Dec. 28, 1954 A. W. FRANCIS 2,698,276

SOLVENT EXTRACTION

Filed June 20, 1952 4 Sheets-Sheet 1

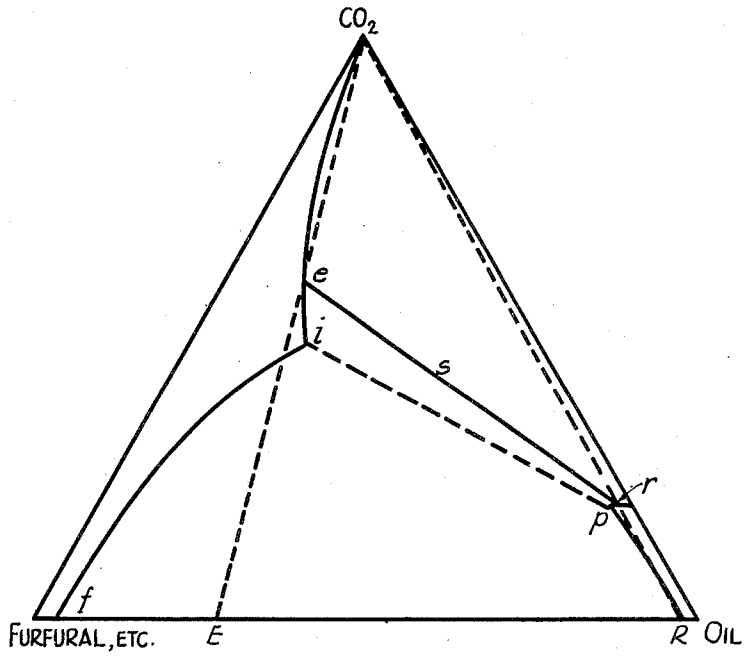


Fig. 1

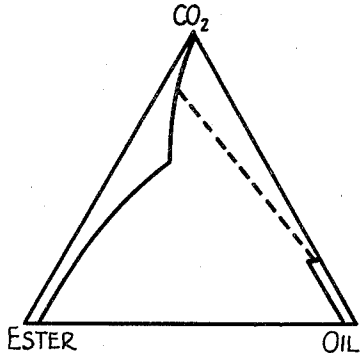


Fig. 2

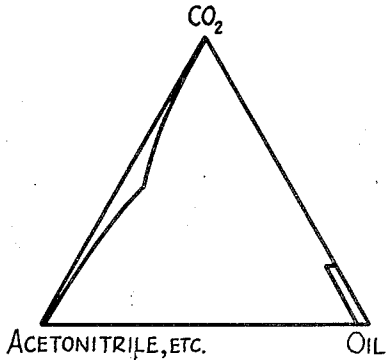


Fig. 3

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SOLVENT EXTRACTION

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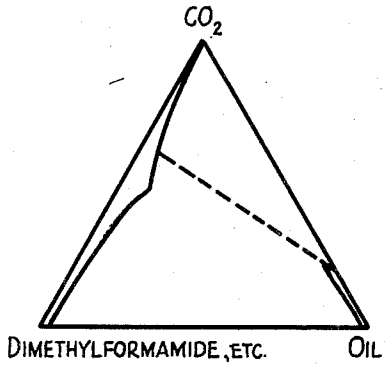


