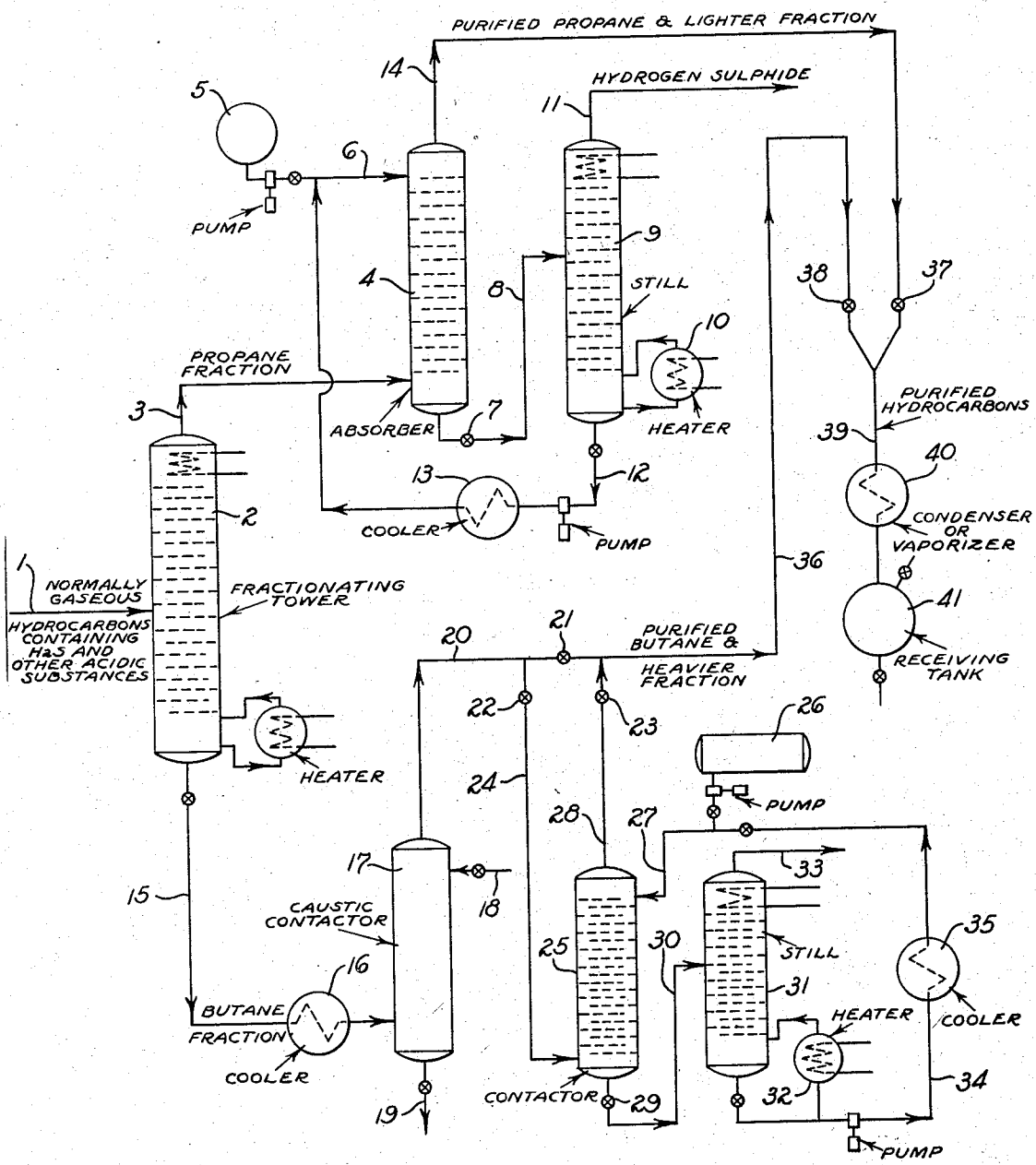
March 16, 1943. H. Y. HYDE ET AL 2,314,217

