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A system and/or process for decreasing the level of at least one organic fluoride present in a hydrocarbon mixture (118) by first passing the hydrocarbon mixture (118) to an eductor (120) and educting into the hydrocarbon mixture a catalyst (122) comprising a volatility reducing additive and hydrofluoric acid to produce a hydrocarbon–catalyst mixture (132), permitting the hydrocarbon–catalyst mixture (132) to undergo a phase separation to produce a hydrocarbon phase (128) having a lower concentration of at least one organic fluoride than the hydrocarbon mixture (132) and to produce a catalyst phase (130), and withdrawing at least a portion of the hydrocarbon phase to thereby form a hydrocarbon product stream (134), are disclosed. In an alternate embodiment, a system and/or process for controlling the concentration of at least one organic fluoride and/or the RON of the hydrocarbon mixture by adjusting the amount of the volatility reducing additive present in the catalyst are disclosed.
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METHOD FOR REDUCING ORGANIC FLUORIDE LEVELS IN HYDROCARBONS

The present invention relates to a method and/or system for reducing the concentration of organic fluorides present in a hydrocarbon mixture. More particularly, the invention relates to a method and/or system for reducing the concentration of organic fluorides present in an alkylation reactor effluent.

Background of the Invention

The use of catalytic alkylation processes to produce branched hydrocarbons having properties that are suitable for use as gasoline blending components is well known in the art. Generally, the alkylation of olefins by saturated hydrocarbons, such as isoparaffins, is accomplished by contacting the reactants with an acid catalyst to form a reaction mixture, settling the mixture to separate the catalyst from the hydrocarbons and further separating the alkylation reactor effluent, for example, by fractionation, to recover the separate product streams. Normally, the alkylation reactor effluent of the alkylation process contains hydrocarbons having five to ten carbon atoms per molecule, preferably seven to nine carbons atoms per molecule. In order to have the highest quality gasoline blending stock, it is preferred for the alkylate hydrocarbons formed in the alkylation process to be highly branched and contain seven to nine carbon atoms per molecule.

Recent efforts to improve conventional hydrogen fluoride catalyzed alkylation processes have resulted in the development of new catalyst compositions that contain hydrogen fluoride and a volatility reducing additive. These new catalyst compositions have been found to be quite effective as an alkylation catalyst and to provide many other favorable benefits. However, it has also been found that in the alkylation process that uses the catalyst mixture containing hydrogen fluoride and such additive there is an increase in the production of undesirable organic fluorides. In fact, as the concentration of hydrogen fluoride in the new catalyst composition becomes more dilute, the amount of organic fluorides produced in the alkylation process increases. Organic fluorides produced can include, but are not limited to, organic fluorides having in the range of from about 3 to about 14 carbon atoms per molecule. Typical organic fluorides produced can include, but are not limited to, 2-fluoropropane, 2-fluorobutane, 2-fluoro-2-methylpropane, 2-fluoropentane,
2-fluoro-2-methylbutane, 2-fluoro-3-methylbutane, methylfluorobutane isomers, 2-fluorohexane, 3-fluorohexane, methylfluoropentanes, dimethylfluorobutanes, fluoroheptanes, fluoromethylhexanes, dimethylfluoropentanes, fluorooctanes, fluoromethylheptanes, dimethylfluorohexanes, fluorotrimethylpentanes, fluorononanes, fluoromethyloctanes, dimethylfluoroheptanes, fluorotrimethylhexanes.

In many instances, it is not desirable for the product streams to have an excessively high concentration of organic fluorides.

Therefore, development of an efficient process for reducing the level of organic fluorides present in a hydrocarbon mixture would be a significant contribution to the art.

**Brief Summary of the Invention**

It is, thus, an object of the present invention to provide an improved process for reducing the level of at least one organic fluoride in a hydrocarbon mixture which is economical and efficient.

A further object of the present invention is to provide an improved system to be used in reducing the level of at least one organic fluoride in a hydrocarbon mixture which is economical in construction and reliable and efficient in operation.

A yet further object of the present invention is to provide an improved system to be used in reducing the level of at least one organic fluoride in a hydrocarbon mixture which includes means for controlling the level of at least one organic fluoride present in the hydrocarbon mixture and/or for controlling the research octane of the hydrocarbon mixture.

According to a first embodiment of the present invention, a method for decreasing the level of at least one organic fluoride present in a hydrocarbon mixture is provided. The method of the first embodiment comprises the steps of:

passing the hydrocarbon mixture to an eductor;

educting into the hydrocarbon mixture a catalyst comprising a volatility reducing additive and hydrofluoric acid to thereby form a hydrocarbon-catalyst mixture;

permitting the hydrocarbon-catalyst mixture to undergo a phase separation to thereby produce a hydrocarbon phase having a lower concentration of at
least one organic fluoride than the hydrocarbon mixture and to thereby produce a catalyst phase;

withdrawing at least a portion of the catalyst phase for use as the catalyst; and

withdrawing at least a portion of the hydrocarbon phase to form a hydrocarbon product stream.

According to a second embodiment of the present invention, a process for alkylating at least a portion of a hydrocarbon feedstock comprising olefins and isoparaffins is provided. The process of the second embodiment comprises the steps of:

introducing the hydrocarbon feedstock into an alkylation reaction zone;

contacting the hydrocarbon feedstock with a first catalyst comprising a volatility reducing additive and hydrofluoric acid in the alkylation reaction zone to thereby produce alkylation of at least a portion of the olefins and isoparaffins in the form of an alkylation reaction effluent;

passing the thus-produced alkylation reaction effluent from the alkylation reaction zone to a first settling zone and permitting a phase separation to occur so as to produce a first catalyst phase and to produce a first hydrocarbon phase having a concentration of at least one organic fluoride in the range of from about 150 ppmw to about 10,000 ppmw, based on the total weight of the first hydrocarbon phase, and having a research octane in the range of from about 85 to about 98; and

contacting at least a portion of the first hydrocarbon phase with a second catalyst comprising a volatility reducing additive and hydrofluoric acid to thereby produce a hydrocarbon product stream having a lower concentration of at least one organic fluoride than the first hydrocarbon phase.

