Nov. 27, 1945. L. F. DOWDING 2,389,604

TEMPERATURE CONTROL FOR HYDROCARBON OIL PROCESSING

Filed April 1, 1944 3 Sheets-Sheet 1

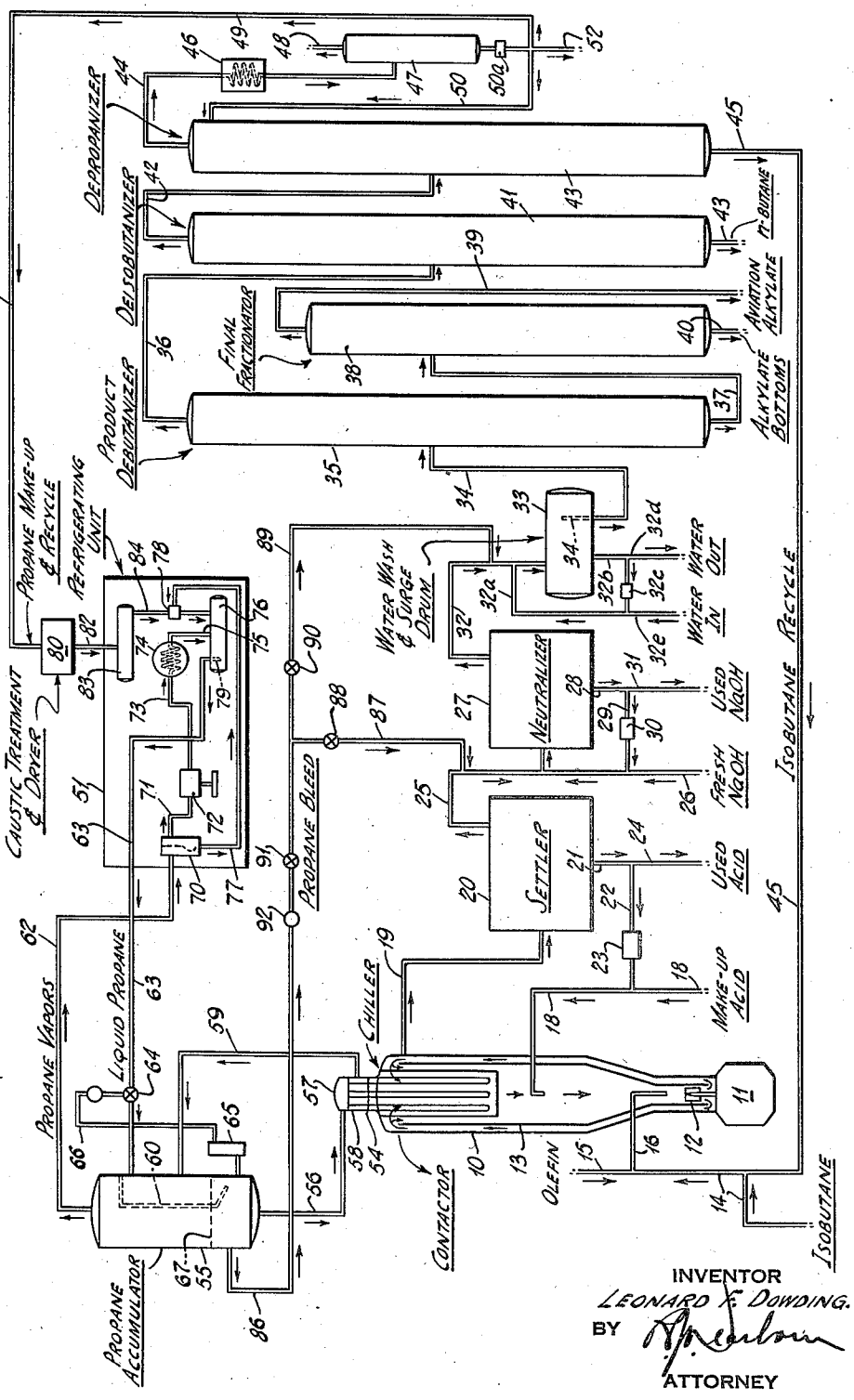


Fig. 1.

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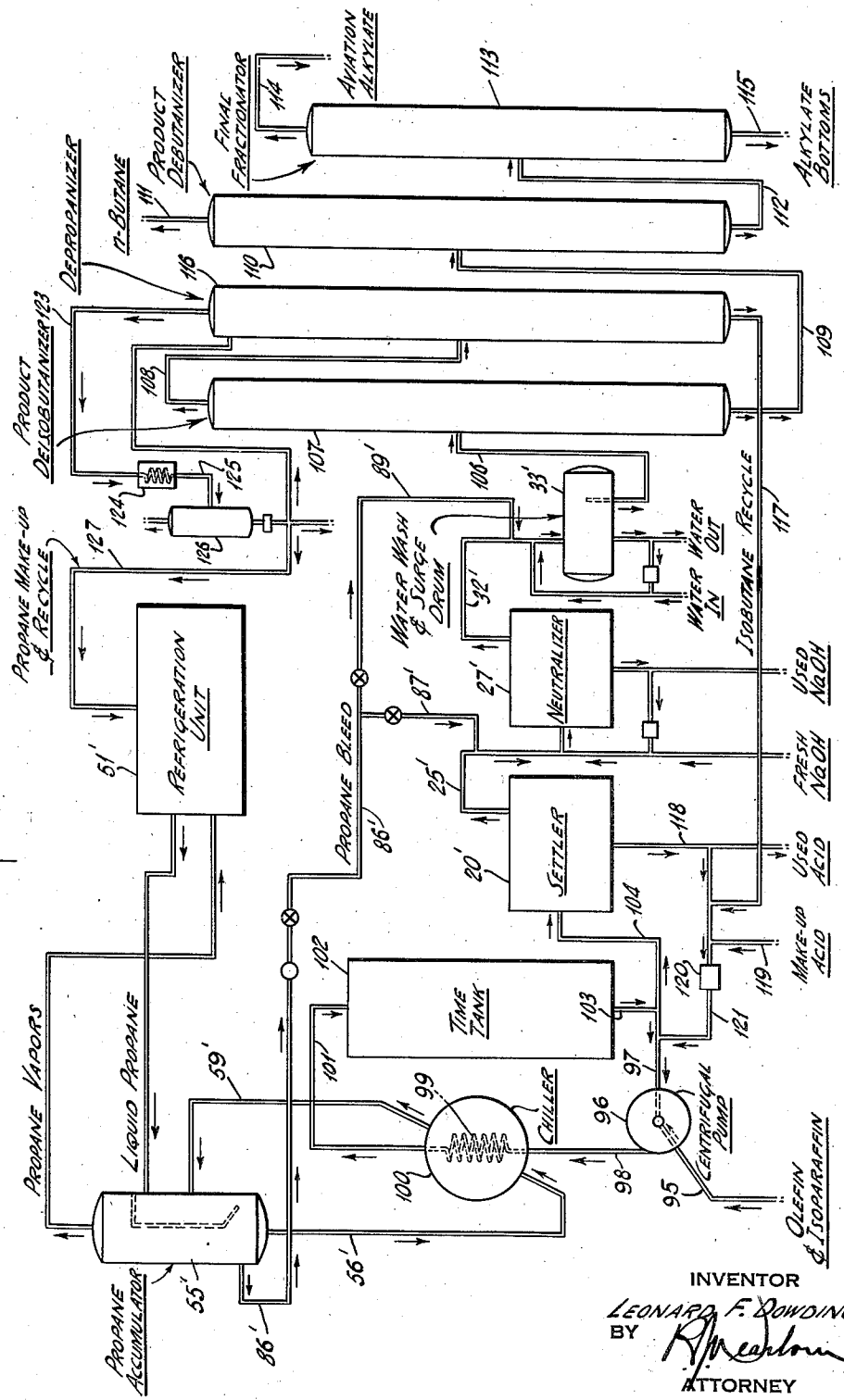


Fig. 2.