TREATMENT OF HYDROCARBON GASES

Filed May 10, 1940



INVENTORS
HERSCHEL Y. HYDE
CLARE K. VILAND
LIONEL S. GALSTAUN

BY Charles L. Thomas

ATTORNEY

Patented Mar. 16, 1943 2,314,217

UNITED STATES PATENT OFFICE

2,314,217

TREATMENT OF HYDROCARBON GASES

Herschel Y. Hyde, Associated, Clare Kenneth Viland, Martinez, and Lionel S. Galstaun, San Francisco, Calif., assignors to Tide Water Associated Oil Company, San Francisco, Calif., a corporation of Delaware

Application May 10, 1940, Serial No. 334,408

12 Claims. (Cl. 260—676)

This invention relates to the separation of hydrogen sulphide from light hydrocarbon gases and has as a principal object the provision of a method whereby hydrogen sulphide may be efficiently removed from hydrocarbon gases resulting from cracking hydrocarbon oil.

Another object of the invention is the removal of hydrogen sulphide from normally gaseous hydrocarbons which contain small amounts of low boiling aliphatic acids.

Another object is to provide a means whereby such hydrogen sulphide removal may be conducted with satisfactory regeneration of an absorbing agent.

Still another object is to efficiently prepare a mixture of C_3 and C_4 hydrocarbons suitable for polymerization purposes.

In the manufacture of gasoline motor fuel by the so-called cracking processes, wherein high boiling hydrocarbons are converted into lower boiling hydrocarbons by the application of high temperatures, with or without pressure, there are formed large quantities of normally gaseous hydrocarbons (containing one, two, three, and four carbon atoms to the molecule and commonly referred to as C_1, C_2, C_3, and C_4 hydrocarbons respectively). Most of these have too high a vapor pressure to be included in marketable gasoline. However, the C_4 hydrocarbons have sufficiently low vapor pressures that a certain percentage may be incorporated in the finished gasoline without raising the vapor pressure of the finished product above the desired value.

In addition to the light hydrocarbons formed by cracking processes, sulphur compounds present in the oil charge are broken up into H_2S, mercaptans, and other sulphur compounds. There are also formed, at times, as a result of cracking, small amounts of aliphatic acids such as acetic, propionic, and butyric acids, particularly when the charge stocks to the cracking operations contain organic acids, such as naphthenic acids and the like.

With the development of polymerization, alkylation, and other processes utilizing C_3 and C_4 hydrocarbons in the manufacture of gasoline, iso-octane, alcohols, and other chemicals, it has become desirable to segregate a fraction predominating in C_3 and C_4 hydrocarbons for charge material to these processes. When such a fraction is segregated by distillation from cracking still gases it will contain the major portion of the H_2S together with some mercaptans especially methyl mercaptan. When cracking sulphur bearing oils, such as residuum from typical California crude oils, the content of H_2S in the C_3—C_4 fraction ordinarily ranges from 2,000 to 3,000 grains of H_2S per 100 standard cubic feet of gas. With certain high sulphur crudes this fraction may contain as high as 30% by volume of H_2S. The presence of H_2S and mercaptans is detrimental to polymerization, alkylation, and such synthetic processes in that it causes corrosion of equipment, poisoning of catalysts, and contamination of products.

The removal of the hydrogen sulphide and mercaptans may be effected by washing the C_3—C_4 fraction with caustic soda solution, but this entails the consumption of large amounts of caustic soda due to the large quantity of hydrogen sulphide present.

To prevent the consumption of chemicals, and also to allow the recovery of hydrogen sulphide as a by-product, regenerative purification processes are commonly employed. According to these regenerative processes the C_3—C_4 fraction is washed with an alkaline solution which is capable of absorbing hydrogen sulphide by a reversible reaction. After the alkaline solution is saturated, or nearly so, with hydrogen sulphide it is passed to a still wherein the hydrogen sulphide is boiled off, and recovered if desired, and the regenerated alkaline solution returned to the washing cycle. Various alkaline solutions are suitable for this purpose, such as aliphatic amines, mono-, di-, and tri-ethanolamines, diaminopropanol, sodium phenolate, tripotassium phosphate, etc.