According to a third embodiment of the present invention, a system or apparatus is provided comprising:

an alkylation reactor;

a first settler, having an upper portion, an intermediate portion and a lower portion;

an eductor;

a second settler, having an upper portion, an intermediate portion and a
lower portion;

first conduit means operably related to the alkylation reactor for introducing a hydrocarbon feedstock comprising olefins and isoparaffins into the alkylation reactor;

second conduit means operably related to the alkylation reactor for introducing a first catalyst comprising a volatility reducing additive and hydrofluoric acid into the alkylation reactor;

third conduit means operably related to the alkylation reactor and operably related to the first settler for withdrawing an alkylation reaction effluent from the alkylation reactor and for introducing the alkylation reaction effluent into the intermediate portion of the first settler, the upper portion of the first settler being operable for containing a first hydrocarbon phase separated from the alkylation reaction effluent and the lower portion of the first settler being operable for containing a first catalyst phase separated from the alkylation reaction effluent;

fourth conduit means operably related to the first settler and operably related to the eductor for withdrawing at least a portion of the first hydrocarbon phase from the upper portion of the first settler and for introducing the at least a portion of the first hydrocarbon phase into the eductor;

fifth conduit means, operably related to the second settler and operably related to the eductor for withdrawing at least a portion of a second catalyst phase comprising a volatility reducing additive and hydrofluoric acid from the lower portion of the second settler and for introducing the at least a portion of the second catalyst phase into the eductor for mixing with the at least a portion of the first hydrocarbon phase to thereby produce a hydrocarbon-catalyst mixture;

sixth conduit means operably related to the eductor and operably related to the second settler for withdrawing the hydrocarbon-catalyst mixture from the eductor and for introducing the hydrocarbon-catalyst mixture into the intermediate portion of the second settler, the upper portion of the second settler being operable for containing a second hydrocarbon phase separated from the hydrocarbon-catalyst mixture and the lower portion of the second settler being operable for containing the second catalyst phase separated from the hydrocarbon-catalyst mixture; and

seventh conduit means operably related to the second settler for
withdrawing at least a portion of the second hydrocarbon phase from the second settler to thereby form a hydrocarbon product stream.

Other objects and advantages will become apparent from the detailed description and the appended claims.

**Brief Description of the Drawing**

Fig. 1 is a schematic flow diagram presenting an embodiment of the present invention.

**Detailed Description of the Invention**

According to the first embodiment of the present invention, the hydrocarbon mixture can comprise paraffins and/or olefins, wherein each of these hydrocarbons contains at least 3 carbon atoms per molecule. The hydrocarbon mixture further comprises at least one organic fluoride in the range of from about 150 ppmw to about 10,000 ppmw, based on the total weight of the hydrocarbon mixture. More typically, the concentration of the at least one organic fluoride is in the range of from about 200 ppmw to about 1,000 ppmw; and most typically from 250 ppmw to 500 ppmw, based on the total weight of the hydrocarbon mixture.

The research octane number (RON) of the hydrocarbon mixture is typically in the range of from about 85 to about 98, more typically from about 87 to about 96; and most typically from 89 to 94. RON, as used herein, is defined as the octane number of a hydrocarbon stream as determined using the ASTM D2699-97 method.

The hydrocarbon mixture is most suitably an alkylation reaction product produced from the alkylation of olefins having at least 3 carbon atoms per molecule with isoparaffins having at least 4 carbon atoms per molecule.

The hydrocarbon mixture can be contacted with a catalyst comprising a volatility reducing additive and hydrofluoric acid by any suitable manner, including mixing and blending. The volatility reducing additive can be any compound effective in reducing the volatility of a mixture resulting from the addition of the volatility reducing additive to hydrofluoric acid. More particularly, the volatility reducing additive can be a compound selected from the group consisting of sulfone, ammonia, methylamines, ethylamines, propylamines, butylamines, pentylamines, pyridine, alkylpyridines, picoline, melamine, hexamethylene-tetramine and the like.
The sulfones suitable for use in this invention are the sulfones of the general formula

\[ R \text{-SO}_2\text{-R}^1 \]

wherein R and R\(^1\) are monovalent hydrocarbon alkyl or aryl substituents, each containing from 1 to 8 carbon atoms, and wherein R and R\(^1\) can be the same or different. Examples of suitable sulfones include, but are not limited to, dimethylsulfone, di-n-propylsulfone, diphenylsulfone, ethylmethylsulfone and alicyclic sulfones wherein the SO\(_2\) group is bonded to a hydrocarbon ring. In such a case, R and R\(^1\) are forming together a branched or unbranched hydrocarbon divalent moiety preferably containing from 3 to 12 carbon atoms. Among the latter, tetramethylenesulfone or sulfolane, 3-methylsulfolane and 2,4-dimethylsulfolane are more particularly suitable since they offer the advantage of being liquid at process operating conditions of concern herein. These sulfones may also have substituents, particularly one or more halogen atoms, such as for example, chloromethylethylsulfone. These sulfones may advantageously be used in the form of mixtures of any two or more thereof. The most preferred volatility reducing additive is sulfone.

It is preferred to contact the hydrocarbon mixture with the catalyst by mixing in an eductor which can also be referred to as an ejector, siphon, exhauster or jet pump. As used herein, the operation and apparatus of the eductor are such to allow a pumping fluid to enter through a nozzle, pass through a venturi nozzle, and discharge through a discharge opening. As the pumping fluid passes into the venturi nozzle, it develops a suction that causes fluid in a suction chamber to be entrained with the pumping fluid stream and to be delivered through the discharge opening.

The hydrocarbon mixture is passed to the pumping fluid inlet of an eductor wherein the catalyst is educted into the hydrocarbon mixture to thereby produce a hydrocarbon-catalyst mixture. The hydrocarbon-catalyst mixture is then permitted to undergo a phase separation in a settler vessel thereby producing a hydrocarbon phase and a catalyst phase. The hydrocarbon phase has a lower concentration of at least one organic fluoride than the hydrocarbon mixture. More particularly, the concentration of at least one organic fluoride in the hydrocarbon phase is preferably in the range of from about 0 ppmw to about 1,000 ppmw; more preferably from about 0 ppmw to about 100 ppmw; and most preferably from 0
ppmw to 50 ppmw, based on the total weight of the hydrocarbon phase.

The RON of the hydrocarbon phase is preferably in the range of from about 85 to about 98, more preferably from about 87 to about 96, and most preferably from 89 to 94.

