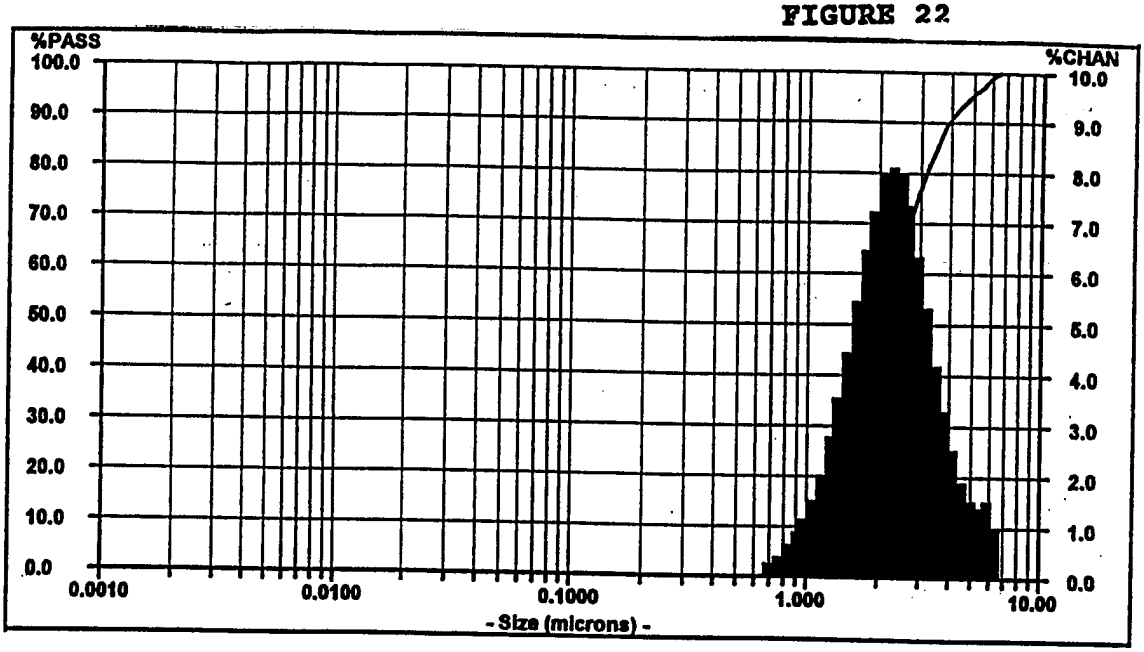

FIGURE 23

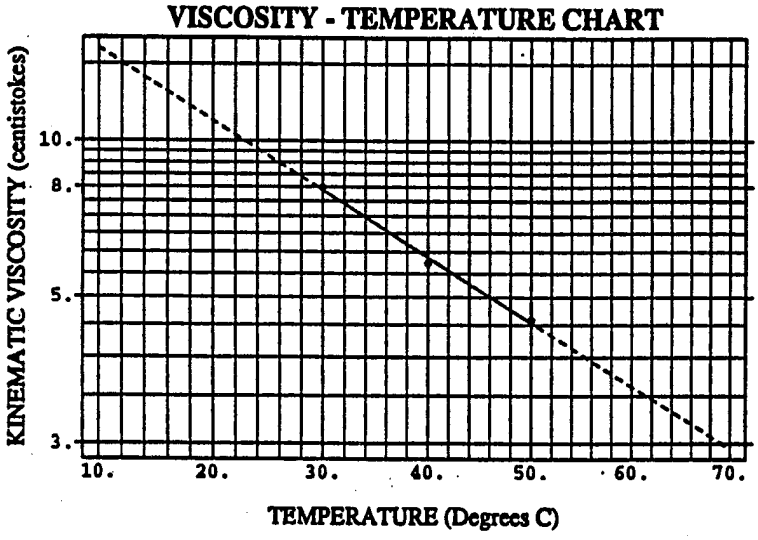

FIGURE 24

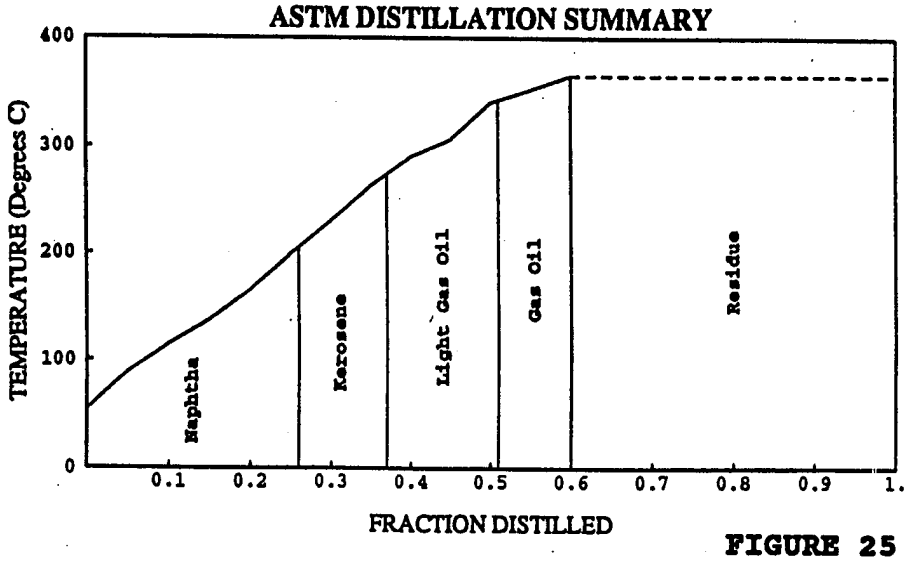

FIGURE 25

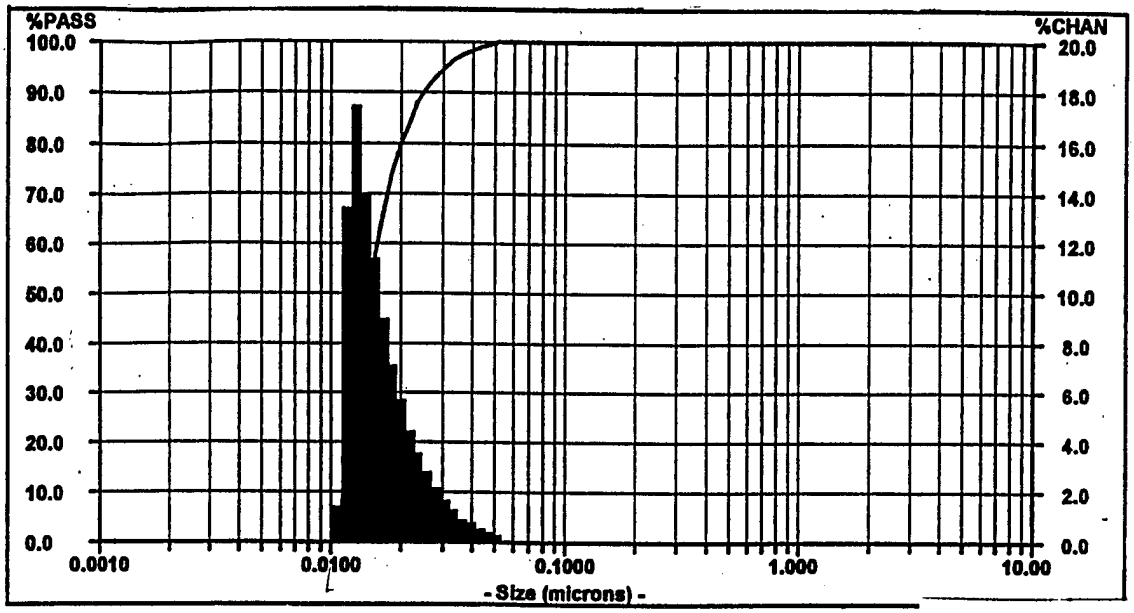

FIGURE 26

INTERNATIONAL SEARCH REPORT

I. ,national Application No
PCT/CA 98/00300

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01D17/02 B01D61/14 B01D63/02 B01D69/08 C02F1/44
E02B15/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01D C02F E02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 00119 A (SUTHERLAND GEORGE) 4 January 1996 see page 3, line 7 - page 5, line 3 see page 11, last paragraph - page 14, line 5 see page 14, paragraph THIRD - page 16, line 17 see page 18, paragraph SECOND - page 19, paragraph SECOND; claims 1-3,13-15,20-22; figures 1-5,7,8,10	1-25
X	WO 94 15702 A (SARTORIUS GMBH ;GRABOSCH MATTHIAS (DE)) 21 July 1994 see page 4, line 5 - page 5, line 18 see page 7, line 3 - page 8, line 4; figures 1-3	1-4,11, 12,16

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
18 September 1998	29/09/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Edmueller, P

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INTERNATIONAL SEARCH REPORT

national Application No
PCT/CA 98/00300

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 886 603 A (TAYLOR JOHN A) 12 December 1989 cited in the application see column 2, line 61 - column 4, line 19 see column 4, line 54 - line 19	1-4,11, 12,14,16
A	US 4 229 297 A (NOHMI TAKASHI ET AL) 21 October 1980 cited in the application see the whole document	1-25

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/CA 98/00300

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