However, it has been found that, at times, due apparently to the type of cracking stocks used or to conditions obtained during cracking, the C_3—C_4 fraction contains in addition to the H_2S and mercaptans small amounts of aliphatic acids. Acetic acid has been identified in this fraction, and the presence of other homologues is indicated. Although these aliphatic acids are at times present in this fraction in only very small concentration, such as in the order of 0.01% by weight, they are considerably stronger acids than the H_2S and unite with the alkaline absorptive solution to form comparatively stable compounds which are not satisfactorily removed in the regenerative stage. Consequently, there is a gradual accumulation of aliphatic acids in the absorptive solution during repeated use. Besides consuming the chemical and thus lowering the efficiency for hydrogen sulphide removal, the accumulation of these aliphatic acids creates a tendency of the alkaline solution to foam in the absorber and thereby often so greatly interferes with the throughput capacity of the plant that

the reagent must be entirely replaced at a great increase in cost of operation.

It is thus seen to be desirable to remove, or at least reduce the concentration of, the aliphatic acids in the C_3—C_4 fraction prior to removal of the H_2S by the regenerative process. While this may be accomplished by washing the fraction with water, such procedure requires the disposal of rather large quantities of waste wash water saturated with hydrogen sulphide. Washing the fraction with caustic soda, or sodium sulphide, solution likewise is partially effective in removing the aliphatic acids, but the caustic soda, or sodium sulphide, solution very soon becomes ineffective and requires frequent replacing.

According to the present invention a means is provided whereby the H_2S may be removed by the regenerative process without contamination of the absorptive alkaline solution with the aliphatic acids. To this end the C_3—C_4 fraction, containing hydrogen sulphide and aliphatic acids is fractionally distilled into two portions the lighter of which will contain the C_3 hydrocarbons, the hydrogen sulphide, any lighter hydrocarbons, and substantially no C_4 hydrocarbons. The heavier portion will contain the C_4 hydrocarbons, any heavier hydrocarbons, and substantially no C_3 hydrocarbons or hydrogen sulphide. When such a split is made between the C_3 and C_4 hydrocarbons, it will be found that the heavier portion will contain the bulk of the mercaptans, chiefly methyl mercaptan. Likewise, the aliphatic acids will be concentrated in the heavier portion.

The lighter portion containing the C_3 hydrocarbons and the hydrogen sulphide is subjected to the regenerative H_2S removal described above, and, since the aliphatic acids are sufficiently absent, the separation of the H_2S and the regeneration of the alkaline solution proceeds in an orderly manner.

The heavier portion containing the C_4 hydrocarbons, the mercaptans and the aliphatic acids is washed with an alkali solution, such as aqueous NaOH for example. Any suitable strength of alkali may be used, 20% NaOH being preferred. Since the quantity of aliphatic acids and mercaptans is very much less than the quantity of H_2S in the C_3—C_4 fraction, the consumption of alkali in treating the heavy portion is not excessive as would be the case if the entire C_3—C_4 fraction were treated with NaOH. However, if the mercaptan content of the heavy portion is high, advantageous results may be obtained by treating the heavy portion according to the process of U. S. Patent Number 2,183,968 issued December 19, 1939, to McCormick and Lazar, according to which the aliphatic acids are first removed in a non-regenerative stage with NaOH and then the mercaptans are removed in a second stage with an alkali which may be regenerated and returned for further treatment. For such second stage any alkali capable of absorbing mercaptans at low temperatures and releasing them at high temperatures may be used. Aqueous caustic soda, mixtures of potassium hydroxide and potassium isobutyrate, etc., may be used.

Having removed the H_2S from the C_3 portion and the mercaptans from the C_4 portion, the two portions are then blended together to form a purified C_3—C_4 fraction suitable as charge material for polymerization, alkylation, and other synthetic processes.

In the attached drawing there is shown for the purposes of illustration an application of the invention. A hydrocarbon gas derived from the stabilization of untreated cracked gasoline and comprised largely of C_3 and C_4 hydrocarbons together with hydrogen sulphide and also traces of acetic acid and/or other aliphatic acids is charged to the purification system for removal of hydrogen sulphide to prepare the gas for subsequent manufacturing processes.