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Filed April 1, 1944 3 Sheets-Sheet 3

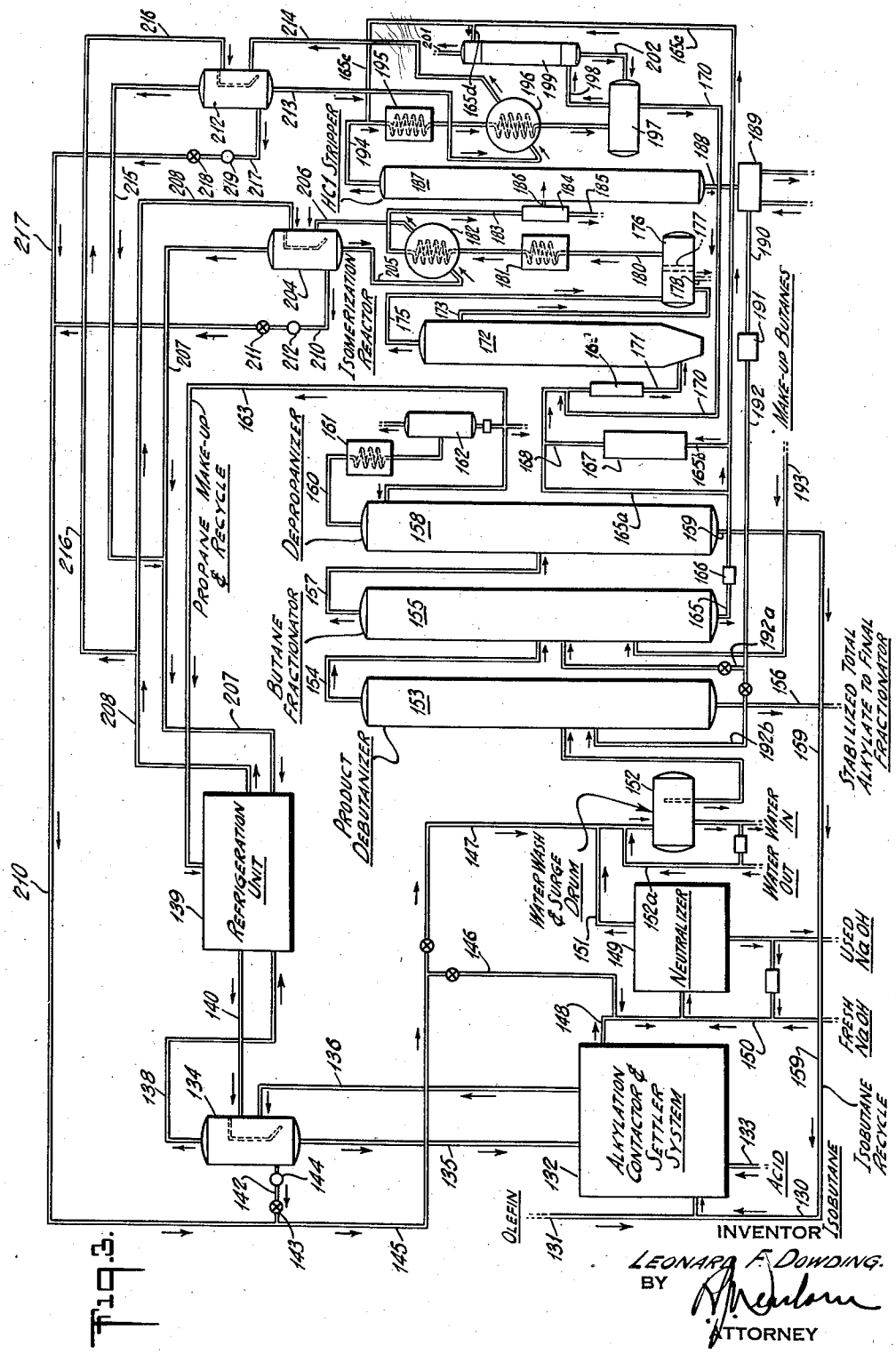


Fig. 3.

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UNITED STATES PATENT OFFICE

2,389,604

TEMPERATURE CONTROL FOR HYDROCARBON OIL PROCESSING

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Application April 1, 1944, Serial No. 529,075

18 Claims. (Cl. 260—683.4)

This invention relates to hydrocarbon oil processing, and more particularly to temperature control for such processing by indirect heat exchange with a liquefied normally gaseous hydrocarbon refrigerant obtained from the hydrocarbon oil stabilizing and fractionating system. The invention is particularly applicable to alkylation units and combination alkylation-isomerization units for the manufacture of motor fuel or aviation gasoline, and wherein propane or other liquefied normally gaseous hydrocarbon obtained from the alkylate fractionating system is utilized as the refrigerant for temperature control in the alkylation or combination alkylation-isomerization units.

In the modern refinery, one or more alkylation units are generally provided for the purpose of converting refinery gases or other hydrocarbon products into high octane motor fuel or aviation gasoline by isoparaffin-olefin alkylation. Also, such an alkylation unit may be combined with an isomerization unit, the latter furnishing the low-boiling isoparaffin, such as isobutane, to the alkylation unit. Temperature control for the alkylation unit, and also for certain operations in the isomerization unit, is generally accomplished by indirect heat exchange with a suitable refrigerant. The latter is recirculated from a refrigerating unit to the heat exchange chiller and back again through repeated stages of compression and cooling for liquefaction and indirect heat exchange for vaporization. A very satisfactory and economical source of refrigerant is a liquefied normally gaseous hydrocarbon, such as propane, obtained directly from the refinery, such as from the alkylate stabilizing and fractionating system. For example, refrigerant propane makeup to the refrigeration unit may be obtained from the overhead condensate of the depropanizer tower, which latter is a part of the stabilizing and fractionating system of the alkylation unit or combination alkylation-isomerization unit.

During continued recirculation in the refrigeration unit and chillers, the refrigerant propane frequently becomes contaminated with heavier normally liquid impurities which accumulate and remain in the chiller side of the refrigeration unit. The liquefied propane refrigerant is partially vaporized in the chilling coils by indirect heat exchange with the hydrocarbon oil being processed, and the resulting propane vapors are passed to the refrigerating unit where they are compressed in propane compressors and then cooled by indirect heat exchange with cooling water. The compressors are conventionally supplied with lubricating oil on the interior of the compressor cylinder for lubrication of the piston movement therein. A small proportion of this lubricating oil may become entrained in the compressed propane and carried out of the compressor cylinder therewith to the propane condenser and thence to a liquefied propane receiver. The refrigerant so contaminated is then returned to the cooling coils by way of a propane accumulator. Since this lubricating oil is higher boiling than the propane, it is not evaporated and returned with the propane vapors to the refrigerating unit, but remains in the propane accumulator and chiller.