Fig. 4

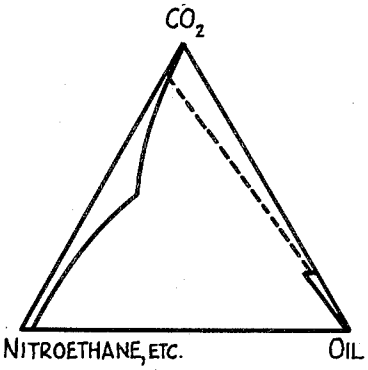


Fig. 5

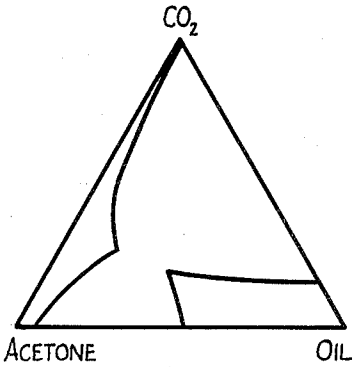


Fig. 6

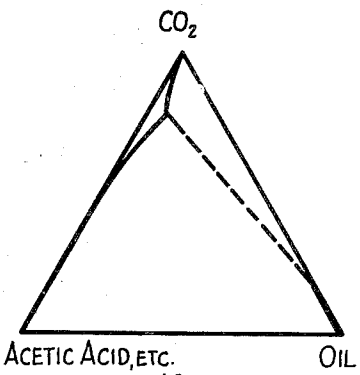


Fig. 7

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SOLVENT EXTRACTION

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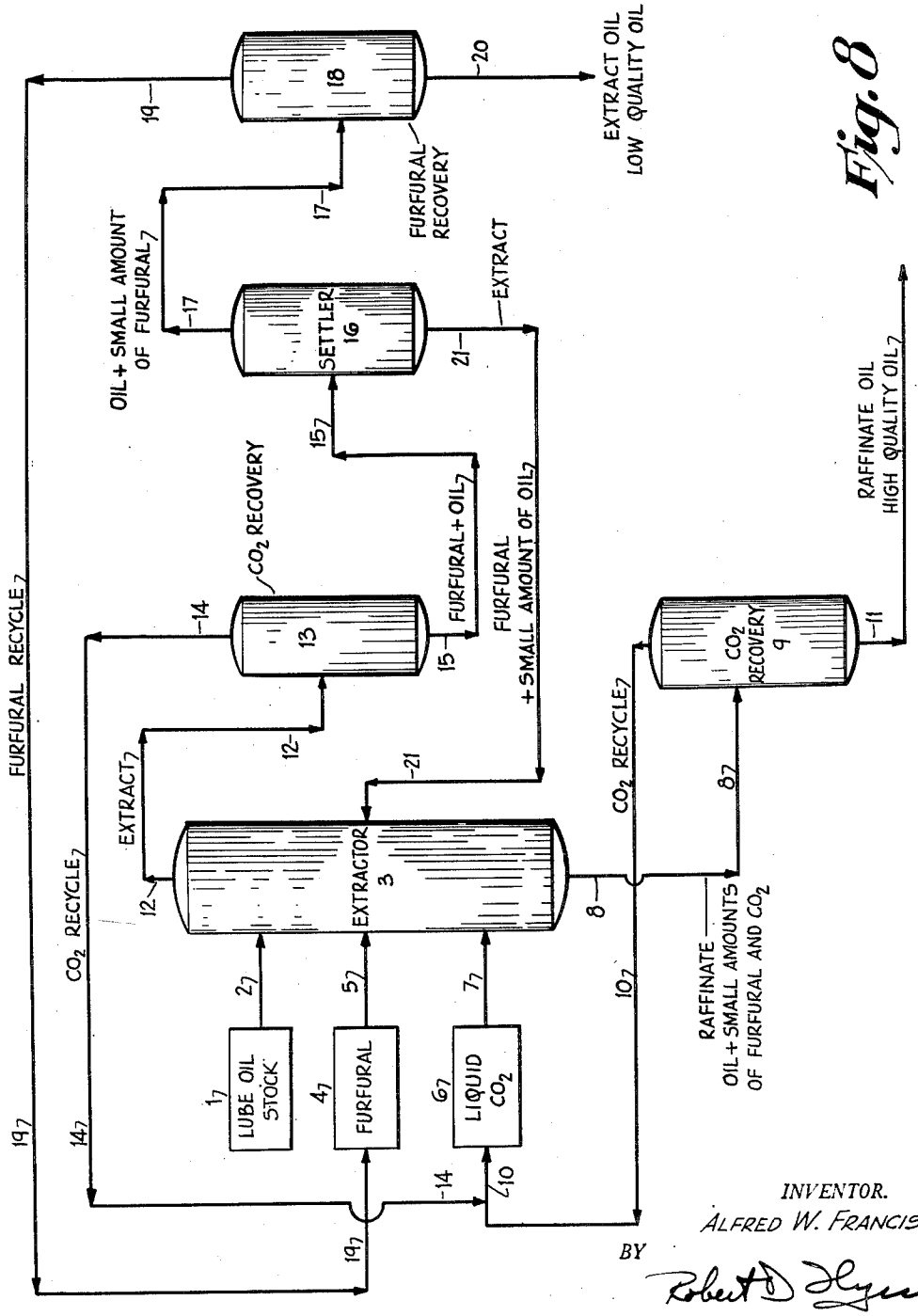


Fig. 8

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SOLVENT EXTRACTION

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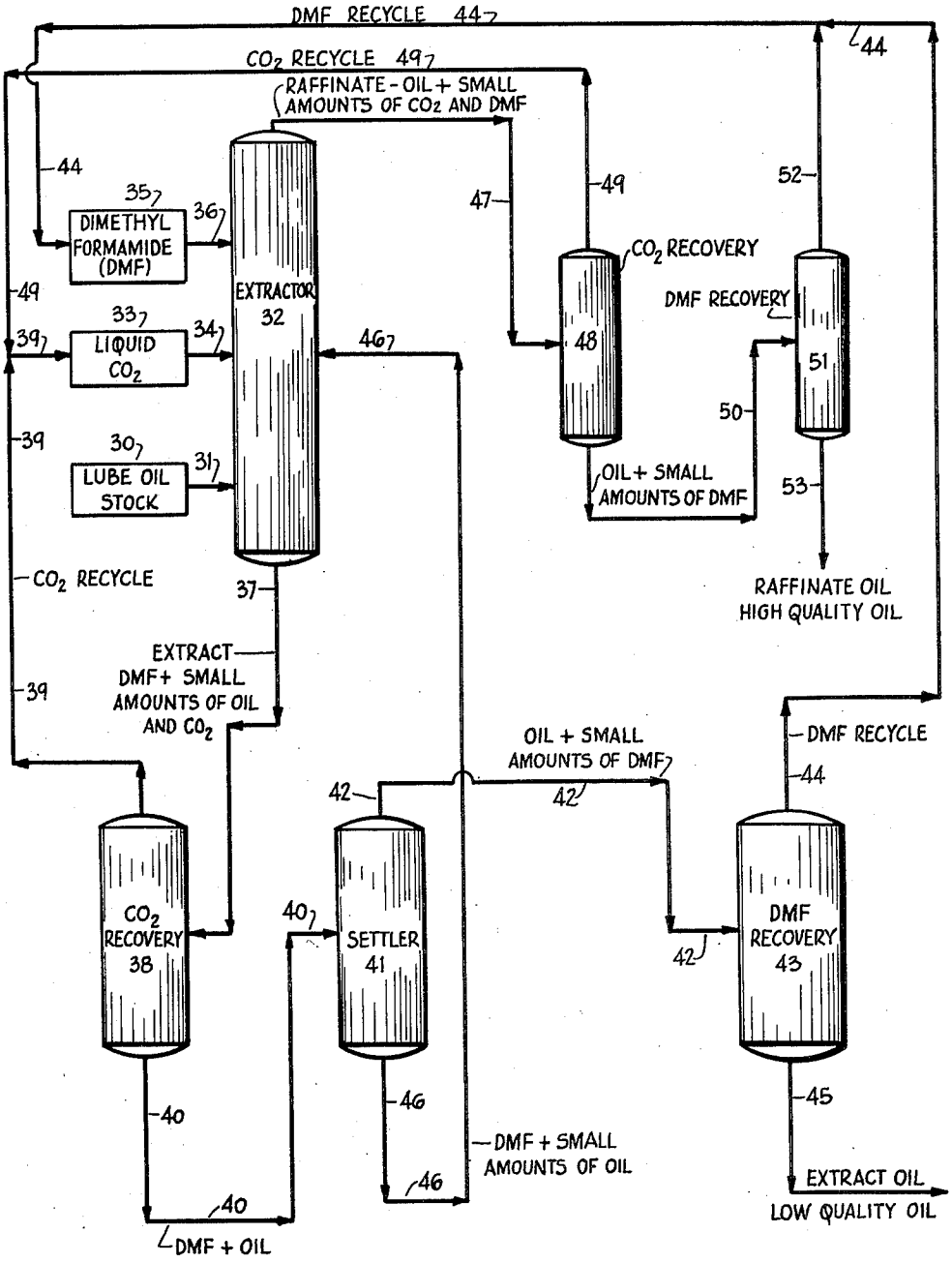


