

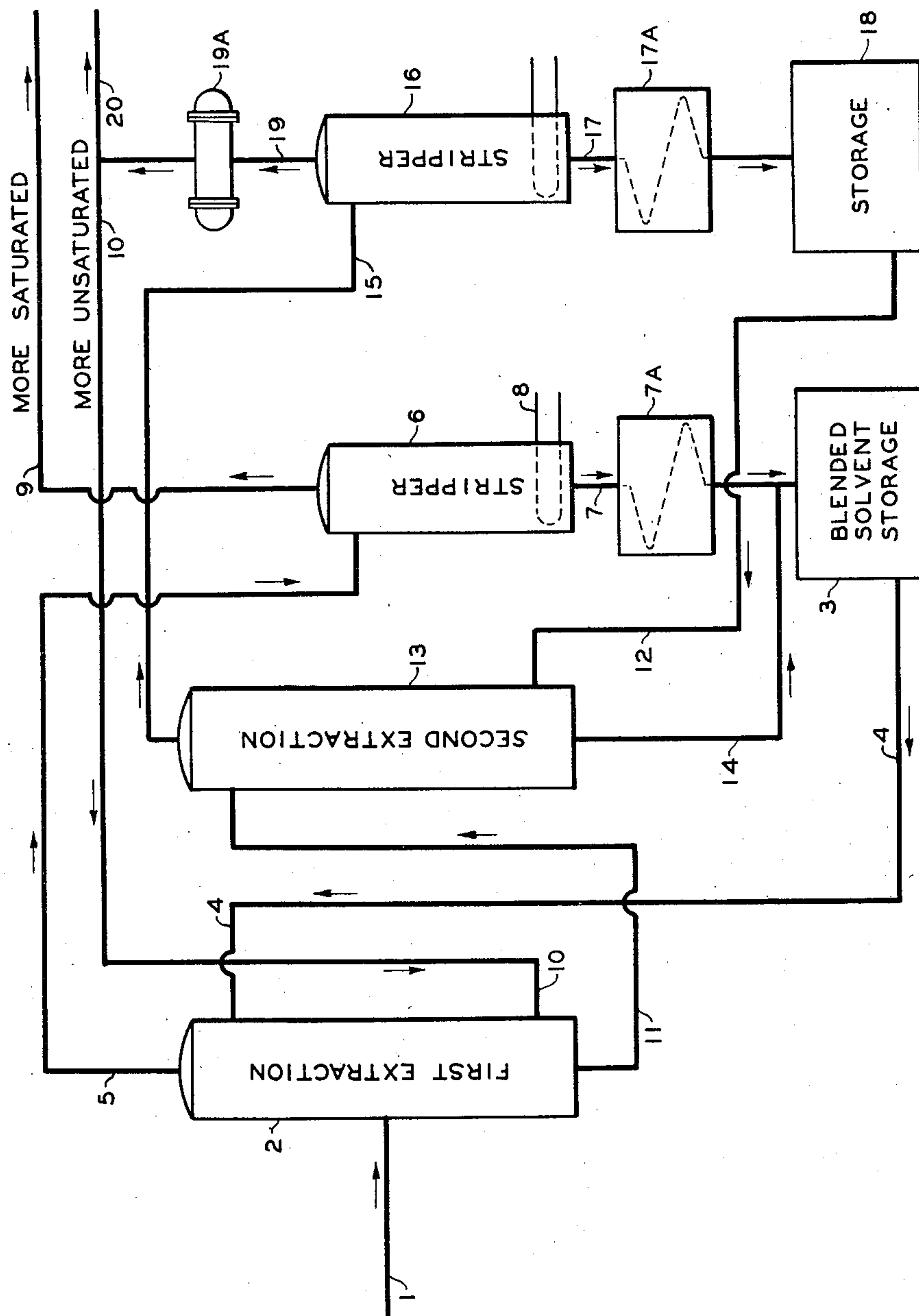
**Oct. 31, 1950**

**B. J. MAYLAND ET AL**  
**HYDROCARBON SEPARATION**

**2,527,951**

Filed Sept. 27, 1948

**2 Sheets-Sheet 1**



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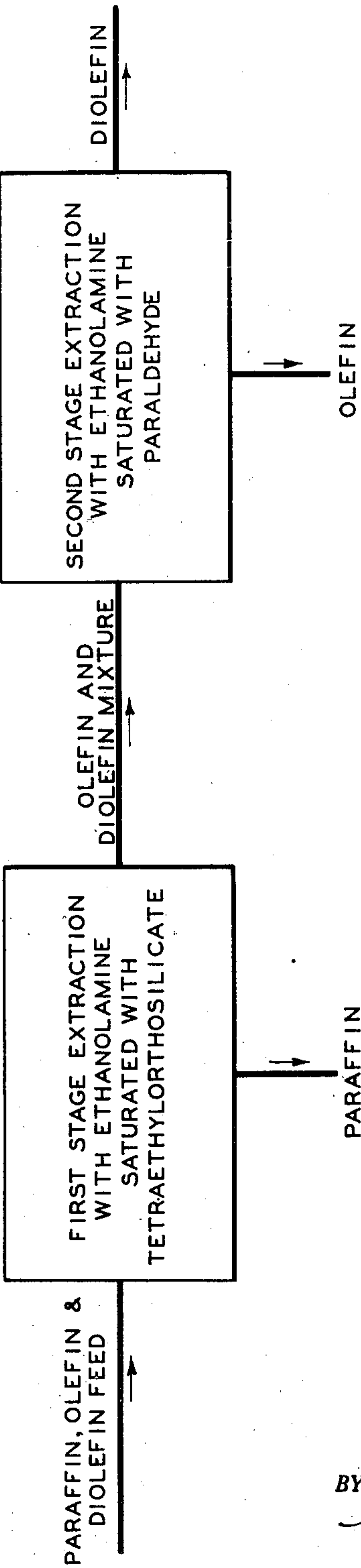


FIG. 2

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## UNITED STATES PATENT OFFICE

2,527,951

## HYDROCARBON SEPARATION

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Application September 27, 1948, Serial No. 51,444

7 Claims. (Cl. 260—681.5)

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This invention relates to a process for resolving mixtures of aliphatic hydrocarbons having at least three degrees of saturation. In a specific embodiment it relates to a process for resolving mixtures of aliphatic paraffin, olefin and diolefin hydrocarbons into the respective components. This invention is useful for the resolution of mixtures of butanes, butenes and butadiene.

This application is a continuation-in-part of our copending application, Serial No. 691,148, filed August 16, 1946, now U. S. Patent 2,484,305.

The separation of olefins or diolefins from paraffinic hydrocarbon streams to obtain a substantially pure paraffinic stream and unsaturated stream usually cannot be simply accomplished because of the close boiling range of the compounds and because of the tendency to form azeotropes. For example the separation of butadiene and butenes from n-butane by straight fractionation is not possible due to the formation of a constant boiling mixture between butadiene and n-butane. Similarly the separation of diolefins from olefins by ordinary fractionation is often not possible.

It has heretofore been attempted to solve this problem by the use of azeotropic or extractive distillation whereby another component is added to the system which makes possible fractionation by changing the relative volatilities of the hydrocarbon. If the added component goes overhead this method of separation is referred to as azeotropic distillation, and the added component is commonly termed an entraining agent. If the added material is removed in the kettle product, the process is known as extractive distillation, and the added material is termed a selective solvent. Generally, a greater change in relative volatilities is obtained by adding a component of higher selectivity. Polar compounds (i. e., compounds having a high dipole moment and a high internal solution pressure) are used as selective solvents for extractive distillation. In general, the greater the polarity of the selective solvent, the greater the selectivity but the lower the solvent power or capacity. To decrease the height of a column necessary to effect the desired separation a highly selective added component is desired as the selective solvent. On the other hand, the hydrocarbons must have a moderate solubility in the solvent to limit the amount of solvent required to be added and to keep the diameter of the column within reason. The polar solvent chosen represents a compromise between these two extremes; i. e., selectivity is sacrificed for solvent power or capacity.