In addition to this lubricating oil contamination, the propane refrigerant may also become contaminated with other liquid impurities, such as water, and also acid and liquid hydrocarbons resulting from leakage of the hydrocarbon-acid emulsion into the propane chiller at the alkylation unit, or similar leakage in the chiller at the isomerization unit. The resulting build-up of such liquid impurities in the liquefied propane on the chiller side of the refrigerating unit during long periods of continuous operation eventually may seriously impair or entirely stop the proper flow of propane through the chilling coils and refrigerant flow passages. The resulting decrease in refrigerating effect disturbs the temperature control and deleteriously affects the alkylation or other operations.

One of the principal objects of the present invention is to overcome the above-noted defects and provide an improved temperature control for hydrocarbon oil processing, wherein the liquefied normally gaseous hydrocarbon refrigerant is maintained throughout long periods of continuous operation substantially free from such normally liquid contamination, and high refrigerating efficiency and effective temperature control are thereby secured.

Another object of the present invention is to provide, in combination with an isoparaffin-olefin alkylation unit for the manufacture of motor fuel or aviation gasoline, an improved propane or other liquefied normally gaseous hydrocarbon refrigerating system, wherein the makeup propane or other liquefied normally gaseous hydrocarbon for the refrigerating system is obtained from the stabilizing and fractionating system of the alkylation unit, and wherein the liquefied propane in the refrigerating system is maintained in a purified condition by recirculation and purification of a portion thereof in the

said alkylate stabilizing and fractionating system.

Still another object of the present invention is to provide, in combination with a catalytic alkylation unit employing an acid catalyst and having the usual neutralizing and fractionating system for the resulting alkylate, an improved propane refrigerating system wherein a portion of the liquefied propane of the refrigerating system is neutralized and purified in the neutralizing and fractionating system of the alkylation unit.

A further object of the present invention is to provide, in a combined alkylation-isomerization unit, improved propane refrigeration for either or both of the alkylation and isomerization treatments, and wherein the liquefied propane refrigerant is maintained in a purified condition by treatment of a portion thereof in the neutralizing and fractionating system of the combined alkylation-isomerization unit.

Still another object of the present invention is to provide an improved propane or other liquefied normally gaseous hydrocarbon refrigerating system especially adapted for use in a refinery or other source of supply of the hydrocarbon refrigerant, and wherein the liquefied refrigerant is maintained free from liquid contamination over long periods of operation by cyclic recirculation and purification treatment.

Other objects and advantages of the invention will be apparent from the following description when taken in conjunction with the appended claims and the several figures of the attached drawings.

The present invention is more particularly illustrated by way of preferred embodiments thereof in the drawings, in which

Figure 1 is a diagrammatic elevational view, with certain parts in section, of an isoparaffin-olefin alkylation unit with associated refrigerating system constructed in accordance with the present invention;

Figure 2 is a diagrammatic elevational view similar to Figure 1 of a modification, showing a different order of alkylate stabilization and fractionation; and

Figure 3 is a diagrammatic elevational view of a combined alkylation-isomerization unit, showing a plurality of propane accumulators and chillers connected to a single refrigeration unit, and having provisions for continuous purification of the liquefied propane from any or all of the accumulators in accordance with the method of the present invention.

While the invention is specifically described as applied to an alkylation unit or a combination alkylation-isomerization unit, it is to be understood that this is merely by way of example and not by way of limitation. The improved refrigerating system of the present invention can be utilized for indirect heat exchange with or chilling of any treating or processing operation where temperature control, particularly the maintenance of relatively low temperatures, is found desirable. Thus, the invention may be applied to low-temperature short-contact-time hydrocarbon oil acid-treating, or to other catalytic hydrocarbon conversion processes, such as aromatic-olefin alkylation, naphthene-olefin alkylation, normal paraffin-olefin alkylation, naphtha or other normal paraffin isomerization, hydrogen exchange reactions, and other hydrocarbon synthesis reactions. It is to be understood that in these various applications, the propane or other liquefied normally gaseous hydrocarbon refrigerant withdrawn from the refrigerating unit will be purified by mixing with a broad boiling range hydrocarbon oil, and the mixture then passed to the stabilizing and fractionating system supplying makeup propane or other liquefied hydrocarbon to the refrigerating unit. Also, treatment for the prevention of corrosion and fouling in the system, such as caustic or other alkaline neutralization and water washing, can be given the withdrawn refrigerant in advance of the stabilizing and fractionating treatment

Referring to Figure 1, an alkylation contactor of the impeller internal-recirculation type, such as a Stratco reactor, is diagrammatically indicated at 10. This is equipped with a motor 11 driving an impeller 12 which forces the contents of the reactor to circulate upwardly through the annular chamber between the outer casing and an inner shell 13, and thence return downwardly through the central passage to the impeller. Fresh feed isobutane is introduced by line 14 and is mixed with an olefin feed stock from line 15, the resulting mixture having a molar excess of isobutane to olefin passing by line 16 into the contactor. Makeup acid, such as strong sulfuric acid, is introduced by line 18 to supply the required alkylation catalyst which forms an emulsion with the hydrocarbons in the contactor that is internally recirculated in conventional manner.

A stream of the emulsion is continuously withdrawn by line 19 to a settler 20 where an upper hydrocarbon phase settles from a lower acid phase. Acid is continuously removed from the lower acid layer by line 21; and all or any portion thereof may be recycled to the reactor by line 22 containing pump 23 and line 18, the balance being discharged to recovery by line 24.

The hydrocarbon phase of settler 20 is continuously withdrawn by line 25 and introduced together with caustic soda from line 26 into a neutralizer 27. The neutralized hydrocarbons separate as an upper layer from a lower aqueous caustic layer which is withdrawn by line 28. Any portion of the withdrawn caustic soda stream may be recirculated by line 29 containing pump 30 and line 26 for the treatment of further quantities of hydrocarbons, the balance being discharged by line 31. A stream of the neutralized hydrocarbon layer is withdrawn from neutralizer 27 by line 32 and passed to a water wash and surge drum 33. Any remaining caustic and water soluble reaction products are removed from the hydrocarbon oil at this point by introducing water from line 32*a* into line 32 through a suitable mixer. The mixture then passes into the surge drum 33, where the hydrocarbon oil stratifies as an upper layer from a lower water layer which is removed by bottom line 32*b*. A portion of the water may be recirculated by pump 32*c* and line 32*a*, the balance being discharged by line 32*d*. Fresh makeup water is introduced by line 32*e*.

From the surge drum 33, a stream of the hydrocarbons is withdrawn by line 34 which extends upwardly from the bottom of the drum into the hydrocarbon layer. Line 34 serves to introduce the hydrocarbons into a stabilizing tower 35 customarily termed a product debutanizer. This tower 35 is operated under conditions to stabilize the resulting alkylate, removing overhead by line 36 normal butane and lighter. The stabilized alkylate is passed by bottom line 37 to a final

fractionator 38, where the desired aviation or motor fuel fraction is removed overhead by line 39, and any heavier material, termed alkylate bottoms, is removed by line 40. The overhead gases from the product debutanizer, which in the case of C_4 alkylate consist largely of normal butane, the excess isobutane and some propane, are introduced by line 36 into a deisobutanizer 41, which is operated to remove overhead by line 42 isobutane and lighter, a normal butane stream being withdrawn by bottom line 43. It will be understood that the various towers heretofore described are equipped with condensers and accumulators, reflux lines and pumps, bottom heating coils or reboilers and suitable control equipment in conventional manner.