Fig. 9

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United States Patent Office 2,698,276
Patented Dec. 28, 1954

2,698,276

SOLVENT EXTRACTION

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Application June 20, 1952, Serial No. 294,585

8 Claims. (Cl. 196—13)

The invention has to do with extraction with certain selective solvents of various mixtures, and particularly hydrocarbon mixtures such as lubricating oil stocks, to separate the mixtures into fractions having different properties.

This application is a continuation-in-part of application Serial No. 160,619, filed May 8, 1950, now Patent Number 2,631,966, issued March 17, 1953.

Solvent extraction is commonly used in refining lubricating oils, the most generally used solvents being nitrobenzene, furfural, phenol, sulfur dioxide, chlorex, and propane-cresylic acid. The choice has been based mainly on cost, solubility of oil in solvent, and ease of recovery. The recovery is usually by distillation; and this operation limits (1) the boiling point of the solvent, which must be substantially below that of the oil, and (2) the volume of solvent, all of which must be distilled before recycling the solvent. This means that the solubility of oil in the solvent should not be too low.

One of the above-mentioned solvents, furfural, and several other solvents which might otherwise be considered, such as acetonitrile, nitromethane, and acetic acid, have a low solvent power for lubricating oil stocks, about three per cent in the case of furfural at ordinary temperatures. This solubility is increased somewhat at higher temperatures, but it is still necessary to distill all of the furfural (several times the volume of oil) each time the solvent is used. The process of the present invention employs liquid carbon dioxide to increase greatly the solubility of oil in the solvent and so to diminish the amount of furfural (or other solvent) used and also to avoid the necessity of distilling most of the solvent.

Liquid carbon dioxide has unusual miscibility relations with hydrocarbons and other substances. While liquid carbon dioxide is favored by low cost, non-corrosiveness, non-toxicity, and ease of recovery from extract and raffinate phases, its use is limited by its complete miscibility with most gasoline hydrocarbons, and on the other hand by its slight solubility for lubricating oils. For example, it has been shown that the maximum solubility for a typical lubricating oil in liquid carbon dioxide is only 0.9 per cent at 10° C.; and at 25° C., the solubility is only 0.72 per cent. To one skilled in the art, it is obvious that these solubilities are too low for practical purposes.

Carbon dioxide has a critical temperature of 31.1° C. (88° F.).

This invention is predicated upon the discovery of an advantageous and practical solvent extraction procedure in which liquid carbon dioxide is used in combination with certain solvents with which it cooperates.

I. PRIOR ART

One of the first to extract oils with liquid carbon dioxide was Auerbach. As shown by Auerbach in U. S. Letters Patent 1,805,751 and related foreign patents (Canadian 285,782, and British 277,946 and 285,064), certain light lubricating oil fractions are soluble in liquid carbon dioxide to the extent of only about three per cent. Schilling and Stadler (2,029,120) also described a selective separation with liquid carbon dioxide, showing the removal of unsaturated hydrocarbons from gas mixtures.

Several investigators have also described a selective separation of hydrocarbons in which liquid carbon dioxide is used in combination with liquid SO_2 (2,034,495—

e. g., extraction of light gasoline; 2,346,639; German 546,123). Refining of petroleum fractions to effect removal of sulfur compounds, using SO_3 in combination with liquid carbon dioxide is disclosed by Gary (1,893,138).

Milmore (2,130,147) has described solvent extraction techniques in which a hydrocarbon mixture containing a solvent such as chlorex, is treated with a low molecular substance in the para-critical state in order to precipitate out one or more hydrocarbon fractions. One such low molecular substance is carbon dioxide.