In addition, at least a portion of the catalyst phase can be used as the catalyst and at least a portion of the hydrocarbon phase is withdrawn from the process to form a hydrocarbon product stream.

The volatility reducing additive concentration of the catalyst is such as to provide a hydrocarbon phase having a lower concentration of at least one organic fluoride than the hydrocarbon mixture.

More particularly, the volatility reducing additive is present in the catalyst in an amount in the range of from exceeding about 0 weight percent to about 50 weight percent; preferably from about 5 weight percent to about 35 weight percent; and most preferably from 10 weight percent to 25 weight percent, based on the total weight of the catalyst.

The concentration of the volatility reducing additive in the catalyst can be varied so as to adjust and/or control the concentration of at least one organic fluoride in the hydrocarbon product stream and/or to adjust and/or control the RON of the hydrocarbon product stream.

More particularly, the concentration of the volatility reducing additive in the catalyst can be varied by replacing at least a portion of the catalyst phase with a makeup catalyst comprising a compound selected from the group consisting of the volatility reducing additive, hydrofluoric acid, and mixtures thereof.

The amount of volatility reducing additive can be adjusted such that the RON of the hydrocarbon product stream is controlled to a level in the range of from about 85 to about 98; preferably from about 87 to about 96; and most preferably from 89 to 94; and/or such that the concentration of the at least one organic fluoride present in the hydrocarbon product stream is controlled to a level in the range of from about 0 percent to about 65 percent; preferably from about 0 percent to about 50 percent; and most preferably from 0 percent to 25 percent of the concentration of the at least one organic fluoride of the hydrocarbon mixture.

According to the second embodiment of the present invention, the
hydrocarbon feedstock can comprise iso-paraffins having at least 4 carbon atoms per molecule and olefins having at least 3 carbon atoms per molecule. Preferably, the iso-paraffins have in the range of from 4 to 5 carbon atoms per molecule and the olefins have in the range of from 3 to 4 carbon atoms per molecule.

The olefins contained in the hydrocarbon feedstock can be alkylated with the iso-paraffins by contacting the hydrocarbon feedstock, by any suitable manner in an alkylation reaction zone, with a first catalyst comprising hydrofluoric acid and a volatility reducing additive (as described above) to thereby produce alkylation of at least a portion of the olefins and iso-paraffins in the form of an alkylation reaction effluent comprising alkylate, unreacted iso-paraffins, the first catalyst, and, in runaway type situations, unreacted olefins.

The alkylation reaction effluent can be passed from the alkylation reaction zone to a first settling zone wherein a phase separation occurs. The phase separation produces a first hydrocarbon phase having a concentration of at least one organic fluoride in the range of from about 150 ppmw to about 10,000 ppmw; more particularly from about 200 ppmw to about 1,000 ppmw; and most particularly from 250 ppmw to 500 ppmw, based on the total weight of the first hydrocarbon phase; and the first hydrocarbon phase has a RON in the range of from about 85 to about 98; more particularly from about 87 to about 96; and most particularly from 89 to 94.

The first hydrocarbon phase can comprise alkylate, unreacted iso-paraffins, and unreacted olefins.

The phase separation in the first settling zone also produces a first catalyst phase which can be used, at least in part, as the first catalyst. At least a portion of the first hydrocarbon phase can be contacted with a second catalyst comprising a volatility reducing additive and hydrofluoric acid by any suitable manner, including mixing and blending to thereby produce a hydrocarbon product stream. It is preferred to contact at least a portion of the first hydrocarbon phase with the second catalyst by mixing in an eductor.

At least a portion of the first hydrocarbon phase is passed to an eductor wherein the second catalyst is educted into at least a portion of the first hydrocarbon phase to thereby form a hydrocarbon-catalyst mixture. The hydrocarbon-catalyst mixture is then passed to a second settling zone wherein a phase
separation occurs thereby producing a second hydrocarbon phase and a second catalyst phase. The second hydrocarbon phase has a lower concentration of at least one organic fluoride than the first hydrocarbon phase. More particularly, the concentration of at least one organic fluoride in the second hydrocarbon phase is preferably in the range of from about 0 ppmw to about 1,000 ppmw; more preferably from about 0 ppmw to about 100 ppmw; and most preferably from 0 ppmw to 50 ppmw, based on the total weight of the second hydrocarbon phase.

The second hydrocarbon phase has a RON in the range of from about 85 to about 98; preferably from about 87 to about 96; and most preferably from 89 to 94.

In addition, at least a portion of the second catalyst phase can be used as the second catalyst and at least a portion of the second hydrocarbon phase is withdrawn from the process to form a hydrocarbon product stream.

The volatility reducing additive concentration of the second catalyst is such as to provide the second hydrocarbon phase having a lower concentration of at least one organic fluoride than the first hydrocarbon phase. For best results in decreasing the concentration of at least one organic fluoride in the first hydrocarbon phase, the concentration of volatility reducing additive in the second catalyst is less than the concentration of volatility reducing additive in the first catalyst. More particularly, the volatility reducing additive is present in the second catalyst in an amount in the range of from exceeding about 0 weight percent to about 50 weight percent; preferably from about 5 weight percent to about 35 weight percent; and most preferably from 10 weight percent to 25 weight percent based on the total weight of the second catalyst.

The amount of volatility reducing additive present in the second catalyst can be varied in order to control at least one processing variable, such as, but not limited to, the concentration of at least one organic fluoride of the hydrocarbon product stream and/or the RON of the hydrocarbon product stream.

Where the processing variable is the concentration of at least one organic fluoride, the concentration of the volatility reducing additive present in the second catalyst can be decreased responsive to an increase in the concentration of at least one organic fluoride of the hydrocarbon product stream above a desired
concentration of at least one organic fluoride of the hydrocarbon product stream to
thereby decrease the concentration of at least one organic fluoride of the hydrocarbon
product stream. Alternately, the concentration of the volatility reducing additive
present in the second catalyst can be increased responsive to a decrease in the
concentration of at least one organic fluoride in the hydrocarbon product stream
below the desired concentration to thereby increase the concentration of at least one
organic fluoride of the hydrocarbon product stream.