The overhead stream from deisobutanizer 41, consisting mainly of isobutane with a small proportion of propane, is passed by line 42 to a depropanizer 43, where an essentially pure propane stream is removed overhead by line 44. The bottoms from this tower consisting essentially of isobutane are withdrawn by line 45 and recycled to the alkylation contactor by way of lines 14 and 16. The overhead propane vapors are condensed in a water-cooled condenser 46 and passed to an accumulator 47. Any uncondensed vapors may be removed from accumulator 47 by vapor relief line 48. A minor proportion of the liquefied propane from accumulator 47 is passed by line 49 to the refrigerating unit indicated generally at 51 and to be hereinafter more specifically described. The major proportion of the condensate propane is returned by line 50 and pump 50*a* to the upper portion of tower 43 to serve as reflux therein. Any excess propane not required for refrigeration or reflux may be passed by line 52 to tankage or other suitable disposal.

As shown, alkylation contactor 10 is equipped with a chilling tube bundle 54 mounted on the upper head of the contactor with the chilling tubes depending into the circulating emulsion stream within the reactor. Liquefied propane is supplied from a propane accumulator 55 through line 56 to a header 57, from which the propane passes into a plurality of the tubes of the bank in parallel. The propane flows downwardly through these tubes which open at their lower ends into surrounding return tubes providing a double tube type of chiller, the outer tubes serving to return the propane to header 58. During its passage through the chilling tubes, the liquefied propane is heated by indirect heat exchange with the recirculating emulsion, with the result that a portion of the propane is vaporized during its flow through the outer return tubes. The mixed propane liquid and vapor returns from header 58 by line 59 to accumulator 55, being discharged against suitable liquid entrainment baffles 60 designed to effect a separation between liquid and vapor. The resulting propane vapors are released from accumulator 55 by vapor line 62 and passed to the refrigerating unit 51. Liquefied propane is returned from the refrigerating unit through line 63 under the control of valve 64 to accumulator 55. A liquid level controller 65 of conventional type and equipped with fluid line 66 serves to actuate valve 64 to maintain a constant level of liquid propane within accumulator 55, as indicated at 67.

It is thus seen that a thermo-siphonic circulation of liquefied propane is set up between the propane and accumulator 55 and the chilling tube bundle 54, and in which a substantial part of the propane remains in liquid state. For example, about one-fifth of the propane flowing by line 56 to the chilling bundle may be vaporized in each pass by heat exchange in the chilling tubes, the remaining four-fifths of the liquefied propane returning in liquid state together with the resulting dispersed vapors by line 59 to the accumulator. The baffles 60 provide for separation between the liquefied and vaporized propane, the vapor accumulating in the vapor space and being withdrawn by compressor suction through line 62 to the refrigerating unit.

Any conventional type of rerfigerating unit of the compressor-condenser type can be employed. As shown, line 62 discharges into a suction trap 70 designed to effect a separation of any entrained liquid propane from the vapors, so that liquid does not enter the compressor cylinders. The vapors are withdrawn from the suction trap 70 by line 71 to the compressor 72, which forces the compressed vapors through line 73 to water-cooled condensers indicated at 74. The resulting liquid propane then flows by line 75 into a propane receiver 76. Any liquid propane separated in suction trap 70 may be passed by line 77 and transfer pump 78 to the receiver 76. From the latter, liquefied propane is withdrawn by depending line 79, which communicates with line 63 for return of liquid propane to accumulator 55 in accordance with the liquid level control.

As previously described, propane refrigerant for the refrigerating unit is obtained from the overhead condensate of depropanizer tower 43 of the alkylate stabilizing and fractionating system. In order to remove any SO_2 which is sometimes found in this overhead, the propane makeup from line 49 may be treated with caustic soda in a small vessel 80, the caustic soda being recirculated by means of a suitable eductor. The caustic soda is settled from the liquid propane and the latter may then be passed through a drier containing flake calcium chloride or unslaked lime to remove water. The makeup propane, free from SO_2 and water, passes by line 82 to a storage drum 83, from which it is withdrawn as needed by line 84 and transfer pump 78 and passed to the propane receiver 76.

In accordance with the present invention, a stream of liquid propane is withdrawn from accumulator 55 by bleed line 86. This stream may be passed by line 87 controlled by valve 88 to line 25, where the propane is mixed with the hydrocarbon oil steam passing from settler 20 to neutralizer 27. Or the propane can be passed by line 89 controlled by valve 90 to line 32, where it is mixed with the hydrocarbon oil stream flowing from neutralizer 27 to surge drum 33 in advance of the water wash line 32*a*. The rate of withdrawal of propane is conveniently controlled by a throttle valve 91 which is regulated in accordance with an indicating flow meter 92. Generally, the bleeding off of only a small proportion of the liquefied propane in the refrigerating system is sufficient to maintain the liquid propane in the system effectively free from the contaminating impurities. The withdrawal of propane from the refrigeration system is preferably continuous and at a uniform rate as controlled by the throttle valve 91; although the withdrawal can be intermittent or at variable rates throughout a long period of continuous operation.

Where the propane in the refrigeration system has become contaminated with acid, or where such contamination is likely to occur, valve 90 will be closed and valve 88 opened, so that the

propane bleed stream passes by line 87 to be mixed with the unstabilized alkylate in advance of the neutralizer. The mixing of the propane stream with the hydrocarbon oil in either line 25 or line 32 results in the absorption of the propane in the heavier hydrocarbon oil, thereby facilitating the purification treatment and enabling the use of lower pressures, and higher temperatures, thereby avoiding difficulties which would be involved in the treatment of the volatile propane at the high pressures or low temperatures otherwise required. Both the neutralizer 27 and the surge drum 33 of the alkylation unit are operated at lower pressures than the propane accumulator 55, the pressure differential being used to transfer the propane bleed under the control of the throttle valve 91. The mixed propane and unstabilized alkylate from line 25 are then subjected to the neutralizing action of the caustic solution from line 26 in neutralizer 27, whereby retained acid is removed from both the alkylate and the propane bleed stream. The mixed alkylate and absorbed propane then passes to the water wash and surge drum 33 and thence to the alkylate fractionating system.

Where acid contamination is not involved, and the only liquid impurities are heavier hydrocarbons and water, valve 88 will be closed and valve 90 opened so that the propane bleed stream flows by line 89 and is mixed with the hydrocarbon oil stream in line 32 following the neutralization of the latter. Here again the propane bleed stream is preferably introduced into the flowing hydrocarbon oil stream to obtain the desired turbulent mixing and absorption effects. In neither case, the resultant mixture from surge drum 33 passes to the product debutanizer 35 where the propane is removed overhead along with isobutane and normal butane, and thereby separated from heavier liquid impurities, such as lubricating oil and water. The latter remain in the stabilized alkylate which passes by line 37 to the final fractionator 38. The lubricating oil will of course remain in the alkylate bottoms withdrawn by line 40; and these bottoms can be subsequently fractionated if desired to separate a heavier motor fuel fraction from the lubricating oil and any other heavier material contained therein. Any water will pass overhead from fractionator 38 along with the aviation alkylate, which is led by line 39 to a suitable condenser and accumulator. The water will then separate out as a lower layer in the accumulator and may be withdrawn from the system.