Pilat and Godliewicz (2,188,013 and 2,315,131) have also extracted hydrocarbon mixtures with a conventional solvent and a gaseous treating agent such as a hydrocarbon or carbon dioxide. The gaseous treating agent, such as CO_2, is used in small amounts under conditions at which it is incapable of being liquefied. Similarly, if a naphthenic solvent such as liquid SO_2, furfural or the like, is used, it is employed in small quantity in order to substantially saturate the oil without causing the oil to separate into two phases at the treating temperature. This imposes a severe limitation upon the amount of furfural, for example, which can be used; generally, only about two per cent by weight of furfural can be used under such conditions.

Low molecular weight paraffins, such as propane or isopentane, have also been used with liquid carbon dioxide in extracting hydrocarbon mixtures. This is shown by Lantz (2,188,051) and by Webb (2,246,227). The processes described by these patentees are essentially precipitation processes, rather than simple extractions. Lantz points out: "It will be noted that as progressively larger quantities of liquid carbon dioxide are used, the amount dissolved therein decreases." Webb makes a very similar statement.

Typical of the diluents shown by Webb (2,246,227) for use with liquid carbon dioxide are: hydrocarbons such as propane; solvents such as acetone, pyridine, liquid SO_2, cresylic acid and other solvents of the type of preferential solvents for non-paraffinic hydrocarbons. A similar disclosure is found in 2,281,865 (Van Dijck); used with liquid carbon dioxide are hydrocarbons and solvents known as selective or naphthenic (or aromatic) solvents such as furfural, nitrobenzene, chlorex, cresylic acid, phenol, aniline and quinoline. The solvents used by Van Dijck are necessarily employed in relatively small quantities, actually only those quantities which are miscible with an oil. In the cases of furfural, aniline and phenol, the quantities used are minute—of the order of one or two per cent. One salient feature of the Van Dijck process is change in solubility relationships affected by pressure changes, with pressures used being sufficiently high, as 1200–1800 p. s. i., to preclude the formation of a gas phase.

II. OUTLINE OF INVENTION

It has now been discovered that solvent extraction refining procedures in which certain solvents (S) are used, or might otherwise be considered suitable, are made much more efficacious by the use therein of liquid carbon dioxide in combination with such solvents. In the process of this invention, liquid carbon dioxide is used in such quantities and with such solvents as to increase greatly the solvent power of the solvent for the hydrocarbon fractions which are treated therewith.

The solvents (S) with which liquid carbon dioxide is used, are characterized by: (1) complete miscibility with liquid carbon dioxide, and (2) a low solvent power for components of the mixture treated, such as a lubricating oil stock—generally, less than about five per cent (by weight) of such mixture will dissolve in the solvent.

The sequence of operations used in effecting separation of the several fractions includes:

(*a*) Contacting lubricating oil stock with liquid carbon dioxide and solvent (S) under pressure, whereupon a raffinate phase and an extract phase are formed;

(*b*) Separating the raffinate and extract phases under pressure;

(*c*) Removing carbon dioxide from the extract phase, whereupon two additional phases are formed upon set-

tling of the carbon-dioxide-free extract, the two new phases are substantially pure solvent (S) and the extract containing a relatively small amount of solvent (S);

(*d*) Separating the solvent (S) and the extract phase;

(*e*) Removing solvent (S) from the raffinate phase of (*b*), whereupon a high viscosity-index fraction is obtained;

(*f*) Removing solvent (S) from the extract phase of (*d*), whereupon a low viscosity-index fraction is obtained;

(*g*) Recycling the solvent (S) phase of (*d*) to the system such as at (*a*)—the solvent (S) need not be recovered before recycling.

III. OBJECTS

It is an object of this invention, therefore, to provide an effective means for separating a multiplicity of fractions or compounds of different properties from mixtures containing the same.

It is also an object of this invention to provide for the selective separation of several hydrocarbon fractions of different properties from hydrocarbon mixtures. An important object is the selective separation of several hydrocarbon fractions, differing in properties, from high molecular weight hydrocarbon mixtures, and particularly from lubricating oil stocks. A further object is to selectively separate polycyclic aromatic hydrocarbons from mixtures containing the same. Still another object is to selectively separate alkyl benzenes from mixtures containing the same.

An important object of the invention is the improvement of solvent extraction processes in which solvents of type (S) are used, by increasing substantially the solubility of an oil therein, by decreasing appreciably the amount of such solvent required for the extraction and by reducing or obviating the necessity for recovering such solvent by distillation.

Other objects and advantages of the invention will be apparent from the following description.

IV. INVENTION IN DETAIL

As indicated above, liquid carbon dioxide and a second solvent are used together in the selective separation process of this invention. Solvents used with liquid carbon dioxide and designated by the symbol (S), are miscible with liquid carbon dioxide and incompletely miscible with the mixture to be extracted. In addition, solvents in this group do not form solid salts with carbon dioxide at temperatures of 20° and greater. Preferably, too, if the solvent are not normally liquid, they should become so in contact with liquid carbon dioxide. This generally occurs if their melting points are less than about 60° C.