An object of this invention is to provide an improved method for resolving mixtures of ali-

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phatic hydrocarbons having at least three degrees of saturation into the respective components of the mixture. Another object is to provide an improved method of resolving mixtures of aliphatic paraffins, olefins and diolefins into the respective components of the mixtures. It is a further object of this invention to resolve mixtures of butanes, butenes and butadiene by liquid-liquid extraction. Numerous other objects will appear more fully hereinafter.

The accompanying drawings portray diagrammatically one arrangement of equipment which has been found very satisfactory for carrying out liquid-liquid extraction as a means of separating aliphatic hydrocarbons of different degrees of saturation; the arrangement shown represents a preferred embodiment of our invention, but obviously other arrangements may be used without going beyond the scope of our invention.

The present invention provides a solution to the problem outlined above in that it makes available solvents having both high selectivity and good solvent power or capacity for the hydrocarbons. We have discovered that a solvent having greatly improved properties over ordinary polar solvents is obtained by blending a polar solvent with a solvent which exhibits compound-forming tendencies with the unsaturated hydrocarbons. The resulting solvent has improved selectivity over either of the solvents alone and greater solvent power or capacity for the hydrocarbons. The blended solvent may be used in an extractive distillation process of the type now well known in the art. In conventional extractive distillation, the mixture of aliphatic hydrocarbons of varying degrees of saturation ranging from diolefins to paraffins is fed continuously to a combined fractional distillation-extraction column at an intermediate point therein, the relatively non-volatile selective solvent is continuously introduced at the top of the column and flows downwardly therein, the bottom of the column is reboiled in the usual way to drive out any of the more saturated hydrocarbon dissolved therein and to supply the heat required for the distillation, the top of the column is refluxed by returning a portion of the condensed more saturated hydrocarbon taken overhead, and the solvent rich in more unsaturated hydrocarbon is continuously fed to a stripping column where the unsaturated hydrocarbon content is stripped from the solvent.