The overhead propane and other gases from product debutanizer 35 pass by line 36 to the deisobutanizer 41, from where isobutane and propane pass overhead by line 42 to depropanizer 43. In the latter tower, the propane, including that introduced by propane bleed line 86 and that present in the alkylation feed stock from lines 14 and 15, will be separated by overhead line 44 from the isobutane which is recycled to the alkylation unit by line 45. A purified propane condensate, free from heavier liquid impurities, is thereby returned from accumulator 47 by line 49 to the refrigerating unit 51. This return may be by pressure differential between accumulator 47 and the liquefied propane storage drum 83; or line 49 can be branched off of the usual reflux line 50 containing reflux pump 50a. This propane supply to the refrigerating unit 51 will include propane recycle, that is, propane bled off from the refrigerating unit by line 86, and any necessary makeup propane from the alkylate feed stocks required to keep the propane tanks 83 and 76 properly supplied with the refrigerant.

The alkylate fractionating system described above is that customarily employed when alkylating isobutane with an olefinic charge stock, such as a refinery C_4 cracking gas fraction. It is to be understood that the present invention is applicable to the alkylation of other low-boiling isoparaffin, such as isopentane, with any olefin, either normally gaseous or normally liquid, or other alkylating agent, such as an alkyl ester, alcohol or ether. Suitable provisions are made in the alkylate fractionating system to separate the propane or other normally gaseous hydrocarbon refrigerant from the alkylate and from the isoparaffin recycle to the alkylation unit. While sulfuric acid has been specifically described above as the alkylation catalyst, it is to be understood that any other suitable alkylation catalyst may be employed, such as hydrofluoric acid, boron trifluoride-water complex, aluminum chloride-hydrocarbon complex preferably with a small proportion of HCl, and the like. Moreover, any suitable contactor can be employed for the alkylation in place of the Stratco reactor, such as a pump and time tank reactor, jet reactor, tower reactor, and the like. Moreover, the alkylate fractionating system can be modified from that shown in Figure 1.

This is illustrated more particularly in Figure 2 which discloses an alkylation reactor of the pump and time tank type and a fractionating system of the so-called reverse flow type. As shown in this figure, a mixed stream of isoparaffin and olefin is introduced by line 95 into the suction side of a centrifugal pump 96 where it is mixed with a recirculating emulsion stream from line 97, the mixture being passed by line 98 through cooling coils 99 in a chiller 100. The resulting cooled emulsion then passes by line 101 to a baffled time tank 102 from which a stream of the emulsion is withdrawn by line 103. The latter stream is divided, the major portion being recirculated by line 97 and a minor portion being passed by line 104 to settler 20'.

Refrigerant propane is supplied from accumulator 55' by line 56' to the jacket of chiller 100 surrounding the coils 99, the mixed propane liquid and vapors being returned by line 59' to accumulator 55'. Except as described herein, the construction of the other elements in Figure 2 is the same as that heretofore described in connection with Figure 1, and similar primed reference numerals are used to designate these corresponding parts. Propane bleed from accumulator 55' is passed by line 86' and either lines 87' or 89' to mix with the unstabilized alkylate, either in advance of the neutralizer 27' or following the neutralizer and immediately in advance of the water wash and surge drum 33'.

In this case, the hydrocarbon stream from surge drum 33' passes by line 106 to a product deisobutanizer 107 which is operated to remove overhead by line 108 isobutane and lighter. The bottoms from tower 107 pass by line 109 to a product debutanizer 110, where the desired stabilization of the alkylate is accomplished by removing normal butane overhead by line 111. The stabilized alkylate then passes by line 112 to a final fractionator 113, where the aviation alkylate is removed overhead by 114 and the alkylate bottoms are discharged by 115. The overhead stream from deisobutanizer 107 passes by line 108 to a depropanizer 116, from which a bottom recycle stream of isobutane is removed by line

117. This isobutane recycle is preferably mixed with recycle acid from bottom line 118 of settler 20' in advance of the addition of any makeup acid by line 119, and the mixture or emulsion then passed by pump 120 and line 121 into the main emulsion recycle line 97 in advance of pump 96.

The overhead propane vapors from depropanizer 116 are passed by line 123 to water-cooled condenser 124, and thence by run-down line 125 to accumulator 126. Propane condensate is supplied as recycle and makeup propane from accumulator 126 by line 127 to the refrigerating unit 51' in the manner heretofore described.

Figure 3 discloses the invention as applied to a combination alkylation-isomerization unit, wherein a plurality of propane accumulators and associated chillers are connected to a common refrigeration unit. As shown, isobutane from line 130 and olefin from line 131 are introduced into an alkylation contactor and settling system indicated diagrammatically at 132, to which acid alkylation catalyst is supplied by line 133. Temperature control of the alkylation contactor is accomplished by a chilling coil supplied with propane from accumulator 134 by line 135. The mixed propane liquid and vapor is returned from the chiller by line 136 to accumulator 134. Propane vapors are released from accumulator 134 by line 138 and passed to a common refrigerating unit 139 similar to the unit 51 of Figure 1. Liquid propane is returned from refrigeration unit 139 by line 140 to accumulator 134 in accordance with the liquid level control as heretofore described.

Liquid propane is bled off from accumulator 134 by line 142 containing its individual throttle valve 143 and flow meter indicator 144. This propane bleed is passed by line 145 and either of branch lines 146 or 147 to mix the propane with the unstabilized alkylate stream in the manner heretofore described. Line 146 thus empties into line 148 carrying a hydrocarbon stream from the settler of the alkylation unit to the neutralizer 149 in advance of the caustic soda inlet 150. Line 147 discharges into line 151 carrying the neutralized hydrocarbon stream from neutralizer 149 to surge drum 152 in advance of the water wash inlet 152a.

The resulting hydrocarbon from surge drum 152 passes to product debutanizer 153 from which butane and lighter pass overhead by line 154 to butane fractionator 155. The stabilized total alkylate is removed from 153 by bottom line 156 to a final fractionator not shown. From the butane fractionator 155, an overhead stream of isobutane and lighter passes by line 157 to depropanizer 158, from which an isobutane recycle stream is removed as bottoms by line 159 and recycled to the alkylation unit. The overhead propane stream passes by line 160 to condenser 161 and accumulator 162, from which the propane makeup and recycle stream is passed by line 163 to the refrigeration unit 139.

The bottoms consisting largely of normal butane from butane fractionator 155 are passed by line 165 and pump 166 to branch lines 165a and 165b, the latter containing an aluminum chloride absorber 167. The latter contains lump aluminum chloride which is utilized as makeup catalyst for the isomerization unit to maintain the activity of the aluminum chloride-hydrocarbon complex catalyst employed in the isomerization reactor at the desired level. The normal butane, which is preferably at a temperature of around 200° F., dissolves aluminum chloride to substantial saturation; and this solution then passes by line 168 to a mixer 169 where it meets the main stream of n-butane from line 165a and a stream of normal butane containing HCl from line 170 and prepared as hereinafter described. The resulting mixture then passes by line 171 into the bottom of isomerization reactor 172 which is filled to the overflow level of line 173 with a liquid body of aluminum chloride-hydrocarbon complex catalyst. This tower is maintained at a temperature of about 200–240° F., which is conducive to rapid isomerization of the normal butane to isobutane to an equilibrium conversion of around 40–60%, depending upon the conditions of the reaction and the activity of the catalyst.