The solvent power of the solvent (S) is increased substantially by the addition to one part by weight thereof of amounts of liquid carbon dioxide varying from about 0.25 part (weight) to about 5 parts (weight), according to the particular solvent (S) used. Thus, the present process is distinctively different from earlier processes in which liquid carbon dioxide has been used with certain of the same co-solvents (S), such as sulfur dioxide. For example, Andrews and Fenske (2,346,639) have described their process with the following statements:

"The solvents employed usually contain two ingredients, one of which is a better solvent for the hydrocarbons than the other so that the dissolving capacity of the mixture can be varied by changing the ratio of the ingredients. . . . This range may be extended in the direction of lower dissolving capacity by mixing with the methylamine (or sulfur dioxide) a liquid, miscible therewith, which has a lower capacity for dissolving hydrocarbons. . . . These modifying solvents 'are chemically inert,' are soluble in them, and possess a lower dissolving capacity for a particular hydrocarbon type."

It is evident that Andrews and Fenske, and others, have contemplated intermediate solvent power for mixtures of two solvents. In no sense have they contemplated the possibility that mixtures of any two solvents might have much greater solvent power than either one alone, as I have discovered with liquid carbon dioxide and the co-solvents (S) described herein. This solvent power relationship is particularly remarkable inasmuch as the two solvents are mutually-inert chemically.

Included among the above-described class of solvents (S) are the following: furfural, triacetin, ethyl maleate, beta-chloroethylacetate, acetonitrile, ethanol, methanol, methyl formate, dimethylformamide, beta-methoxyethanol (methyl Cellosolve), chloroacetone, ethyl sulfate, nitroethane, sulfur dioxide, acetone, acetic acid, acetic anhydride, acetonylacetone, ethylene diformate, methyl sulfate and nitromethane.

The foregoing solvents and liquid carbon dioxide are effective in resolving various mixtures into a multiplicity of fractions, or compounds, of different properties. They are particularly advantageous in the resolution of lubricating oil stocks, representative of which are Pennsylvania, Mid-Continent and Coastal types, or paraffinic, naphthenic and aromatic types. Other hydrocarbon mixtures successfully treated include gas oils, fuel oils, shale oils, transformer oils, cable oils, coal tar fractions, etc. In general, therefore, hydrocarbon mixtures treated as described herein range from gas oils through lubricating oil stocks. The hydrocarbon mixtures are generally within the molecular weight range of about 150 to about 500.

The invention is illustrated by experimental data obtained with liquid carbon dioxide and solvents of type (S). These experimental data are presented in the form of charts, or more particularly ternary diagrams, identified here as Figures 1 to 7. These diagrams can be used to determine: the suitability of a solvent for a desired separation; the approximate selectivity of the solvents; the range of compositions of liquid carbon dioxide, solvent (S), and the mixture to be treated; and approximate number of stages or extractions necessary to effect a separation of desired degree; etc.

Figure 1 represents the system liquid carbon dioxide, furfural and lubricating oil. It is to be understood that in Figure 1 and in all of the ternary diagrams involving lubricating oil, the phase boundaries are necessarily approximate since the oil is not a pure substance. In fact, the purpose of the fractionations is to separate it into fractions of different properties, which include miscibilities with the solvents. Therefore, with countercurrent operation in extractor 3 of Figure 8 (described hereinafter), for example, the effective diagram of Figure 1 is appreciably different at the bottom and at the top of the extractor. At the top of the extractor, curve *f*—*i*—*e* CO_2 of Figure 1 is farther from the left side indicating a greater solubility. At the bottom of extractor 3, the reverse change appears. No substantial difference in temperature or pressure in different sections of the extractor is necessary.

The oil is a highly naphthenic distillate stock having the following properties:

A. P. I. gravity	23.80
Density	0.910
Refractive index, n_D^{20}	1.5076
Critical solution temperature (with aniline), °C	72
Pour point, °F	20
Flash (open cup), °F	395
Fire, °F	455
Viscosity, centistokes at 100° F	28.65
Viscosity, centistokes at 210° F	4.51
Viscosity gravity constant	0.871
Color, Lovibond	18

Figure 1 reveals that furfural and liquid carbon dioxide are completely miscible, that furfural has a low solvent power for the oil, and that liquid carbon dioxide has a low solvent power for the oil. The solubility of oil in furfural is three per cent at temperatures of the order of 20–25° C., as indicated by point *f* of Figure 1. This solubility is increased by the addition of liquid carbon dioxide. From three per cent at *f*, the solubility is increased to about sixteen per cent at *i*, by using about sixty per cent by weight of liquid carbon dioxide in the solvent mixture; similarly, the solubility is increased to about fourteen per cent at *e*, by using about seventy per cent of liquid carbon dioxide. A system *s* is assembled with about thirty per cent oil, twenty per cent furfural and fifty per cent carbon dioxide. This separates into two layers *e* (upper) an extract layer and *r* (lower) a raffinate layer.

Following separation of layers *e* and *r* and release of carbon dioxide (to E and R, respectively), about eighty per cent of the oil dissolved in the extract layer *e* is separated (at the top), leaving a dilute furfural solution *f* which is recycled without distillation. The only furfural which need be recovered by distillation or by other means is the relatively small amount dissolved in the raffinate R, and the small amount dissolved in the second oil layer (the extract-raffinate); about two per cent of furfural is pres-

ent in each of such layers. This represents a saving of about ninety per cent in distillation requirements over conventional furfural extractions.