The blended solvents of the present invention may also be used in liquid-liquid extraction processes. For example, a mixture of two or more of paraffins, olefins and diolefins may be contacted countercurrently with a blended solvent in any suitable type of equipment such as a



vertical column provided with means of obtaining intimate contact such as baffles, packing, bubble trays, etc. The resulting extract consisting essentially of solvent and dissolved more unsaturated hydrocarbons may then be stripped in a separate zone to recover the more unsaturated hydrocarbons. The extracted hydrocarbon stream, i. e., the raffinate, is composed essentially of the more saturated hydrocarbon, which was undissolved by the solvent, together with a small amount of dissolved solvent. This raffinate may be stripped or otherwise treated to separate essentially pure more saturated hydrocarbon from the dissolved solvent.

We much prefer, however, to use a special liquid-liquid extraction process which we have discovered and which provides a large saving of heat over either extractive distillation or conventional liquid-liquid extraction processes. Such a special process is described in detail below.

It can be shown that the selectivity of a polar solvent depends on the degree of polarity as well as on the difference of polarity between the compounds being separated. In the order of increasing polarity the C<sub>4</sub> hydrocarbons are n-butane, butenes, and butadiene. These compounds actually are relatively non-polar and form non-ideal solutions with highly polar compounds. The differences in polarity of these hydrocarbons determine their relative deviation from ideal solution laws. Butadiene being more polar will be more soluble in a polar solvent than n-butane under comparable conditions of temperature, pressure and concentration.

Blending two polar solvents results in a polar mixture having a polarity somewhere between the polarity of the individual solvents. The mixture exhibits about the same degree of selectivity as a single solvent having a polarity corresponding to the mixture and the hydrocarbon solvent power or capacity is similarly related. Thus the solvent obtained by blending two polar solvents has little or no advantage over a single solvent of the same degree of polarity.

Some compounds show a tendency to form loose chemical compounds with the hydrocarbons. If this tendency is more pronounced with one type of hydrocarbon than with another or if the tendency is present with one of the hydrocarbon types and not with another, the solvent will have a certain amount of selectivity depending on the strength of the effect. A compound of this type may or may not be polar. If it is polar, the selectivity is due to the polarity as well as to the bonding tendency and the selectivity will be greater than that of an ordinary polar compound which does not exhibit the bonding tendency.

In accordance with our invention selective solvents for the separation of aliphatic hydrocarbons of varying degrees of saturation are made by blending a polar solvent having no bonding tendency or only poor bonding tendency with the unsaturates with a solvent having such bonding tendency with the unsaturates. The resulting mixture shows selectivity due to the resulting polarity of the mixture and due to the bonding tendency with the unsaturates and is greatly superior to either component by itself.

By the term "polar" as used herein we mean a compound having a high polarity, i. e. a compound in which a dissolved non-polar compound such as gaseous normal butane at atmospheric condition has a high activity coefficient, namely above 10. Methods of determining the activity coefficient of a compound such as normal butane

in solution are well-known to those skilled in the art and need not be detailed herein. The activity coefficient is a measure of the deviation of the solution from ideality, a coefficient of unity indicating ideality. A coefficient greater than unity indicates solubility or solvent power less than ideal (positive deviation), and a coefficient less than unity indicates solubility or solvent power greater than ideal (negative deviation).

In general the polar compounds used in practicing our invention do not exhibit a bonding tendency with unsaturates. Conversely the compounds exhibiting a bonding tendency with unsaturates used in accordance with the present invention are, generally speaking, non-polar.

We have found that blending highly polar solvents with relatively non-polar solvents that exhibit strong valence forces with the unsaturates is a means of approaching the ideal solvent.

The compound exhibiting bonding tendency may display such tendency with diolefins but not with olefins or paraffins or with both diolefins and olefins but not with paraffins. In the first case the resulting blended solvent may be employed to separate diolefins from olefins and/or paraffins. In the second case it may be employed to separate diolefins and/or olefins from paraffins.

For example a blended solvent consisting of ethanolamine saturated with tetraethylorthosilicate may be used to separate diolefins or olefins or both from paraffins in accordance with our invention. However a solvent consisting of ethanolamine saturated with paraldehyde has an activity coefficient of less than unity with butadiene but greater than unity with butene-1 and n-butane and therefore can be used to separate butadiene from butene-1 or n-butane or both.