The normal butane, containing dissolved aluminum chloride and HCl, is dispersed into the bottom of tower 172 from line 171, and passes upwardly in the form of a multitude of fine liquid drops through the maintained liquid catalyst body as the continuous phase. During this passage through the liquid catalyst, the hydrocarbon gives up its aluminum chloride to the catalyst body, thereby maintaining the activity of the latter. The hydrocarbon drops, upon reaching the upper surface of the liquid catalyst body, form a superposed hydrocarbon layer of mixed isobutane and normal butane, from which a stream is withdrawn by line 175. This stream of crude isomate is introduced into a complex trap 176 containing a Raschig ring nest 177 or other suitable packing, which removes any complex liquid carried along with the hydrocarbon stream. Any separated complex may be withdrawn by line 178.

The hydrocarbons along with the HCl removed overhead in stream 175 then pass by line 180 through water-cooled condenser 181 and propane chiller 182, which cool the stream to a temperature of about 50° F. The cooled stream then passes by line 183 to a complex knock-out drum 184, where any remaining complex separates and is removed by line 185. The hydrocarbons containing HCl then pass by line 186 into a HCl stripper 187, which is operated to distill all the HCl overhead together with a small proportion of the butanes. This requires reboiling in the base of tower 187. The heated isomate from the bottom of the stripper passes by line 188 to a water-cooler 189, where the temperature is lowered sufficiently for caustic neutralization, water washing, and introduction into the alkylate fractionating system.

As shown, the cooled butane stream then is passed by line 190 to a caustic and water wash unit 191 where the butanes are neutralized and then washed with water. The purified butanes are then passed by line 192 which communicates with valve controlled branch lines 192a and 192b opening respectively into the butane fractionator 155 and the product debutanizer 153. Where the crude isomate contains some pentanes and heavier, the latter will remain in the butane stream discharged by line 188 from the base of HCl stripper 187. In such case, all or a portion of the stream may be passed by lines 192 and 192b to the product debutanizer, so that the pentanes and heavier will remain in the stabilized total alkylate which is passed by line 156 to the final fractionator, and thus separated from the butanes and lighter passed overhead by line 154. This prevents undesirable build-up of pentanes and heavier in the isomerization system. Or the stream from line 192 may be passed for a period of time

by line 192a to the butane fractionator 155 until the pentanes build up to a certain maximum proportion, and then diverted by line 192b to product debutanizer 153 for another period of time to reduce the pentane content to a certain minimum proportion, with repetition of this alternate shifting to maintain the pentane content within the isomerization unit within a predetermined range which tends to minimize the formation of pentanes and heavier in the isomerization reactor 172 and render the isomerization reaction more selective for the production of isobutane.

In either case, the isobutane produced in the isomerization unit is separated from n-butane in the butane fractionator 155 and is eventually supplied by line 159 to serve as make-up isobutane for the alkylation unit. The n-butane charge to the isomerization unit may come entirely from the fresh feed to the alkylation unit, such as from the cracking gas fraction introduced by line 131, and which n-butane passes unreacted through the alkylation system and is eventually removed as bottoms from butane fractionator 155 by line 165. If additional makeup butanes are required, these may be supplied by line 193 from any suitable source, such as a C_4 fraction from the stabilization of natural gasoline, and introduced into the butane fractionator 155.

The overhead from the HCl stripper 187, consisting of HCl and mixed butanes, passes by line 194, together with added n-butane from line 165c, through water-cooled condenser 195 and propane chiller 196 to a so-called HCl mix surge drum 197. The butanes accumulate as a liquid in this drum and contain absorbed HCl. Any unabsorbed HCl passes off by vapor line 198 to an absorber 199, where the vapors flow countercurrent to a descending normal butane stream introduced by line 165d, the latter being branched from line 165c and supplied by pump 166. Any remaining unabsorbed vapors pass off by line 201. The resulting normal butane stream with absorbed HCl is returned from absorber 199 by line 202 to the surge drum 197. From the latter, a stream of the butanes with absorbed HCl is passed by line 170 to mixer 169 for introduction into the isomerization reactor 172. In this manner, the desired HCl concentration is maintained within the isomerization reactor, while loss of HCl from the system is minimized.

The propane chiller 182 for the crude isomate stream is supplied with liquid propane from accumulator 204 by line 205. Mixed propane liquid and vapors return from chiller 182 to accumulator 204 by line 206. Propane vapors from accumulator 204 are withdrawn by line 207 to the refrigeration unit 139; and propane liquid is supplied from the unit by line 208 to accumulator 204 in accordance with a liquid level control as previously described. While lines 138—140 and lines 207—208 are shown for convenience as connected to the refrigeration unit at different locations, it will be understood that these lines lead to a common compressor and cooling unit of the character shown in Figure 1. Liquid propane is bled from accumulator 204 by line 210 under the control of throttle valve 211 and indicating flow meter 212. Line 210 joins line 145 for return of this propane to the alkylate neutralizing and fractionating system along with the propane bleed from accumulator 134.

Propane chiller 196 for the overhead from HCl stripper 187 is supplied with refrigerant propane from accumulator 212 by line 213; and the propane liquid and vapor are returned from chiller 196 by line 214 to accumulator 212. Vapors from 212 are removed through line 215, which joins line 207 leading to the refrigeration unit 139. Liquid propane is returned from the refrigeration unit by lines 208 and 216 to accumulator 212 in accordance with its individual liquid level regulator. Liquid propane is also bled from accumulator 212 by line 217 under the control of its individual throttle valve 218 and indicating flow meter 219. Line 217 joins line 210 for the return of this bleed propane through the said lines and line 145 to the alkylate neutralizing and fractionating system as heretofore described.

It is thus seen that the depropanizer 158 of the combined alkylate and isomate fractionating system supplies the propane refrigerant to a common refrigeration unit 139, which in turn supplies the accumulators 134, 204, and 212 for the various thermo-siphonic chilling circuits. The bleed of liquid propane from each individual accumulator and associated chilling circuit can be independently controlled and regulated; and makeup liquid propane from the common refrigeration unit is likewise under independent control. The cyclic process of bleeding propane from the various chilling units to the combined alkylation-isomerization fractionation system, with return of purified recycle and makeup propane to the common refrigeration unit, maintains the propane refrigerant in all of the chilling circuits in a proper and highly efficient condition over long periods of continuous operation and in a very economical manner.

While liquid phase isomerization has been specifically disclosed, it is to be understood that vapor phase operation may be used. While an aluminum chloride-hydrocarbon complex has been specifically mentioned above as the isomerization catalyst, it is to be understood that the invention is applicable to other isomerization catalysts, such as aluminum bromide, zirconium chloride, complexes thereof, etc. Moreover, while isomerization of normal butane to produce isobutane for the alkylation unit has been specifically described, it is to be understood that the invention is applicable to the isomerization of other normal paraffins, such as the isomerization of normal pentane to produce isopentane for alkylation with olefins or for blending directly with the motor fuel.