The line *i—p*, represented by dashes, is an "isopycnic" or line connecting compositions *i* and *p* of liquid phases in equilibrium having equal densities. Such a line, shown also by dashes in Figures 2, 4, 5 and 7 (described hereinafter), occurs on these diagrams when the solvent is heavier than the oil, since carbon dioxide is lighter than the oil. The isopycnic may be at the kink of the curve, as in Figures 1 and 7, or elsewhere. It is of practical importance since an attempt at solvent extraction using a system of composition on an isopycnic would be prevented by failure of the phases to settle into layers. It should be noted that if a smaller proportion of liquid carbon dioxide were used, the extract would be on the curve *f—i* and the raffinate would be on the curve *p—r*, of Figure 1. In such case, the extract layer is heavier than the raffinate layer; and the flow sheet for such an operation would be similar to that of Figure 9 rather than that of Figure 8.

A ternary diagram similar to Figure 1 is obtained for the system: liquid carbon dioxide -triacetin -oil.

Figures 2 through 7, inclusive, are ternary diagrams of lubricating oil stocks and liquid carbon dioxide and other solvents of type (S) used in place of furfural.

Figure 2 shows the ternary system of liquid carbon dioxide and lubricating oil with ethyl maleate. A similar diagram is obtained when beta-chloroethyl acetate is used in place of ethyl maleate.

Figure 3 represents the systems formed by liquid carbon dioxide and lubricating oil, with such solvents as:

Acetonitrile
Ethanol
Methanol
Methyl formate

Figure 4 represents the systems formed by liquid carbon dioxide and lubricating oil, and a solvent from the following group:

Dimethylformamide
Beta-methoxyethanol

Figure 5 represents the systems formed by liquid carbon dioxide and lubricating oil, and a solvent such as:

Chloroacetone
Ethyl sulfate
Nitroethane
Sulfur dioxide

Figure 6: liquid carbon dioxide—acetone—lubricating oil.

Figure 7 represents the systems formed by liquid carbon dioxide and lubricating oil with one of the following solvents:

Acetic acid
Acetic anhydride
Acetonylacetone
Ethylene diformate
Methyl sulfate
Nitromethane

The data from which Figures 1–7 were prepared, were obtained with a visual autoclave, operating at room temperature, about 25° C. The autoclave is a Jerguson gauge of 116 parts by volume capacity, with thick narrow Pyrex glass windows front and back. Incandescent lamps are mounted behind the vertical position of the autoclave. Agitation of the materials is obtained by rotation of the autoclave, end-over-end, within a heat-insulated case. The latter is provided with strip heaters which permit heating by radiation, and with means for cooling to low temperature. The autoclave was charged with the liquid reagents, the carbon dioxide being introduced from a cylinder. Solubility of carbon dioxide in another liquid was estimated by charging a definite volume of that liquid and then adding carbon dioxide until after agitation a new liquid phase appeared (at the top). Then additional increments of liquid carbon dioxide were added. By extrapolation, the drop in equilibrium position of the interface could be used to estimate approximately the solubility of the other liquid in liquid carbon dioxide. If there was no separation into two liquid phases, the miscibility was considered to be complete only after about three volumes of carbon dioxide were added for one of the other liquids.

In each case the solvent (S) was removed from the raffinate by distillation or by washing with water or alkali, as appropriate to the solvent. The raffinate oil was light colored, less dense, and more paraffinic than the charge stock as shown by lower refractive index and higher critical solution temperature with aniline.

Additional illustrative examples of the invention are the following:

Example 1

Ten volumes of the lubricating oil stock described above, five volumes of acetone and twenty-one volumes of liquid carbon dioxide were charged to a visual autoclave. After agitating these materials for above five minutes at 25° C., two layers were obtained. The lower layer comprised thirteen volumes and the upper layer comprised twenty-three volumes. These layers were removed separately from the autoclave. Carbon dioxide was removed from the extract, and the carbon- dioxide-free extract was allowed to settle, whereupon an extract and an acetone phase formed. Acetone was removed from the extract and raffinate, whereby a low and a high quality oil were obtained, respectively.

Properties of the oil products, after removal of both solvents (carbon dioxide and acetone) are as follows:

	Refractive Index, n_D^{20}	Aniline Point, ° C.
Oil charge (ten volumes)	1.5076	72
Raffinate (two volumes)	1.5056	74
Extract (seven volumes)	1.5119	68

Example 2

Ten volumes of the lubricating oil stock described above, six volumes of liquid sulfur dioxide, and twenty-one volumes of liquid carbon dioxide were charged to a visual autoclave, and were agitated therein for about five minutes at 25° C. Two layers were formed. The lower layer comprised twenty-five volumes and the upper layer comprised twelve volumes. The layers were withdrawn separately from the autoclave, and the solvents were evaporated therefrom. Properties of the oil fractions, after removal of the solvents (carbon dioxide and sulfur dioxide) are shown below:

	Refractive Index, n_D^{20}	Aniline Point, ° C.
Oil charge (ten volumes)	1.5076	72
Raffinate (nine volumes)	1.5063	73
Extract (one volume)	1.5136	66

Example 3

The lubricating oil described above was treated with a solvent mixture comprising about thirty per cent (weight) of furfural and about seventy per cent (weight) of liquid carbon dioxide, in the same manner as described in Examples 1 and 2, above. The results of this treatment are indicated by the following tabulated data:

	Refractive Index, n_D^{20}	Aniline Point, ° C.
Oil charge (20 volumes)	1.5076	72
Raffinate (13 volumes)	1.5037	76
Extract (7 volumes)	1.5256	60

In order that the invention may be more fully understood, typical separations are described below with reference being made to the drawings attached hereto.