The process of our invention may be defined as a two-stage process for resolving a hydrocarbon mixture containing at least one saturated aliphatic hydrocarbon, at least one unsaturated aliphatic hydrocarbon containing one double bond per molecule and at least one unsaturated aliphatic hydrocarbon containing at least two double bonds per molecule into the respective components. In the first stage the hydrocarbon mixture is intimately contacted with a blended solvent which will effect preferential solution of either the unsaturated hydrocarbons or the more unsaturated hydrocarbons, viz. those containing the two double bonds per molecule. As a consequence one of the hydrocarbon types in the mixture is separated from the other two types, and in the second stage the other two types are separated from each other by intimately contacting them with a selective solvent which will effect preferential solution of the more unsaturated of the two hydrocarbon types. Hence, the ultimate result of practicing our invention is a resolution of the hydrocarbon mixture into its respective components.

The second component, which is the compound that exhibits bonding tendencies, of the selective solvent of the present invention exhibits compound-forming tendencies with olefins or diolefins or both but is to be distinguished from a compound which actually forms compounds with olefins or diolefins. Examples of the latter type of compound are sulfur dioxide, cuprous salts, maleic anhydride. The compounds which we employ are generally characterized by being non-polar, i. e. in which n-butane has an activity coefficient greater than 1.0 but not greater than 2.0 and either butene or butadiene less than 1.0.



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The hydrocarbon separation may be conducted with the hydrocarbon mixture in either the vapor or liquid phase. Where the mixture is in the vapor phase simple gas scrubbing may be practiced but extractive distillation is preferable. We prefer liquid-liquid extraction. The temperature may range from the freezing point of the solvent or components thereof up to the point of complete miscibility between the solvent and the hydrocarbon mixture. Temperatures below the critical temperature of the hydrocarbon mixture should of course be employed. Generally the temperature of extraction will be atmospheric or substantially atmospheric.

The pressure may vary over wide limits but should be sufficient to hold the hydrocarbon mixture in the liquid phase in order that liquid-liquid extraction may be practiced. At ordinary atmospheric temperatures of, say, 60 to 110° F., pressures of the order of 80 to 200 pounds per square inch gauge will be sufficient to prevent appearance of a gaseous phase to any appreciable extent.

The relative amounts of the blended solvents and the hydrocarbon feed employed will depend upon the concentration of the hydrocarbon to be preferentially separated. It is of course preferable to use enough solvent to dissolve a substantial proportion or all of the hydrocarbon to be separated. In the interest of economical operation the amount of solvent should preferably be kept as close as is practical to the minimum required to dissolve completely the hydrocarbon to be separated.

We have found it highly desirable and advantageous to carry out the separation steps in vertical elongated columns or contacting zones, introducing the hydrocarbon mixtures to be separated at an intermediate point in these columns and the solvent at one end, most conveniently at the top, contacting the feed countercurrently with the feed in one end of the extraction zone and passing the resulting extract past the feed entry into the other portion, usually the lower, of the zone, and to introduce near the other end of the extraction zone a continuous stream (which may be termed "reflux") of more unsaturated hydrocarbon or hydrocarbons separated from the resulting extract. Introduction of this more unsaturated stream effects displacement from the solvent of any dissolved more saturated hydrocarbon and gives a much purer fraction of more unsaturated hydrocarbon or hydrocarbons.

The raffinate from the extraction step consists essentially of the more saturated hydrocarbon or hydrocarbons containing a small amount of dissolved solvent. This may be stripped to recover the more saturated hydrocarbon or hydrocarbons.

The extract consists essentially of the more unsaturated hydrocarbon or hydrocarbons dissolved in the solvent. While this may be stripped directly to give a fraction consisting essentially of the more unsaturated hydrocarbon or hydrocarbons we have found it much superior to extract the extract with a solvent composed chiefly of the component of the blended solvent which exhibits bonding tendencies with the unsaturated hydrocarbon content of the extract. This effects transfer of the more unsaturated hydrocarbon or hydrocarbons from the original extract to the second solvent leaving a raffinate consisting essentially of the blended solvent suitable for recycle to the first extraction. Upon

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stripping the resulting extract the more unsaturated hydrocarbon or hydrocarbons is obtained. A portion of this is withdrawn as the more unsaturated hydrocarbon product of the process and the balance is returned for injection as "reflux" into the first extraction zone as described above.

Extraction of the first extract with the single component of the blended solvent in the manner just described effects great savings in heat since the large amount of blended solvent in the first extract is replaced by a relatively small amount of the single solvent. The single solvent is capable of dissolving very much more of the more unsaturated hydrocarbon or hydrocarbons. In fact the single solvent is generally completely miscible in all proportions with aliphatic unsaturated hydrocarbons. Thus, the second extraction greatly reduces the volume of solvent associated with the more unsaturated hydrocarbon or hydrocarbons and effects a correspondingly great saving in the heat required for stripping.

We have found that tetraethylorthosilicate exhibits a bonding tendency with olefins and diolefins but not with paraffins. The bonding tendency of this compound is shown by the following tabulation which gives the solubility of three gaseous C<sub>4</sub> hydrocarbons in this compound and their calculated activity coefficients.

[85° F., 1 atm., 5 ml. solvent.]