Where the processing variable is RON, the concentration of the
volatility reducing additive present in the second catalyst can be decreased responsive
to an increase in the RON of the hydrocarbon product stream above a desired RON
of the hydrocarbon product stream to thereby decrease the RON of the hydrocarbon
product stream. Alternately, the concentration of the volatility reducing additive
present in the second catalyst can be increased responsive to a decrease in the RON
of the hydrocarbon product stream below the desired RON to thereby increase the
RON of the hydrocarbon product stream.

One skilled in the art can establish the concentration of the volatility
reducing additive present in the second catalyst at a level which maximizes the RON
of the hydrocarbon product stream, or, which minimizes the concentration of at least
one organic fluoride of the hydrocarbon product stream, or, which reaches a desired
balance between the RON and the concentration of at least one organic fluoride of
the hydrocarbon product stream.

The desired concentration of at least one organic fluoride of the
hydrocarbon product stream is preferably in the range of from about 0 percent to
about 65 percent; more preferably from about 0 percent to about 50 percent; and
most preferably from 0 percent to 25 percent of the concentration of at least one
organic fluoride of the first hydrocarbon phase.

The desired RON of the hydrocarbon product stream is preferably in
the range of from about 85 to about 98; more preferably from about 87 to about 96;
and most preferably from 89 to 94.

For best results in decreasing the concentration of at least one organic
fluoride in the first hydrocarbon phase, the ratio by weight of iso-butane to alkylate
in the first hydrocarbon phase is in the range of from about 1:1 to about 8:1,
preferably from about 1.5:1 to about 6:1; and most preferably from 2:1 to 5:1.

According to the third embodiment of the present invention, the system of the present invention will be described with reference to the drawing.

Referring to Fig. 1 therein is illustrated the inventive system or apparatus 10 including an alkylation reactor 100 having an inside wall 102 which defines an alkylation reaction zone. The alkylation reactor 100 is operably related by connection in fluid flow communication to a conduit 104 providing first conduit means for introducing a hydrocarbon feedstock into the alkylation reaction zone. The alkylation reactor 100 is also operably related by connection in fluid flow communication to a conduit 106 providing second conduit means for introducing a first catalyst comprising a volatility reducing additive, as described above, and hydrofluoric acid into the alkylation reaction zone. The alkylation reactor 100 provides means for alkylationing at least a portion of the hydrocarbon feedstock to thereby produce an alkylation reaction effluent.

The alkylation reactor 100 is operably related by connection in fluid flow communication to a conduit 108 providing third conduit means for removing the alkylation reaction effluent from alkylation reactor 100 and for introducing the alkylation reaction effluent into an intermediate portion 109 of a first settler 110. First settler 110 also has an inside wall 112 which defines a first settling zone, having an upper portion 114, intermediate portion 109 and a lower portion 116, for allowing a phase separation of the alkylation reaction effluent. The upper portion 114 of first settler 110 is operable for containing a first hydrocarbon phase separated from the alkylation reaction effluent and the lower portion 116 of first settler 110 is operable for containing a first catalyst phase separated from the alkylation reaction effluent.

The lower portion 116 of first settler 110 is operably related by connection in fluid flow communication, via conduit 106, with alkylation reactor 100 for returning the first catalyst phase to alkylation reactor 100 for use as the first catalyst.

The upper portion 114 of first settler 110 is operably related by connection in fluid flow communication to a conduit 118 providing fourth conduit means for withdrawing at least a portion of the first hydrocarbon phase from upper portion 114 of first settler 110 and for introducing at least a portion of the first
hydrocarbon phase into an eductor 120. Eductor 120 is operably related by
connection in fluid flow communication via conduit 122 with a second settler 124
having an inside wall 126 which defines a second settling zone having an upper
portion 128, an intermediate portion 129 and a lower portion 130. Conduit 122
provides fifth conduit means for withdrawing at least a portion of a second catalyst
phase comprising a volatility reducing additive and hydrofluoric acid from the lower
portion 130 of second settler 124 and for introducing at least a portion of the second
catalyst phase into eductor 120 for mixing with at least a portion of the first
hydrocarbon phase introduced via conduit 118 into eductor 120 to thereby produce a
hydrocarbon-catalyst mixture.

Eductor 120 is operably related by connection in fluid flow
communication to a conduit 132 which provides sixth conduit means for withdrawing
the hydrocarbon-catalyst mixture from eductor 120 and for introducing the
hydrocarbon-catalyst mixture into the intermediate portion 129 of second settler 124.
The upper portion 128 of second settler 124 is operable for containing a second
hydrocarbon phase separated from the hydrocarbon-catalyst mixture and the lower
portion 130 of the second settler 124 is operable for containing the second catalyst
phase separated from the hydrocarbon-catalyst mixture.

Upper portion 128 of second settler 124 is operably related by
connection in fluid flow communication to a conduit 134 which provides seventh
conduit means for withdrawing at least a portion of the second hydrocarbon phase
from upper portion 128 of second settler 124 to thereby form a hydrocarbon product
stream.

In addition, the inventive system or apparatus 10 can include a control
system operably related to second settler 124 which provides control means for
varying the concentration of the volatility reducing additive present in the second
catalyst phase in order to control at least one processing variable of the hydrocarbon
product stream.

Dash lines, which designate signal lines in the drawings, are electrical
or pneumatic in this preferred embodiment. However, the invention is also applicable
to mechanical, hydraulic, or other signal means for transmitting information. In
almost all control systems some combination of these types of signals will be used.
However, the use of any other type of signal transmission, compatible with the process and equipment in use, is within the scope of the invention.

A digital computer is used in the preferred embodiment of this invention to calculate the required control signal based on measured process parameters as well as set points supplied to the computer. Any computer control system having software that allows operation in a real time environment for reading values of external variables and transmitting signals is suitable for use in this invention.

Signal lines are also utilized to represent the results of calculations carried out in a digital computer and the term “signal” is utilized to refer to such results. Thus, the term signal is used not only to refer to electrical currents or pneumatic pressures but is also used to refer to binary representations of a calculated or measured value.

The controllers shown may utilize the various modes of control such as proportional, proportional-integral, proportional-derivative, or proportional-integral-derivative. In this preferred embodiment, proportional-integral-derivative controllers are utilized but any controller capable of accepting two input signals and producing a scaled output signal, representative of a comparison of the two input signals, is within the scope of the invention.