The contaminated gas in line 1 is charged under suitable pressure to a fractionating tower 2 where the gas is fractionated into two fractions according to boiling range. The overhead product comprising the propane and lower boiling constituents is removed in line 3 and charged to absorber 4 for removal of hydrogen sulphide and other acidic gases contained in the fraction. A suitable solution capable of removing hydrogen sulphide and other acidic constituents from the gas fraction is charged from tank 5 through line 6 into absorber 4. The preferred solution for this purpose is a 20% solution of diethanolamine in water, although other concentrations of the amine either stronger or weaker than 20% are satisfactory, or any other chemical capable of removing hydrogen sulphide and other acidic constituents by means of a reversible reaction may be employed. Ordinarily the reaction in tower 4 is conducted with the hydrocarbons in the vapor phase, and under a pressure approximating that in fractionating tower 2, which may preferably be about 225 pounds per square inch, gage, although other operating conditions may be employed if desired.

The hydrogen sulphide together with any carbon dioxide present is absorbed from the gas into the amine solution at a temperature of 100°–150° F., and the foul amine solution is passed from the absorber through control valve 7 and line 8 into the solution regenerating still 9. Heat is applied to the solution in still 9, by reboiler 10 or other suitable means, to reverse the reaction, and the hydrogen sulphide in relatively pure form leaves still 9 through the overhead line 11. The hydrogen sulphide product at this point is generally 95–99% pure hydrogen sulphide with traces of hydrocarbons and carbon dioxide, the latter being removed along with the hydrogen sulphide. The regenerated amine solution is pumped from still 9 through line 12, cooler 13, and line 6 back into absorber 4 for further use. The purified propane-and-lighter gas fraction leaves absorber 4 through line 14 and may contain 20–50 grains hydrogen sulphide per 100 cubic feet, or higher or lower depending on the efficiency of the treatment.

The butane-and-heavier residue fraction from fractionating tower 2 is withdrawn as a liquid under pressure through line 15 through cooler 16 and passed through caustic contact tower 17 where mercaptans and the aliphatic acids are removed from the fraction by reaction or solution in caustic soda or other alkali supplied through line 18. Tower 17 may, if desired, contain contact material such as Raschig rings, baffles, etc., or, alternately, any well known contact apparatus may be substituted for tower 17. From time to time it will be necessary to withdraw the spent caustic solution through line 19 and inject new caustic into the tower through line 18. The purified butane-and-heavier fraction leaves the caustic tower 17 through line 20, valve 21, and line 36.

If desired, particularly when the quantity of mercaptans is high, the concentration of fresh caustic in tower 17 may be maintained sufficiently low that only the aliphatic acids and small amounts of mercaptans are removed. The hydrocarbons then leaving contactor 17 will con-

tain the major portion of the mercaptans present. By closing valve 21 and opening valves 22 and 23, the mercaptan-containing hydrocarbons are passed through line 24 into contactor 25. A caustic soda, or other alkaline, solution is supplied to contactor 25 from tank 26, through line 27. In contactor 25 the mercaptans are removed by the caustic solution and the purified hydrocarbons pass out through lines 28 and 36. The foul alkaline solution is passed from contactor 25 through control valve 29 and line 30 into regenerating still 31. Heat is applied to the solution in still 31 by reboiler 32 and the mercaptans in relatively pure form leave still 31 through line 33. The regenerated alkaline solution is pumped from still 31 through line 34, cooler 35, and line 27 back into contactor 25 for further use.

In order to obtain the desired mixture of purified C_3 and C_4 hydrocarbons the purified propane-and-lighter fraction in line 14 is passed through pressure regulating valve 37 and into line 39. Simultaneously the purified butane-and-heavier fraction in line 36 is withdrawn through valve 38 and is mixed with the propane-and-lighter fraction in line 39. Depending on the use to be made of the purified C_3—C_4 mixture, the mixture in line 39 may be liquefied in condenser 40 and passed to storage tank 41. Alternatively, if a gaseous C_3—C_4 mixture is desired, condenser 40 may be operated as a vaporizer and the mixture of liquid and gas in line 39 completely vaporized.

In the application of the invention described above and illustrated in the drawing the treatment of the light fraction was shown in the gaseous state and the treatment of the heavy fraction in the liquid state. By proper choice of temperatures and pressures either or both of these fractions may be treated in either liquid or gaseous state, as desired.