	Ml. of Gaseous Hydrocarbon Absorbed	Activity Coefficients
n-Butane.....	268.9	1.15
Butene-1.....	256.4	0.992
Butadiene-1,3.....	325.6	0.883

An activity coefficient less than unity indicates negative deviation from ideal solution laws and is an indication of attraction between the solvent and hydrocarbon. This attraction is called loose chemical bonding but may be thought of as simply an attraction between unlike molecules. Whereas n-butane shows positive deviation, the unsaturated hydrocarbons show negative deviation.

We have found that blending tetraethylorthosilicate with a polar solvent not exhibiting a bonding tendency with the unsaturated hydrocarbons gives a solvent having greater selectivity than either solvent alone and greater solubility or solvent power for the hydrocarbons than the polar solvent. A typical polar solvent, namely ethanolamine, was blended with tetraethylorthosilicate by saturating the ethanolamine with tetraethylorthosilicate. The resulting blend was compared with ethanolamine by itself for the relative solubility of the three gaseous C<sub>4</sub> hydrocarbons. The following tabulation shows the results which were obtained.

[85° F., 1 atm., 5 ml. solvent.]

	Ethanolamine		Ethanolamine saturated with tetraethylorthosilicate at 70° F.	
	Ml. of gaseous Hydrocarbon dissolved	Relative Solubility	Ml. of gaseous hydrocarbon dissolved	Relative Solubility
n-Butane.....	5.65	1.00	6.7	1.00
Butene-1.....	12.55	2.22	15.7	2.34
Butadiene-1,3.....	30.7	5.43	37.9	5.66



It will be seen that the blended solvent has a selectivity between paraffins and the unsaturates greater than either solvent alone. The solubility of the hydrocarbon in the blended solvent is greater than in the polar solvent alone. In addition, whereas the greater amount of hydrocarbon dissolved in the blended solvent tends to decrease the selectivity, actually the selectivity is shown to be greater. Other polar compounds may be used instead of ethanolamine. Ethanolamine is a good example because it has high selectivity but it is of doubtful usefulness by itself because of low solubility for the hydrocarbons. The presence of the tetraethylorthosilicate increases its capacity for dissolving hydrocarbons and also increases its selectivity between paraffins and unsaturates.

We have found that paraldehyde tends to form loose chemical compounds (i. e. exhibits a bonding tendency) with diolefins but not with olefins or paraffins. This is indicated by the data below where butadiene-1,3 has an activity coefficient of less than unity in the hydrocarbon-paraldehyde system whereas butene-1 and n-butane show positive deviation and so do not tend to form loose chemical compounds with the solvent.

[Vapor-Liquid Equilibrium 180° F., 100 p. s. i. a.]

	Gas Phase, Mol. Per Cent	Liquid Phase, Mol. Per Cent	Activity Co- efficient
Butadiene-1,3.....	22.2	13.9	0.91
Butene-1.....	50.9	27.4	1.015
n-Butane.....	25.2	13.2	1.220
Paraldehyde.....	1.7	45.3	-----

This solvent by itself would be useless for liquid-liquid extraction operations because it is miscible in all proportions at ordinary temperatures. However, by blending with a polar solvent to cut down the solubility, the selectivity due to formation of loose chemical bonds of the diolefin plus the selectivity due to the polarity of the solution is obtained and the degree of miscibility can be adjusted.

For example, the solvent ethanolamine, a polar compound characterized by low solubility for hydrocarbons, was saturated with paraldehyde and tested for selectivity. The following tabulation compares the blended solvent with pure ethanolamine.

[85° F., 1 atm., 10 ml. solvent.]

	Ethanolamine		Ethanolamine Saturated with Paraldehyde at 75° F.	
	Ml.	Relative Sol.	Ml.	Relative Sol.
n-Butane.....	11.3	1.00	13.4	1.00
Butene-1.....	25.1	2.22	27.2	2.03
Butadiene-1,3.....	61.4	5.43	76.0	5.67

From the data it will be seen that the selectivity of the blended solvent is greater than either solvent alone with respect to n-butane and butadiene and much greater with respect to butene and butadiene. The solubility is also greater than ethanolamine alone. The blended solvent is better for the separation of the diolefin from the olefin and paraffin than either of the single solvents because it has greater selectivity, is not completely miscible with the hydrocarbons, and yet has a greater capacity for dissolving hydrocarbon than the polar solvent.

The above data concerns C<sub>4</sub> hydrocarbons but

the principle of blending the solvents of the present invention can be applied to any mixture of saturated and unsaturated aliphatic hydrocarbons. Usually, if not always, the hydrocarbon mixture treated by the process of the present invention will consist of hydrocarbons having the same number of carbon atoms per molecule, because it is a simple matter to separate hydrocarbons having different numbers of carbon atoms per molecule by ordinary fractional distillation. The hydrocarbon mixtures treated may range from C<sub>2</sub> to C<sub>8</sub> or even higher. Generally a C<sub>4</sub> or a C<sub>5</sub> hydrocarbon stream will be treated by the present invention.