The scaling of an output signal by a controller is well known in control system art. Essentially, the output of a controller may be scaled to represent any desired factor or variable. An example of this is where a desired flow rate and an actual flow rate are compared by a controller. The output could be a signal representative of a desired change in the flow rate of some liquid necessary to make the desired and actual flows equal. On the other hand, the same output signal could be scaled to represent a percentage or could be scaled to represent a temperature change required to make the desired and actual flows equal. If the controller output can range from 0 to 10 volts, which is typical, then the output signal could be scaled so that an output signal having a voltage level of 5.0 volts corresponds to 50 percent of some specified flow rate.

The various transducing means used to measure parameters which characterize the process and the various signals generated thereby may take a variety
of forms or formats. For example, the control elements of the system can beimplemented using electrical analog, digital electronic, pneumatic, hydraulic,mechanical or other similar types of equipment or combinations of one or more suchequipment types. While the presently preferred embodiment of the inventionpreferably utilizes a combination of pneumatic final control elements in conjunctionwith electrical analog signal handling and translation apparatus, the apparatus andmethod of the invention can be implemented using a variety of specific equipmentavailable to and understood by those skilled in the process control art.

Likewise, the format of the various signals can be modifiedsubstantially in order to accommodate signal format requirements of the particularinstallation, safety factors, the physical characteristics of the measuring or controlinstruments and other similar factors. For example, a raw flow measurement signalproduced by a differential pressure orifice flow meter would ordinarily exhibit agenerally proportional relationship to the square of the actual flow rate. Othermeasuring instruments might produce a signal which is proportional to the measuredparameter, and still other transducing means may produce a signal which bears amore complicated, but known, relationship to the measured parameter. Regardless ofthe signal format or the exact relationship of the signal to the parameter which itrepresents, each signal representative of a measured process parameter orrepresentative of a desired process value will bear a relationship to the measuredparameter or desired value which permits designation of a specific measured ordesired value by a specific signal value. A signal which is representative of a processmeasurement or desired process value is therefore one from which the informationregarding the measured or desired value can be readily retrieved regardless of theexact mathematical relationship between the signal units and the measured or desiredprocess units.

Referring again to Fig. 1, the control system comprises a conduit 136which is operably related by connection in fluid flow communication to lower portion130 of second settler 124. Conduit 136 provides an eighth conduit means forintroducing a hydrofluoric acid stream into the second catalyst phase, and a conduit138 which is operably related by connection in fluid flow communication to lowerportion 130 of second settler 124 provides a ninth conduit means for introducing a
volatility reducing additive stream into the second catalyst phase. The hydrofluoric acid stream in conduit 136 can be combined with the volatility reducing additive stream in conduit 138 prior to introduction into the second catalyst phase contained in lower portion 130 of second settler 124. A conduit 140 is operably related by connection in fluid flow communication to lower portion 130 of second settler 124 and provides tenth conduit means for withdrawing a purge stream from the second catalyst phase.

Conduit 136 is operably related to a first control valve 142 interposed therein which provides first control valve means for adjusting the flow rate of the hydrofluoric acid stream through conduit 136. Conduit 138 is operably related to a second control valve 144 interposed therein which provides second control valve means for adjusting the flow rate of the volatility reducing additive stream through conduit 138. Conduit 140 is operably related to a third control valve 146 interposed therein which provides third control valve means for adjusting the flow rate of the purge stream through conduit 140.

 Operably associated with each of the conduits 136, 138 and 140 is a respective flow transducer 148, 150 and 152, each of which produces a respective flow signal 154, 156 and 158 which is representative of the volume flow rate of the material carried through the conduits with which it is associated. Flow transducers 148, 150 and 152 can comprise flow measuring devices, such as orifice plates, located within conduits 136, 138 and 140, respectively, for measuring the volume flow rates.

Analyzer 160, which is preferably a chromatograph, provides means for establishing a processing variable signal 162 representative of the actual value of at least one processing variable of the hydrocarbon product stream. Analyzer 160 is preferably adapted to take a sample of fresh hydrocarbon product stream from conduit 134 and to deliver, in response to the analysis of the hydrocarbon product stream, processing variable signal 162 which is representative of the actual value of the at least one processing variable of the hydrocarbon product stream. Analyzer 160 can include off-line analysis of the sample of the hydrocarbon product stream.

A computer calculation block 164, preferably associated with a distributed control system, receives as inputs thereto the flow rate signals 154, 156
and 158, processing variable signal 162 and an operator entered signal 166 which is representative of the desired value for the at least one processing variable of the hydrocarbon product stream flowing in conduit 134. Computer calculation block 164 establishes output signals 168, 170 and 172, each responsive to signals 154, 156 and 158 and to the difference between signals 162 and 166. Signals 168, 170 and 172 are scaled to be representative of the flow rates of the hydrofluoric acid stream in conduit 136, the volatility reducing additive stream in conduit 138 and the purge stream in conduit 140, respectively, required to maintain the actual value of the at least one processing variable represented by signal 162 substantially equal to the desired value of the at least one processing variable represented by signal 166.

Signal 168 is provided as a set point input to flow controller 174. Also provided as a processing variable input to flow controller 174 is flow rate signal 154 which is representative of the actual flow rate of hydrofluoric acid in conduit 136. Flow controller 174 provides an output signal 176 which is responsive to the difference between signals 168 and 154. Signal 176 is scaled to be representative of the position of first control valve 142 required to maintain the flow rate represented by signal 154 substantially equal to the flow rate represented by signal 168.

Signal 170 is provided as a set point input to flow controller 178. Also provided as a processing variable input to flow controller 178 is flow rate signal 156 which is representative of the actual flow rate of the volatility reducing additive in conduit 138. Flow controller 178 provides an output signal 180 which is responsive to the difference between signals 170 and 156. Signal 180 is scaled to be representative of the position of second control valve 144 required to maintain the flow rate represented by signal 156 substantially equal to the flow rate represented by signal 170.

Signal 172 is provided as a set point input to flow controller 182. Also provided as a processing variable input to flow controller 182 is flow rate signal 158 which is representative of the actual flow rate of the purge stream in conduit 140. Flow controller 182 provides an output signal 184 which is responsive to the difference between signals 172 and 158. Signal 184 is scaled to be representative of the position of third control valve 146 required to maintain the flow rate represented by signal 158 substantially equal to the flow rate represented by signal 172.
The following example is provided to further illustrate this invention and is not to be considered as unduly limiting the scope of this invention.