The following specific example is given as illustratory of the present invention. In a commercial alkylation plant having a rated capacity of 1180 BPOD, utilizing three type 50 Stratco contactors in parallel, and a refrigeration unit having a rated capacity of 607 A. S. R. E. tons (each ton equivalent to 12,000 B. t. u. per hour), difficulty had been experienced due to the accumulation of lubricating oil in the refrigerant propane in the chillers for the three contactors. The plant was modified in accordance with the present invention to install propane bleed lines from the several accumulators to the alkylate fractionating system. A bleed of about ½ barrel (21 gallons) per hour of liquid propane was then taken from each accumulator. The plant was designed for total olefin feed of 96.8 barrels per hour, and total isobutane feed of 158.5 barrels per hour, making a total combined feed of 255.3 barrels per hour, which is split between the three contactors. Consequently, each contactor has a designed fresh feed rate of about 85.1 barrels per hour. Each contactor was designed to operate with an internal recirculation rate of about 45,000–50,000 gallons per minute. The volume of propane in the chilling coils and lines for each contactor is

approximately 800 gallons, and the volume of the propane in the associated accumulator is approximately 250 gallons, giving a total volume of propane under thermo-siphonic circulation of about 1,050 gallons. The refrigeration unit was designed to maintain a reactor temperature of about 50° F. For this condition, the pressure on the propane accumulator is maintained at about 54 pounds per square inch, resulting in the evaporation of propane in the chilling coils at about 35° F.; and the compressors of the refrigeration unit are designed for a suction pressure of about 57 pounds per square inch and a discharge pressure of 175 pounds per square inch with condensation of the compressed propane at 90° F., basis a maximum cooling water temperature of 80° F. Under design conditions, the pressure in the neutralizer and water wash surge drum of the alkylation unit is maintained at about 15 pounds per square inch gage, thus affording a pressure differential of roughly 40 pounds per square inch for the propane bleed. With the plant operating at least at designed capacity, a bleed of ½ barrel per hour from the chilling circuit of each contactor to the alkylate fractionating system, with the return of sufficient purified propane from the alkylate depropanizer to supply recycle and makeup propane for the refrigeration unit, has served to maintain the refrigerant effectively free from liquid contamination, and satisfactory operation has now been secured over several months of continuous service since installation of the said propane bleeds. The propane from the alkylate depropanizer tower has been found to meet all of the specifications for commercial propane; and the maintenance of this propane in a pure condition is significant, since less power is required when using a relatively pure propane than when impure propane is employed.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. The cyclic method of controlling the temperature in a refinery hydrocarbon oil processing step, which comprises stabilizing and fractionating a hydrocarbon fraction to separate a normally gaseous hydrocarbon from heavier hydrocarbons, passing said normally gaseous hydrocarbon in liquefied form through a chilling zone in indirect heat exchange with the hydrocarbon oil being processed, whereby a portion of the liquefied normally gaseous hydrocarbon is vaporized, removing the vapors to a zone of compression and cooling for liquefaction and returning the liquefied refrigerant to the chilling zone, recirculating the refrigerant through repeated stages of said compression and cooling for liquefaction and indirect heat exchange for evaporation, whereby the refrigerant tends to become contaminated with heavier liquid impurities which accumulate in the chilling zone, withdrawing a minor portion of the contaminated liquefied refrigerant from the chilling zone, mixing the same with the said hydrocarbon fraction and then subjecting the resulting mixture to the stabilizing and fractionating operation, whereby the hydrocarbon refrigerant is separated from the heavier liquid impurities, and returning the separated purified hydrocarbon refrigerant together with any additional make-up normally gaseous hydrocarbon from said stabilizing and fractionating operation to the chilling zone.

2. The method according to claim 1, wherein the withdrawn portion of contaminated liquid refrigerant is subjected to a neutralizing and water washing treatment before being subjected to the stabilizing and fractionating operation.

3. In a continuous process for catalytically reacting hydrocarbons in the presence of a catalyst, wherein the hydrocarbons undergoing reaction are maintained at a controlled temperature by indirect heat exchange in a chilling zone with a liquefied normally gaseous hydrocarbon refrigerant maintained in a closed expansion-compression refrigeration circuit, the resulting hydrocarbon reaction products are separated from the catalyst and then stabilized and fractionated to recover a finished hydrocarbon product, and wherein the recirculating normally gaseous hydrocarbon refrigerant tends to become contaminated with heavier normally liquid impurities which build up in the liquefied refrigerant on the chilling zone side of the refrigeration circuit, the improvement which comprises bleeding off a minor proportion of the liquefied refrigerant from the chilling zone side of the refrigeration circuit, mixing said bled-off refrigerant with said resulting hydrocarbon reaction products, stabilizing said mixture to remove overhead a vapor fraction including the normally gaseous hydrocarbon refrigerant and thereby separate the same from a liquid bottoms containing the desired hydrocarbon product and heavier impurities, fractionating said bottoms to recover the desired hydrocarbon product, recovering normally gaseous hydrocarbon refrigerant from said overhead vapor fraction, and returning said recovered refrigerant to said refrigeration circuit.

4. Process in accordance with claim 3, wherein the overhead vapor fraction includes unreacted hydrocarbon as well as the normally gaseous hydrocarbon refrigerant, said vapor fraction is fractionated to separate the refrigerant as an overhead vapor from a liquid bottoms which is rich in the unreacted hydrocarbon, said liquid bottoms is recycled to the catalytic reaction, and said overhead refrigerant is returned to the refrigeration circuit.

5. In a continuous process for alkylating a low-boiling isoparaffin with an olefin in the presence of an alkylation catalyst, wherein the hydrocarbons undergoing reaction are maintained at a controlled temperature by indirect heat exchange in a chilling zone with a liquefied normally gaseous hydrocarbon refrigerant maintained in a closed expansion-compression refrigeration circuit, the resulting hydrocarbon reaction products are separated from the catalyst, neutralized, water washed, and then stabilized and fractionated to recover a gasoline alkylate, and wherein the recirculating normally gaseous hydrocarbon refrigerant tends to become contaminated with heavier normally liquid impurities which build up in the liquefied refrigerant on the chilling zone side of the refrigeration circuit, the improvement which comprises bleeding off a minor proportion of the liquefied refrigerant from the chilling zone side of the refrigeration circuit, mixing said bled-off refrigerant with said resulting hydrocarbon reaction products, stabilizing said mixture to remove overhead a vapor fraction including the normally gaseous hydrocarbon refrigerant and thereby separate the same from a liquid bottoms containing the gasoline alkylate and heavier impurities, fractionat-

ing said bottoms to recover the gasoline alkylate, recovering normally gaseous hydrocarbon refrigerant from said overhead vapor fraction, and returning said recovered refrigerant to said refrigeration circuit.

6. The method according to claim 5, wherein the hydrocarbons supplied to the alkylation reaction include a proportion of the normally gaseous hydrocarbon employed as refrigerant, additional make-up normally gaseous hydrocarbon is separated along with the purified refrigerant from the stabilizing and recovery operations, and the additional make-up hydrocarbon is returned along with the purified refrigerant to the refrigerating circuit to maintain the latter supplied with refrigerant over long periods of continuous operation.

7. The method according to claim 5, wherein the low-boiling isoparaffin is isobutane, the olefin is a C_4 olefin present in a refinery hydrocarbon fraction also containing some propane, the refrigerant is propane, the overhead vapor fraction separated in the stabilizing operation contains excess unreacted isobutane along with the propane, isobutane is separated from said fraction for recycling to the alkylation step, and propane is separated from said fraction to supply both makeup and recycled purified propane for the refrigeration circuit.

8. The method according to claim 5, wherein the liquefied refrigerant bleed stream is mixed with the said hydrocarbon reaction products following separation of the alkylation catalyst and prior to neutralization and water washing thereof.