Practically any polar solvent may be employed in carrying out the present invention. As stated above we prefer to use a highly polar compound, i. e. a compound in which normal butane at atmospheric condition exhibits an activity coefficient greater than 10. Examples of such highly polar compounds are: ethanolamine, furfural, furfuryl alcohol, aniline, nitrobenzene, phenyl hydrazine, methyl sulfate, ethylene chlorohydrin, tetraethylene pentamine, diethylene glycol monoethyl ether, levulinic acid, o-anisidine, triethylene glycol, B-hydroxypropionitrile.

Instead of tetraethylorthosilicate and paraldehyde, we may employ other solvents having a bonding tendency with hydrocarbon, but not with saturated hydrocarbons. Examples of other solvents are: 1,1-bis-tert-butyl mercapto ethane, tert-dodecyl thioacetate, dioctyl disulfide, diethyl carbitol. In order to practice our two-stage process one of the solvents exhibiting a bonding tendency must exhibit such tendency with unsaturated aliphatic hydrocarbons in preference to saturated aliphatic hydrocarbons, and the other of such solvents must exhibit its bonding tendency with more unsaturated aliphatic hydrocarbons in preference to less unsaturated aliphatic hydrocarbons.

While the preferred solvents for use in carrying out the present invention are saturated solutions of tetraethylorthosilicate and paraldehyde in ethanolamine, we may employ other blends of polar solvents and solvents exhibiting a bonding tendency with unsaturates. The blend should contain a substantial amount of each solvent. Preferably the solvent will consist of the polar solvent saturated with the solvent exhibiting bonding tendency with the unsaturates.

The blended solvents of the present invention may be employed in extractive distillation processes for the separation of aliphatic hydrocarbons of differing degrees of saturation such as paraffins and unsaturates. However, liquid-liquid extraction possesses a number of economical advantages over extractive distillation and is therefore more desirable. Liquid-liquid extraction has not been used heretofore on a commercial scale for the separation of aliphatic hydrocarbons of different degrees of unsaturation. As pointed out above, it is probable that the reason for this failure to use liquid-liquid extraction processes is the limited hydrocarbon solubility in the selective solvents heretofore available. The present invention overcomes this drawback and makes feasible the use of liquid-liquid extraction for this type of separation.

The drawings show in simplified flow diagram how the separation of a mixture of aliphatic hydrocarbons of different degrees of saturation may be accomplished using the blended solvents of the present invention with a double liquid-liquid extraction process which results in a great saving of



heat over either extractive distillation or simple liquid-liquid extraction.

Referring to Figure 1, a feed stream of aliphatic hydrocarbons to be separated and comprising, for example, paraffins together with olefins and diole-  
fins, is fed via line 1 into the center of a multiple  
stage liquid-liquid contacting column 2 operated  
at a pressure sufficient to maintain liquid condi-  
tions. The blended solvent, typically a polar  
compound, such as ethanolamine, saturated with  
tetraethylorthosilicate is fed from storage 3 via  
line 4 into column 2 near or at the top and con-  
tacted countercurrently with the rising hydrocar-  
bon stream. The upper section of column 2 (i. e.  
the part above the point of feed entry) acts as a  
stripping section where the unsaturates are near-  
ly all or completely removed from the hydrocar-  
bon stream. The overhead stream, constituting  
the raffinate, is removed via line 5. This raffinate  
consists essentially of paraffin hydrocarbon and  
dissolved solvent constituents. The paraffinic  
hydrocarbon is recovered as a nearly pure stream  
by stripping the raffinate in a distillation column  
6. The resulting bottoms product, consisting es-  
sentially of recovered solvent components may be  
returned via line 7 to blended solvent storage 3.  
The solvent may be cooled in cooler 7A prior to  
its return. As is usual, stripper column 6 is pro-  
vided with a reboiler 8 and the feed to the column  
is introduced at the top. The stripped essentially  
pure paraffinic hydrocarbon overhead is with-  
drawn from column 6 via line 9. A portion of  
this overhead stream may be condensed and re-  
turned as reflux (not shown) to the top of column  
6. Of course, enough solvent must be used in the  
extraction conducted in extractor 2 so that all the  
non-polar constituent, tetraethylorthosilicate in  
this case, is not dissolved in the hydrocarbon  
stream 5 from the extractor 2.

The lower part of extraction column 2 (i. e.  
the portion below the point of entry of feed line  
1) acts as an enriching section whereby the sol-  
vent from the stripping section is contacted with  
a hydrocarbon reflux stream consisting essential-  
ly of the unsaturated hydrocarbons and intro-  
duced near or at the bottom of column 2 via line  
10. The stream withdrawn via line 11 from the  
bottom of column 2 consists essentially of mixed  
solvent and dissolved unsaturates. The unsat-  
urated hydrocarbons may be recovered by a strip-  
ping operation at this point but the amount  
of solvent is large and the heat consumption  
would be excessive.