Example

This example illustrates the use of catalysts comprising hydrofluoric acid and a volatility reducing additive in the reduction of organic fluoride levels in a hydrocarbon mixture.

A reactor was constructed to enable the steady-state evaluation of HF/sulfolane catalysts comprising varying levels of hydrofluoric acid and sulfolane. The reactor was a section of monel schedule 40 pipe 2 feet in length and 1 inch in diameter connected at one end to a monel sight gauge via 1/4" monel tubing, and connected at the other end to a feed introduction nozzle, having a 0.01 inch diameter orifice, via 1/8" monel tubing.

The catalyst was circulated through the reactor and monel sight gauge at a flow rate in the range of from about 50 mL/min to about 100 mL/min. The catalyst composition was varied for each run, as shown in the Table. A hydrocarbon feed comprising a 2/1 by weight mixture of isobutane/alkylate was blended into a feed cylinder. The alkylate was obtained from an alkylation unit of a refinery. For each run, the hydrocarbon feed was pumped through the feed introduction nozzle into the reactor at a rate of about 300 mL/hour. The reactor effluent flowed into the monel sight gauge wherein the hydrocarbon product and any catalyst carryover were separated.

The hydrocarbon product was drawn off into a suitable sample cylinder, passed over alumina at an ambient temperature (to adsorb free HF), collected, and analyzed by standard gas chromatography using a GC sample injection valve so that no light materials were lost. Test data results for each run are summarized in the Table.
<table>
<thead>
<tr>
<th>Feed</th>
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<th>91.7</th>
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<tr>
<td>Run 1 (inventive)</td>
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<td>23.0</td>
</tr>
<tr>
<td>Run 2 (inventive)</td>
<td>95.9</td>
<td>27.3</td>
</tr>
<tr>
<td>Run 3 (inventive)</td>
<td>95.5</td>
<td>47.0</td>
</tr>
<tr>
<td>Run 4 (inventive)</td>
<td>95.5</td>
<td>50.3</td>
</tr>
<tr>
<td>Run 5 (inventive)</td>
<td>95.9</td>
<td>73.5</td>
</tr>
<tr>
<td>Run 6 (control)</td>
<td>97.3</td>
<td>---</td>
</tr>
</tbody>
</table>

1 - All catalysts contain 1-2% water by weight.
2 - Balance of the catalyst compositions comprise acid soluble oil and dissolved light hydrocarbons.
2FP = 2-fluoropropane
TOS = Time on stream

The test data presented in the Table show that use of catalysts comprising hydrofluoric acid and sulfolane in Runs 1 through 5 significantly reduced the level of 2-fluoropropane contained in the hydrocarbon feed with less degradation in RON of the hydrocarbon product than that of control Run 6 in which the catalyst contained no sulfolane.

It is noted that the use of 12% by weight sulfolane in the catalyst in inventive Run 5 resulted in 100% conversion of 2-fluoropropane and a RON of the hydrocarbon product of 91.1 as compared to control Run 6 where the 2-fluoropropane conversion was also 100% but the RON was only 90.6.

Reasonable variations, modifications, and adaptations can be made within the scope of the disclosure and the appended claims without departing from
the scope of this invention.
CLAIMS

1. A method for decreasing the level of organic fluorides present in a hydrocarbon mixture, said method comprising the steps of:
   passing said hydrocarbon mixture to an eductor;
   educting into said hydrocarbon mixture a catalyst comprising a volatility reducing additive and hydrofluoric acid to thereby form a hydrocarbon-catalyst mixture;
   permitting said hydrocarbon-catalyst mixture to undergo a phase separation to thereby produce a hydrocarbon phase having a lower concentration of at least one organic fluoride than said hydrocarbon mixture and to thereby produce a catalyst phase;
   withdrawing at least a portion of said catalyst phase for use as said catalyst; and
   withdrawing at least a portion of said hydrocarbon phase to form a hydrocarbon product stream.

2. A method as recited in claim 1, wherein said volatility reducing additive is a compound selected from the group consisting of sulfone, ammonia, methylamines, ethylamines, propylamines, butylamines, pentylamines, pyridine, alkylpyridines, picoline, melamine, hexamethylene-tetramine, and mixtures of any two or more thereof.

3. A method as recited in claim 1, wherein said volatility reducing additive is sulfone.

4. A method as recited in claim 1, wherein said volatility reducing additive is present in said catalyst in an amount in the range of from exceeding about 0 weight percent to about 50 weight percent based on the total weight of said catalyst.

5. A method as recited in claim 1, further comprising the step of replacing at least a portion of said catalyst phase with a makeup catalyst comprising a compound selected from the group consisting of a volatility reducing additive, hydrofluoric acid, and mixtures thereof.

6. A process for alkylating at least a portion of a hydrocarbon feedstock comprising olefins and isoparaffins, said process comprising the steps of:
introducing said hydrocarbon feedstock into an alkylation reaction zone;

contacting said hydrocarbon feedstock with a first catalyst comprising a volatility reducing additive and hydrofluoric acid in said alkylation reaction zone to thereby produce alkylation of at least a portion of said olefins and isoparaffins in the form of an alkylation reaction effluent;

passing said thus-produced alkylation reaction effluent from said alkylation reaction zone to a first settling zone and permitting a phase separation to occur so as to produce a first catalyst phase and to produce a first hydrocarbon phase having a concentration of at least one organic fluoride in the range of from about 150 ppmw to about 10,000 ppmw, based on the total weight of said first hydrocarbon phase, and having a RON in the range of from about 85 to about 98; and

contacting at least a portion of said first hydrocarbon phase with a second catalyst comprising a volatility reducing additive and hydrofluoric acid to thereby produce a hydrocarbon product stream having a lower concentration of at least one organic fluoride than said first hydrocarbon phase.

7. A process as recited in claim 6, wherein said volatility reducing additive of said first catalyst and said second catalyst is a compound selected from the group consisting of sulfone, ammonia, methylamines, ethylamines, propylamines, butylamines, pentylamines, pyridine, alkylpyridines, picoline, melamine, hexamethylene-tetramine, and mixtures of any two or more thereof.