9. In a continuous process involving catalytic alkylation of an isoparaffin with an olefin of a normally gaseous hydrocarbon fraction to produce gasoline hydrocarbons, stabilization and fractionation of the resulting hydrocarbon alkylation reaction products to separate from the latter the gasoline hydrocarbons, excess unreacted isoparaffin, and also corresponding normal paraffin and a different normally gaseous hydrocarbon included in said alkylation feed, recycling said isoparaffin to the alkylation step, subjecting said normal paraffin to catalytic isomerization to produce additional quantities of said isoparaffin, and returning hydrocarbon isomerization products to said stabilizing and fractionating operation, the improvement which comprises passing at least a portion of said different normally gaseous hydrocarbon to a refrigeration circuit of the compression-expansion type to serve as a liquefied refrigerant therein, bringing said liquefied refrigerant in the refrigeration circuit in indirect heat exchange in separate chilling zones with products of both said alkylation step and said isomerization step for temperature control of both steps, bleeding off separate streams of said liquefied refrigerant from the said separate chilling zones, and mixing said refrigerant streams with the hydrocarbon reaction products of the alkylation step, whereby the mixed refrigerant and hydrocarbon reaction products are subjected to the stabilizing and fractionating operation, and purified refrigerant along with fresh make-up normally gaseous hydrocarbon is returned from the stabilizing and fractionating operation to the refrigeration circuit.

10. The method according to claim 9, wherein the hydrocarbon alkylation reaction products are subjected to neutralization and water washing prior to the stabilization and fractionation, and the bleed refrigerant streams are mixed with the said hydrocarbon alkylation reaction products in advance of said neutralization and water washing steps.

11. In a process of temperature control by indirect heat exchange with a liquefied normally gaseous hydrocarbon refrigerant, which is repeatedly recirculated in a closed refrigeration circuit including a chilling zone where a portion of the liquefied refrigerant is vaporized, and a compression and cooling zone where the vapors are reliquefied and then returned to the chilling zone, and wherein the refrigerant tends to become contaminated with higher boiling impurities which accumulate in the liquefied refrigerant on the chilling zone side of the refrigeration circuit, the improvement for maintaining the refrigerant effectively free from said impurities which comprises withdrawing a minor portion of the liquefied refrigerant from the chilling zone side of said refrigeration circuit, mixing said withdrawn refrigerant with a broad boiling range hydrocarbon fraction containing higher boiling hydrocarbons as well as some hydrocarbon of the same character and boiling range as said normally gaseous hydrocarbon refrigerant, subjecting said mixture to stabilization and fractionation to thereby separate higher boiling hydrocarbons and impurities from a hydrocarbon cut consisting essentially of said purified normally gaseous hydrocarbon refrigerant along with additional hydrocarbon of the same character obtained from said broad boiling range fraction, and supplying said hydrocarbon cut to the refrigerating circuit to provide make-up and purified recycle refrigerant therefor.

12. The process according to claim 11, wherein the said mixture is treated with a caustic solution and then water washed before being subjected to the said stabilization and fractionation.

13. The process according to claim 11, wherein the refrigerant is propane, and the broad boiling range hydrocarbon fraction is composed primarily of hydrocarbons of gasoline boiling range.

14. The process according to claim 11, wherein the refrigerant is propane, and the broad boiling range hydrocarbon fraction is the unstabilized hydrocarbon reaction products of isobutane-olefin alkylation.

15. In combination, a hydrocarbon oil stabilizing and fractionating system comprising a debutanizer and a depropanizer in series, means for supplying a broad boiling range hydrocarbon oil mixture containing both normally liquid and normally gaseous hydrocarbons to said debutanizer, a refrigeration unit and chiller for indirect heat exchange with said hydrocarbon oil mixture in advance of said stabilizing and fractionating system, means for supplying a liquefied normally gaseous overhead hydrocarbon fraction from said depropanizer to said refrigeration unit to serve as the refrigerant therein, said refrigerant being recirculated in said refrigeration unit and chiller through repeated stages of compression and cooling for liquefaction and indirect heat exchange for evaporation, and wherein heavier normally liquid impurities tend to accumulate in the recirculating refrigerant, and means for bleeding a minor portion of the recirculating liquefied refrigerant into the debutanizer of said hydrocarbon oil mixture stabilizing and fractionating system, whereby the heavier impurities are separated from the normally gaseous hydrocarbon refrigerant in the said stabilizing and fractionating system, and said supply means serves to return the purified re-

frigerant together with required make-up refrigerant from said system to the refrigeration unit.

16. In combination, a hydrocarbon gas conversion unit, an indirect heat exchange chiller for controlling temperature of said unit, a neutralizer for caustic neutralization of hydrocarbon oil produced in said unit comprising a mixture of normally liquid and liquefied normally gaseous hydrocarbons, a stabilizing and fractionating system comprising a debutanizer and a depropanizer connected to receive overhead from said debutanizer, means for passing neutralized hydrocarbon oil from said neutralizer to said debutanizer, a refrigerating unit connected to said chiller for recirculation of refrigerant through repeated stages of compression and cooling for liquefaction and indirect heat exchange for evaporation, means for supplying at least a portion of the overhead from said depropanizer to said refrigerating unit and chiller to serve as the refrigerant therein, and a bleed line for returning a portion of the liquefied refrigerant from said chiller to said neutralizer to be processed in admixture with the hydrocarbon oil in said neutralizer and then in said stabilizing and fractionating system.

17. In combination, an alkylation contactor, means for supplying isoparaffin, olefin and alkylation catalyst to said contactor, a stabilizing and fractionating system comprising a debutanizer and a depropanizer connected to receive overhead from said debutanizer, connections between said contactor and said debutanizer for supplying hydrocarbon alkylation reaction products produced in said contactor to said stabilizing and fractionating system, a chilling coil associated with said contactor for indirect heat exchange with the hydrocarbons undergoing reaction therein, a refrigeration unit including a compressor and cooler connected to said chilling coil to provide a refrigeration circuit of the compression-expansion type, means for supplying liquefied normally gaseous hydrocarbon overhead from said depropanizer to said refrigeration circuit to serve as the refrigerant therein, and a bleed line extending from said refrigeration circuit to said connections between said contactor and said debutanizer for bleeding off a portion of the liquefied refrigerant from the chiller side of said refrigeration circuit and mixing the said bleed stream with the hydrocarbon alkylation reaction products for processing in the stabilizing and fractionating system.

18. In combination, an alkylation reactor, a neutralizer for the hydrocarbon alkylation reaction products, a water wash and surge tank for the neutralized hydrocarbon alkylation products, a stabilizing and fractionating system for the neutralized and washed hydrocarbon products including a product debutanizer, a deisobutanizer and a depropanizer, an isomerization unit, means for supplying liquid bottoms from the butane fractionator to the isomerization unit, means for returning isomate from the isomerization unit to said stabilizing and fractionating system, a refrigeration circuit including separate chilling coils associated respectively with the alkylation reactor and the isomerization unit and connected to a common refrigeration unit having a compressor and cooling means, means for passing overhead normally gaseous hydrocarbon from said depropanizer to said refrigeration unit to supply refrigerant for said refrigeration circuit, and separate and independently controlled bleed lines from the said refrigeration circuit adjacent the respective chilling coils and leading to the said neutralizer for bleeding off liquefied refrigerant from the respective chilling coils and mixing the same with hydrocarbon alkylation reaction products for processing in the said neutralizer, water wash and surge tank, and stabilizing and fractionating system.

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