We have found that a large saving in heat  
consumption may be effected by carrying out an-  
other extraction by contacting the stream flow-  
ing in line 11 with a stream of tetraethylortho-  
silicate introduced via line 12 to a second multiple  
stage liquid-liquid extracting column 13. This  
gives a stream of polar solvent saturated with  
tetraethylorthosilicate (raffinate), withdrawn  
from column 13 via line 14 and a stream of tetra-  
ethylorthosilicate saturated with the polar solvent  
and containing the unsaturated hydrocarbons  
(extract), withdrawn via line 15. The raffinate  
is returned via line 14 to blended solvent storage  
3. The extract is passed via line 15 to distillation  
column 16 which serves to strip the unsaturated  
hydrocarbons from the solvent. The stripped  
solvent is returned via line 17 and cooler 17A  
to tetraethylorthosilicate solvent storage 18.

The unsaturated hydrocarbons stripped in col-  
umn 16 is withdrawn overhead via line 19. Con-  
denser 19A may be employed to cool and condense  
the overhead vapors. A portion of the resulting

liquid condensate may be returned as reflux (not  
shown) to the top of stripper 16. The balance of  
the condensate is split into two streams, one  
stream being returned via line 10 to the bottom  
of extractor 2 and the other stream being with-  
drawn via line 20 as the unsaturated hydrocarbon  
product of the first stage of our process.

An important advantage of the second extrac-  
tion carried out in extractor 13 is that, tetra-  
ethylorthosilicate being completely miscible with  
the hydrocarbon, the second extraction greatly  
reduces the volume of solvent associated with the  
hydrocarbon before the stripping operation car-  
ried out in column 16 thus resulting in a large  
saving in the heat required for the stripping.

It is noted that whereas the feed line 1 enters  
the first extractor 2 at an intermediate point  
therein, say at or near the mid-point, the result-  
ing extract flowing in line 11 enters the second  
extractor 13 at a point adjacent the top thereof.  
The reason for this is that column 2 is effecting  
a separation between paraffins and unsaturates  
and embodies an upper or stripping section  
wherein the unsaturates are substantially com-  
pletely removed from the hydrocarbon stream and  
a lower or enriching section wherein the down-  
wardly flowing solvent is contacted with a stream  
consisting essentially of unsaturated hydrocar-  
bons to effect displacement of paraffin from solu-  
tion in the solvent; whereas column 13 is effect-  
ing only separation of a major portion or sub-  
stantially all of the mixed solvent from the un-  
saturated hydrocarbons by employment of tetra-  
ethylorthosilicate as a solvent which functions to  
selectively dissolve the hydrocarbons from the  
blended solvent.

Countercurrent liquid-liquid extraction is con-  
ducted in each of extractors 2 and 13, conditions  
being such that all components are in liquid phase  
and proportions of incoming streams and condi-  
tions being such that two phases are present, each  
in substantial amount. The extractions are ordi-  
narily carried out at atmospheric temperature.

In operation the stream of tetraethylortho-  
silicate flowing in line 12 from storage 18 to the  
bottom of extractor 13 is saturated with the polar  
solvent. This is for the reason that the equilibri-  
um attained in extraction unit 13 is such that the  
extract withdrawn via line 15 comprises tetra-  
ethylorthosilicate saturated with the polar sol-  
vent as well as containing the unsaturated hydro-  
carbons. The presence of the resulting small  
amount of polar solvent in the tetraethylortho-  
silicate fed via line 12 to unit 13 does not affect  
the operation adversely so that no means for  
separating the polar solvent from the tetraethyl-  
orthosilicate is necessary.

In practice a phase of tetraethylorthosilicate  
saturated with the polar solvent tends to build  
up in the blended solvent storage 3 and must be  
withdrawn occasionally in order that proper oper-  
ation may be attained.

If desired, the unsaturated hydrocarbon prod-  
ucts of our invention may be withdrawn via line  
20, but we prefer to separate these products fur-  
ther in a second stage liquid-liquid separation  
step. The apparatus for and the operation of the  
second stage of our process is identical to that of  
the first stage, and for that reason we will not  
encumber our disclosure with a detailed descrip-  
tion of the second stage. It will be understood  
that the products from the first stage of our  
process are the more saturated hydrocarbons or  
paraffins and a mixture of the unsaturated hydro-  
carbons or olefins and diolefins. We separate



this latter product into its components in a second stage, identical to that described above, wherein the hydrocarbon mixture to be separated is the unsaturated hydrocarbon product from the first stage and it is the feed for the second stage separation. Improved operation may be obtained in some cases by diluting the olefin-diolefin feed with a paraffin that is readily removable by distillation. For example a butene-butadiene stream withdrawn through line 20 may be diluted with a pentane, a hexane, or other easily removable paraffin prior to resolution in the second stage extraction. This feed passes through a separation process identical to the first stage except that the blended solvent for the second stage is a polar compound saturated with a compound that exhibits a compound forming tendency with diolefins in preference to olefins. An example is ethanolamine saturated with paraldehyde which we use in the second stage instead of the ethanolamine saturated with tetraethylorthosilicate of the first stage of our process. The second stage of our process is readily understood by considering the description of the first stage and replacing tetraethylorthosilicate with paraldehyde and realizing further that the hydrocarbon feed contains olefins and diolefins and that the resulting products are a stream of olefins and a stream of diolefins. Hence, the ultimate result of our two-stage process is a resolution of a hydrocarbon mixture containing hydrocarbons of at least three degrees of saturation into the components of the mixture.