In Figure 8, a charge such as a highly naphthenic lubricating oil stock, for example, one having a density of 0.910, a refractive index (n_D^{20}) of 1.5076 and a critical solution temperature (aniline) of 72° C., in tank **1** is introduced through line **2** to extractor **3**. Furfural in tank **4**, is introduced through line **5** into an intermediate section of **3**, and liquid carbon dioxide in tank **6** is introduced through line **7** to a lower section of **3** such that each solvent flows countercurrent to portions of the oil charge. For example, the solvent mixture comprises about thirty per cent of furfural and seventy per cent of

liquid carbon dioxide. It will be understood that the extractor 3 can comprise conventional countercurrent stage or tower extraction equipment. Contact of furfural and liquid carbon dioxide with the oil can also be aided by conventional packing material in extractor 3.

The temperature of the oil and solvents in extractor 3 should not be much greater than about 31.1° C., the critical temperature of carbon dioxide. Slightly higher temperatures, up to about 36° C., can be used in some cases because enough solvent (S) and/or hydrocarbon may dissolve in the carbon dioxide-rich phase to make it liquid above the critical temperature of pure carbon dioxide. This temperature condition can be realized by maintaining both the oil and solvents at the required temperature prior to introduction to the extractor 3, or the latter can be maintained at the required temperature by well known cooling or heat exchange means. The pressure in extractor 3 is maintained sufficiently high so as to maintain a phase rich in carbon dioxide in the liquid state.

The ratio of solvent components, liquid carbon dioxide to furfural or other solvent (S) in the extractor 3, is such that the solvent power for the oil is substantially greater than that of either of the individual solvents alone. For example, with furfural as the solvent (S), the ratio of liquid carbon dioxide to furfural, or related solvent (S), is generally between about 2:1 and about 1:2, preferably between about 3:2 and 2:3. However, with acetone as the solvent (S), the ratio of liquid carbon dioxide to acetone, if maintained from about 1:4 to about 4:1, and preferably from about 1:3 to about 1:2. Correspondingly, the ratio of liquid carbon dioxide to solvent (S) is from about 2:1 to about 5:1, and preferably from about 3:1 to about 4:1, when the solvent (S) is one of the following: acetic acid, acetonylacetone, ethylenediformate, methyl sulfate, or nitro-methane. The quantitative relationships between the quantities of solvents (S) and liquid CO_2 recited here are shown by the several ternary diagrams constituting Figures 1 through 7.

In the extractor 3, a raffinate phase and an extract phase are formed. The raffinate phase (the heavier phase) contains paraffins and naphthenes. Also present in the raffinate phase are small proportions of furfural and carbon dioxide. The raffinate phase is withdrawn from extractor 3 through line 8 to solvent recovery vessel 9. The raffinate is fractionated in 9, with the furfural and carbon dioxide being taken overhead through line 10 and recycled through vessel 6 and line 7. This fractionation can be accomplished by using high temperature, or it can be accomplished by countercurrent extraction with liquid carbon dioxide as described in copending application Serial No. 162,587, filed May 8, 1950, now Patent Number 2,646,387, issued July 21, 1953. A raffinate oil fraction is removed from 9 through 11; this fraction is high quality oil, that is, it has a substantially higher viscosity index than the original charge oil and other fractions thereof.

The extract phase in extractor 3 is removed through line 12 to vessel 13, which is equipped with suitable means for effecting release of carbon dioxide from the extract phase. For example, a heat exchange medium can be circulated through the wall of vessel 13 or through coils therein, to raise the temperature of the extract phase. Also, pressure reducing means can be provided. In vessel 13, then, carbon dioxide is removed through line 14 and recycled to reservoir 6 via line 10. In line 14, a condenser (not shown) is used when carbon dioxide is removed by applying heat to vessel 13, or a compressor (not shown) is positioned in line 14 when carbon dioxide is removed by pressure reduction. The extract phase, substantially free of carbon dioxide, is taken through line 15 to settler 16. When the extract phase is allowed to stand in settler 16, a further separation takes place, with the formation of a solvent phase (furfural) and an extract phase. The extract contains the low quality lubricating components of the charge and some furfural. This is taken through line 17 and fractionated in solvent recovery vessel 18. Again, the fractionation can be accomplished by distillation or by countercurrent extraction with liquid carbon dioxide. Furfural and carbon dioxide (if used) are taken overhead through line 19 and recycled to reservoir 4. The low quality oil is removed from 18 as a bottom product through line 20. The oil removed through line 20 has a substantially lower viscosity index than the original charge and other fractions thereof, and is suitable for use, for example, as an insecticidal oil.

The solvent phase (furfural) separated in settler 16 is recycled through line 21 to an intermediate section of extractor 3. There is no need to distill furfural and any residual carbon dioxide present in the solvent phase.

Figure 9 represents another typical separation, but one in which one or more of the phase relationships differ from those shown in Figure 8, above. The solvent (S) used in the separation illustrated by Figure 9 is dimethyl formamide (DMF); liquid CO_2 is the other solvent and the charge oil is the same as described in connection with Figure 8.

The charge oil in vessel 30 is introduced through line 31 to extractor 32. Liquid CO_2 in tank 33 is introduced through line 34 to an intermediate section of 32, and DMF in tank 35 is brought through line 36 to an upper section of 32. Here too, each of the solvents preferably flows countercurrent to portions of the oil charge.