8. A process as recited in claim 6, wherein said volatility reducing additive is sulfone.

9. A process as recited in claim 6, wherein the concentration of said volatility reducing additive in said second catalyst is less than the concentration of said volatility reducing additive in said first catalyst.

10. A process as recited in claim 6, wherein said step of contacting at least a portion of said first hydrocarbon phase with said second catalyst comprises the steps of:

30 passing said at least a portion of said first hydrocarbon phase to an eductor;

educting through said eductor into said at least a portion of said first
hydrocarbon phase said second catalyst to thereby form a hydrocarbon-catalyst mixture;

passing said hydrocarbon-catalyst mixture to a second settling zone and permitting a phase separation to occur to thereby produce a second hydrocarbon phase and a second catalyst phase;

withdrawing at least a portion of said second catalyst phase for use as said second catalyst; and

withdrawing at least a portion of said second hydrocarbon phase to form said hydrocarbon product stream.

11. A process as recited in claim 10, further comprising the step of varying the amount of said volatility reducing additive present in said second catalyst in order to control at least one processing variable of said hydrocarbon product stream.

12. A process as recited in claim 11, wherein said at least one processing variable is the concentration of said at least one organic fluoride.

13. A process as recited in claim 12, wherein the amount of said volatility reducing additive present in said second catalyst is decreased responsive to an increase in said concentration of said at least one organic fluoride in said hydrocarbon product stream above a desired concentration of said at least one organic fluoride in said hydrocarbon product stream to thereby decrease said concentration of said at least one organic fluoride of said hydrocarbon product stream, and, alternately, the amount of said volatility reducing additive present in said second catalyst is increased responsive to a decrease in said concentration of said at least one organic fluoride in said hydrocarbon product stream below said desired concentration to thereby increase said concentration of said at least one organic fluoride of said hydrocarbon product stream.

14. A process as recited in claim 11, wherein said at least one processing variable is the RON.

15. A process as recited in claim 14, wherein the amount of said volatility reducing additive present in said second catalyst is decreased responsive to an increase in said RON of said hydrocarbon product stream above a desired RON of said hydrocarbon product stream to thereby decrease said RON of said hydrocarbon product stream, and, alternately, the amount of said volatility reducing additive
present in said second catalyst is increased responsive to a decrease in said RON of said hydrocarbon product stream below said desired RON to thereby increase said RON of said hydrocarbon product stream.

16. A process as recited in claim 6, wherein said volatility reducing additive is present in said second catalyst in an amount sufficient to produce said hydrocarbon product stream having a RON in the range of from about 85 to about 98 and a concentration of at least one organic fluoride, based on the total weight of said hydrocarbon product stream, in the range of from about 0 percent to about 65 percent of said concentration of said at least one organic fluoride of said first hydrocarbon phase.

17. A process as recited in claim 6, wherein said volatility reducing additive is present in said second catalyst in an amount in the range of from exceeding about 0 weight percent to about 50 weight percent based on the total weight of said second catalyst.

18. A method for controlling the RON and concentration of at least one organic fluoride of a hydrocarbon mixture, the method comprising the steps of:

   contacting said hydrocarbon mixture with a catalyst comprising a volatility reducing additive and hydrofluoric acid to thereby produce a hydrocarbon product stream; and

   adjusting the amount of said volatility reducing additive present in said catalyst such that said RON is maintained at a desired value, and such that the concentration of said at least one organic fluoride present in said hydrocarbon product stream based on the total weight of said hydrocarbon product stream is controlled to a desired level.

19. A method as recited in claim 18, wherein said volatility reducing additive is a compound selected from the group consisting of sulfone, ammonia, methylamines, ethylamines, propylamines, butylamines, pentylamines, pyridine, alkylpyridines, picoline, melamine, hexamethylene-tetramine, and mixtures of any two or more thereof.

20. A method as recited in claim 18, wherein said volatility reducing additive is sulfone.

21. A method as recited in claim 18, wherein said contacting of said
hydrocarbon mixture with said catalyst comprises the steps of:
   passing at least a portion of said hydrocarbon mixture to an eductor;
   educting into said at least a portion of said hydrocarbon mixture said
   catalyst to thereby form a hydrocarbon-catalyst mixture;
   permitting said hydrocarbon-catalyst mixture to undergo a phase
   separation to thereby produce a hydrocarbon product phase and a catalyst phase;
   withdrawing at least a portion of said catalyst phase for use as said
   catalyst; and
   withdrawing at least a portion of said hydrocarbon product phase to
   form said hydrocarbon product stream.
22. A method as recited in claim 21, wherein said amount of said volatility
   reducing additive present in said catalyst is adjusted by replacing at least a portion of
   said catalyst with a makeup catalyst comprising a compound selected from the group
   consisting of a volatility reducing additive, hydrofluoric acid, and mixtures thereof.
23. A method as recited in claim 22, wherein said volatility reducing
   additive is present in said catalyst in an amount in the range of from exceeding about
   0 weight percent to about 50 weight percent based on the total weight of said
   catalyst.
24. A system comprising:
   an alkylation reactor;
   a first settler, having an upper portion, an intermediate portion and a
   lower portion;
   an eductor;
   a second settler, having an upper portion, an intermediate portion and a
   lower portion;
   first conduit means operably related to said alkylation reactor for
   introducing a hydrocarbon feedstock comprising olefins and isoparaffins into said
   alkylation reactor;
   second conduit means operably related to said alkylation reactor for
   introducing a first catalyst comprising a volatility reducing additive and hydrofluoric
   acid into said alkylation reactor;
   third conduit means operably related to said alkylation reactor and
operably related to said first settler for withdrawing an alkylation reaction effluent from said alkylation reactor and for introducing said alkylation reaction effluent into said intermediate portion of the first settler, said upper portion of said first settler being operable for containing a first hydrocarbon phase separated from said alkylation reaction effluent and said lower portion of said first settler being operable for containing a first catalyst phase separated from said alkylation reaction effluent;

fourth conduit means operably related to said first settler and operably related to said eductor for withdrawing at least a portion of said first hydrocarbon phase from said upper portion of said first settler and for introducing said at least a portion of said first hydrocarbon phase into said eductor;