Figure 2 portrays the complete process of our invention. This drawing is self-explanatory, and it will be understood that both the first and second stage extraction steps are carried out in a manner similar to that of Figure 1, more fully described above.

From the above description numerous modifications of our invention will be apparent to those skilled in the art. For example, in an alternative embodiment the original feed is contacted with a blended solvent of ethanolamine and paraldehyde, and the more unsaturated hydrocarbon or the diolefin is one of the products of this first stage. In the second stage the other product of the first stage which contains the more saturated hydrocarbons, or paraffins and olefins, is contacted with a blended solvent of ethanolamine and tetraethylorthosilicate, and the resulting products are a stream of the paraffins and a stream of the olefins. This embodiment along with other modifications are well within the scope of our invention.

We claim:

1. The method of resolving a mixture of aliphatic hydrocarbons containing hydrocarbon types of at least three degrees of saturation which comprises intimately contacting said mixture with a liquid selective solvent consisting essentially of ethanolamine and a non-polar solvent in which N-butane has an activity coefficient between 1.0 and 2.0 and in which at least one of butene and butadiene has an activity coefficient less than 1.0 and selected from the group consisting of paraldehyde and tetraethylorthosilicate and thereby effecting a preferential dissolution of at least one of the unsaturated hydrocarbon types in said selective solvent as the extract phase and separation of at least one of the more saturated hydrocarbon types in the raffinate phase, and intimately contacting the hydrocarbon content of the phase containing more than

one hydrocarbon type from the first-named contacting step with a second liquid selective solvent consisting essentially of ethanolamine and a non-polar solvent which is paraldehyde when tetraethylorthosilicate is the first-named polar solvent and tetraethylorthosilicate when paraldehyde is the first-named polar solvent, and thereby effecting preferential dissolution of the more unsaturated hydrocarbon type in said second selective solvent.

2. The method of resolving a mixture of aliphatic hydrocarbons containing hydrocarbon types of at least three degrees of saturation which comprises intimately contacting said mixture with a liquid selective solvent consisting essentially of ethanolamine and tetraethylorthosilicate and thereby effecting preferential dissolution of the unsaturated hydrocarbon types in said selective preferential dissolution of the unsaturated hydrocarbon types in said selective solvent, separating said unsaturated hydrocarbon types from said solvent, and intimately contacting the thus-separated unsaturated hydrocarbons with a liquid selective solvent consisting essentially of ethanolamine and paraldehyde and thereby effecting preferential dissolution of said more unsaturated hydrocarbon type of said separated unsaturated hydrocarbons in said second selective solvent.

3. A method according to claim 2 wherein the aliphatic hydrocarbon mixture to be resolved contains paraffins, olefins and diolefins.

4. A method according to claim 3 wherein the aliphatic hydrocarbon mixture to be resolved contains butanes, butenes and butadiene.

5. The method of resolving a mixture of aliphatic hydrocarbons containing hydrocarbon types of at least three degrees of saturation which comprises intimately contacting said mixture with a liquid selective solvent consisting essentially of ethanolamine and paraldehyde and thereby effecting preferential dissolution of the more unsaturated hydrocarbon type in said selective solvent, separating the hydrocarbon types more saturated than the selectively dissolved hydrocarbon from said selective solvent, and intimately contacting the thus-separated more saturated hydrocarbons with a liquid selective solvent consisting essentially of ethanolamine and tetraethylorthosilicate and thereby effecting preferential dissolution of said more unsaturated hydrocarbon type of said separated more saturated hydrocarbons in said second selective solvent.

6. A method according to claim 5 wherein the aliphatic hydrocarbon mixture to be resolved contains paraffins, olefins and diolefins.

7. A method according to claim 6 wherein the aliphatic hydrocarbon mixture to be resolved contains butanes, butenes and butadiene.

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EDWARD E. WHITE.

#### REFERENCES CITED

The following references are of record in the file of this patent:

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**Certificate of Correction**

Patent No. 2,527,951

October 31, 1950

BERTRAND J. MAYLAND ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 12, lines 19 and 20, strike out the words "preferential dissolution of the unsaturated hydrocarbon types in said selective";  
and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 22nd day of May, A. D. 1951.

[SEAL]

THOMAS F. MURPHY,  
*Assistant Commissioner of Patents.*