A raffinate phase and an extract phase are formed in extractor 32. The extract phase is the heavier phase and comprises DMF and relatively small amounts of CO_2 and low quality components of the charge oil. The extract phase is taken from extractor 32 through line 37 to CO_2 recovery vessel 38. The extract is fractionated in 38, such that CO_2 is taken overhead therefrom through line 39 and is recycled through vessel 33 and line 34 to extractor 32. The extract phase, now substantially free of CO_2, is removed from 38 through line 40 to settler 41. Upon standing in settler 41, the extract phase separates into two layers. A solvent phase—DMF—and an extract phase are formed. The extract contains the low quality lubricating components of the charge oil and some DMF. This extract is taken through line 42 to solvent recovery vessel 43, wherein DMF is removed as an overhead product through line 44 and is recycled therethrough to extractor 32 via 35 and 36. Low quality oil is removed as a bottoms product from vessel 43 through line 45.

The solvent phase—DMF—in settler 41 is recycled through line 46 to an intermediate section of extractor 32. Again, there is no necessity for distilling DMF and any residual CO_2 therefrom.

The raffinate phase in extractor 32 is the lighter phase. This is removed through line 47 to CO_2 recovery vessel 48. The raffinate phase is fractionated in 48, with CO_2 being removed overhead through line 49 and being recycled via 39—33—34 to extractor 32. The substantially CO_2-free raffinate, comprising oil and a relatively small amount of DMF, is removed from vessel 48 through line 50 to DMF recovery vessel 51. DMF is fractionated overhead through line 52 and is recycled through 44—35—36 to extractor 32. Raffinate oil is removed from vessel 51 through line 53; this oil is high quality oil—of appreciably higher viscosity index than the original oil charge.

It will be recognized that the foregoing illustrations provided by Figures 8 and 9 are diagrammatic, and that pumps, heaters, coolers, heat exchangers, pressure vessels of various character can be employed.

As indicated above, carbon dioxide is used in liquid form, thus requiring the use of relatively low temperature and high pressures. In effect, the operating temperatures will be not more than slightly above the critical temperature of carbon dioxide, namely, 31.1° C., and preferably below it. While the temperature can be lowered considerably below 31.1° C. satisfactory operation has been realized with temperatures within the range of 10° C. to 35° C. Operating pressures are relatively high, generally about 1000 pounds per square inch (or 70 atmospheres). Usually, pressures are of the order of 600 to 1200 pounds per square inch, depending upon the temperatures employed.

I claim:

1. The process of separating a hydrocarbon mixture selected from the group consisting of hydrocarbon mixtures within the range of gas oils to lubricating oil stocks, into fractions at least one of which has a higher viscosity index than that of the original mixture, which comprises: contacting the mixture with liquid carbon dioxide and a solvent (S) under sufficient pressure to maintain a carbon dioxide-rich phase in the liquid phase, said solvent (S) being selected from the group consisting of furfural, triacetin, ethyl maleate, beta-chloroethyl acetate, acetonitrile, ethanol, methanol, methyl formate, di-

methyl formamide, beta-methoxyethanol, chloroacetone, ethyl sulfate, nitroethane and sulfur dioxide, said solvent (S) being incapable of being rendered miscible with said hydrocarbon mixture upon the addition thereto of liquid CO_2, the ratio of the quantity of liquid carbon dioxide to the quantity of solvent (S) being from about 2:1 to about 1:2 by weight, whereupon a raffinate phase and an extract phase are formed; effecting phase separation of the raffinate and extract under said pressure; removing carbon dioxide and solvent (S) from the raffinate phase, thereby obtaining a hydrocarbon fraction of higher viscosity index than that of the original hydrocarbon mixture.

2. The process as defined by claim 1 wherein the ratio of the quantity of liquid carbon dioxide to the quantity of solvent (S) is from about 3:2 to about 2:3.

3. The process as defined by claim 1 wherein the hydrocarbon mixture is a lubricating oil stock.

4. The process as defined by claim 1 wherein said solvent (S) is furfural.

5. The process as defined by claim 1 wherein the solvent (S) is liquid sulfur dioxide.

6. The process as defined by claim 1 wherein the solvent (S) is dimethyl formamide.

7. The continuous process of separating a hydrocarbon mixture selected from the group consisting of hydrocarbon mixtures within the range of gas oils to lubricating oil stocks, into fractions at least one of which has a higher viscosity index than that of the original mixture, which comprises: contacting the mixture with liquid carbon dioxide and a solvent (S) under sufficient pressure to maintain a carbon dioxide-rich phase in the liquid phase, said solvent (S) being selected from the group consisting of furfural, triacetin, ethyl maleate, beta-chloroethyl acetate, acetonitrile, ethanol, methanol, methyl formate, dimethyl formamide, beta-methoxyethanol, chloroacetone, ethyl sulfate, nitroethane and sulfur dioxide, said solvent (S) being incapable of being rendered miscible with said hydrocarbon mixture upon the addition thereto of liquid CO_2, the ratio of the quantity of liquid carbon dioxide to the quantity of solvent (S) being from about 2:1 to about 1:2 by weight, whereupon a raffinate phase and an extract phase are formed, effecting phase separation of the raffinate and extract under said pressure; removing carbon dioxide and solvent (S) from the raffinate phase, thereby obtaining a hydrocarbon fraction of higher viscosity index than that of the original hydrocarbon mixture; removing carbon dioxide from the extract phase; settling the extract phase substantially free of carbon dioxide, whereupon an extract and a solvent (S) phase are formed; effecting phase separation of said extract and said solvent (S) phase; and recycling directly to said contacting operation, said solvent phase.

8. The process as defined by claim 7 wherein the solvent (S) is furfural.

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