fifth conduit means, operably related to said second settler and operably related to said eductor for withdrawing at least a portion of a second catalyst phase comprising a volatility reducing additive and hydrofluoric acid from said lower portion of said second settler and for introducing at least a portion of said second catalyst phase into said eductor for mixing with said at least a portion of said first hydrocarbon phase to thereby produce a hydrocarbon-catalyst mixture;

sixth conduit means operably related to said eductor and operably related to said second settler for withdrawing said hydrocarbon-catalyst mixture from said eductor and for introducing said hydrocarbon-catalyst mixture into said intermediate portion of said second settler, said upper portion of said second settler being operable for containing a second hydrocarbon phase separated from said hydrocarbon-catalyst mixture and said lower portion of said second settler being operable for containing said second catalyst phase separated from said hydrocarbon-catalyst mixture; and

seventh conduit means operably related to said second settler for withdrawing at least a portion of said second hydrocarbon phase from said second settler to thereby form a hydrocarbon product stream.

25. A system as recited in claim 24, wherein said volatility reducing additive is a compound selected from the group consisting of sulfone, ammonia, methylamines, ethylamines, propylamines, butylamines, pentylamines, pyridine, alkylpyridines, picoline, melamine, hexamethylene-tetramine, and mixtures of any two or more thereof.
26. A system as recited in claim 24, wherein said volatility reducing additive is sulfone.

27. A system as recited in claim 24, further comprising control means operably related to said second settler for varying the concentration of said volatility reducing additive present in said second catalyst phase in order to control at least one processing variable of said hydrocarbon product stream.

28. A system as recited in claim 27, wherein said control means for varying the concentration of said volatility reducing additive present in said second catalyst phase comprises:

- eighth conduit means operably related to said lower portion of said second settler for introducing a hydrofluoric acid stream into said second catalyst phase;

- ninth conduit means operably related to said lower portion of said second settler for introducing a volatility reducing additive stream into said second catalyst phase;

- tenth conduit means operably related to said lower portion of said second settler for withdrawing a purge stream from said second catalyst phase;

- means for establishing a first signal, operably related to said eighth conduit means, representative of the actual flow rate of said hydrofluoric acid stream;

- means for establishing a second signal, operably related to said ninth conduit means, representative of the actual flow rate of said volatility reducing additive stream;

- means for establishing a third signal, operably related to said tenth conduit means, representative of the actual flow rate of said purge stream;

- means for establishing a fourth signal representative of the desired value of said at least one processing variable of said hydrocarbon product stream;

- means for establishing a fifth signal, operably related to said seventh conduit means, representative of the actual value of said at least one processing variable of said hydrocarbon product stream;

- computer means for comparing said fifth signal to said fourth signal and establishing a sixth signal, a seventh signal and an eighth signal, each responsive to said first signal, said second signal, said third signal and to the difference between
said fifth signal and said fourth signal, wherein said sixth signal, said seventh signal
and said eighth signal are scaled to be representative of the flow rates of said
hydrofluoric acid stream, said volatility reducing additive stream and said purge
stream, respectively, required to maintain the actual value of said at least one
processing variable represented by said fifth signal substantially equal to the desired
value of said at least one processing variable represented by said fourth signal;

means for comparing said first signal and said sixth signal and for
establishing a ninth signal which is responsive to the difference between said first
signal and said sixth signal;

first control valve means operably located in said eighth conduit means
for adjusting the flow rate of said hydrofluoric acid stream in response to said ninth
signal;

means for comparing said second signal and said seventh signal and for
establishing a tenth signal which is responsive to the difference between said second
signal and said seventh signal;

second control valve means operably located in said ninth conduit
means for adjusting the flow rate of said volatility reducing additive stream in
response to said tenth signal;

means for comparing said third signal and said eighth signal and for
establishing an eleventh signal which is responsive to the difference between said
third signal and said eighth signal; and

third control valve means operably located in said tenth conduit means
for adjusting the flow rate of said purge stream in response to said eleventh signal.

A system as recited in claim 28, wherein said volatility reducing
additive of said volatility reducing additive stream and said second catalyst is a
compound selected from the group consisting of sulfone, ammonia, methyamines,
ethylamines, propylamines, butylamines, pentylamines, pyridine, alkylpyridines,
picoline, melamine, hexamethylene-tetramine, and mixtures of any two or more
thereof.

A system as recited in claim 28, wherein said volatility reducing
additive of said volatility reducing additive stream and said second catalyst is sulfone.

A system as recited in claim 28, wherein said at least one processing
variable is the concentration of organic fluorides.

32. A system as recited in claim 28, wherein said at least one processing variable is RON.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**
- IPC(7) : B01J 8/00, 8/04, 10/00; C01G 17/00; C07C 7/00, 7/10, 7/17, 2/56

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)
  - U.S. : 422/187, 188, 189; 208/262.1; 585/712, 842, 857, 860, 861, 862, 864

- Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
  - NONE

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

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>X</td>
<td>US 5,689,030A (RANDOLPH) 18 November 1997, the abstract, col. 2, lines 48-53, col. 4, lines 61-67; table I.</td>
<td>1-5</td>
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<tr>
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<td>US 5,654,251A (ABBOTT et al) 05 August 1997, col. 1, line 29 through col. 2, line 22.</td>
<td>1-13, 17, 24-28</td>
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**Further documents are listed in the continuation of Box C.**

- *: Special categories of cited documents:
  - "A": document defining the general state of the art which is not considered to be of particular relevance
  - "E": earlier document published on or after the international filing date
  - "L": document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  - "O": document referring to an oral disclosure, use, exhibition or other means
  - "P": document published prior to the international filing date but later than the priority date claimed
  - "T": later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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  - "Y": document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  - "&": document member of the same patent family

**Date of the actual completion of the international search**
- 22 MARCH 2000

**Date of mailing of the international search report**
- 26 APR 2000

**Name and mailing address of the ISA/US**
- Commissioner of Patents and Trademarks
- Box PCT
- Washington, D.C. 20231
- Facsimile No. (703) 305-3230

**Authorized officer**
- THUAN D. DANG
- Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet) (July 1998)
A. CLASSIFICATION OF SUBJECT MATTER:
US CL:
422/187, 188, 189; 208/262.1; 585/712, 842, 857, 860, 861, 862, 864