By means of the invention it has been found possible to process greatly increased volumes of gas, containing from 0.001% to 0.1% by weight of aliphatic acids, for purification with greatly decreased chemical consumption in the regenerative process, while at the same time eliminating foaming and frothing difficulties which are usually encountered when the whole gas is processed in a single system. It has also been found that when purifying refinery gas according to the invention, that the hydrogen sulphide product is of a higher purity than formerly obtained under conventional operation where the total gas is processed in the absorber, since the hydrogen sulphide product under the invention contains substantially no mercaptans and also decreases quantities of other constituents such as hydrocarbon gases.

In referring herein to the C_3 and C_4 fractions, it will be understood that such fractions include both saturated and unsaturated hydrocarbons, normally existing in gaseous form, which constitute the bulk of the charge necessary for later use in the desired processes, such as polymerization, alkylation, or other processes involving chemical reactions wherein relatively great purity is necessary, because the presence of the now separately removed impurities not only tends to disturb such chemical reactions but produces an impure product.

Further, the separate removal of impurities greatly enhances operating facilities by preventing the foaming of the alkaline solution during absorption and distillation and thus the mechanical carrying over of impurities with the gas to be processed is eliminated as well as corrosion and other deterioration, with its concomitant shut downs, such as will be due to the presence of acids and sulphur compounds.

It will be recognized that, from the practical or commercial refinery standpoint, the process is primarily a continuous process in which a continuous stream of gases is fractionated and the fractions are continuously treated with alkaline solutions which are continuously regenerated and recycled for use, as described. This is essentially true even though a continuous stream of gas is passed through a batch of alkaline solution until the same is saturated when such spent batch would be replaced with a fresh batch. In all cases there must be a continuous onstream flow of gas to pass through alkaline solutions capable of removing the impurities at all times.

We claim:

1. The process of purifying normally gaseous hydrocarbons which comprises: fractionally distilling a mixture of C_3 and C_4 hydrocarbons containing hydrogen sulphide, mercaptans, and aliphatic acids to obtain a light fraction comprising said C_3 hydrocarbons predominantly together with said hydrogen sulphide, and a heavy fraction comprising said C_4 hydrocarbons predominantly together with said mercaptans and said aliphatic acids; contacting a continuous stream of said light fraction in a contact zone with an alkaline reagent capable of absorbing H_2S and liberating the same upon heating; removing contacted alkaline reagent from said contact zone; distilling H_2S from said contacted alkaline reagent to regenerate the same; returning regenerated alkaline reagent to said contact zone; contacting said heavy fraction with an alkali solution to remove said mercaptans and said aliphatic acids; removing the purified heavy fraction from the alkali solution; and blending the thus treated light and heavy fractions to obtain a purified C_3—C_4 mixture.

2. The process according to claim 1 in which the first stated alkaline reagent is an aqueous solution of diethanolamine.

3. The process according to claim 1 in which the first stated alkaline reagent is a solution of about 20% diethanolamine in water.

4. The process according to claim 1 in which the percentage of aliphatic acids in the mixture of C_3 and C_4 hydrocarbons before treatment thereof is from 0.001% to 0.1% by weight.

5. In a process wherein a cracked distillate containing C_4 hydrocarbons together with lighter and heavier hydrocarbons, hydrogen sulphide, and aliphatic acids is separated by fractional distillation to yield a fraction comprising predominantly C_3 and C_4 hydrocarbons together with the hydrogen sulphide and certain aliphatic acids, and the hydrogen sulphide is removed from said fraction by treatment with an alkaline reagent which is regenerated and reused in the process, the method of preventing contamination of said alkaline reagent by said aliphatic acids remaining in said fraction as a result of said distillation, which comprises: first subjecting said C_3—C_4 fraction to fractional distillation to remove therefrom the C_3 hydrocarbons and the hydrogen sulphide whereby said aliphatic acids remain with the C_4 hydrocarbons, then treating the C_3 with said alkaline reagent to remove the hydrogen sulphide.

6. In a process wherein a cracked distillate containing C_4 hydrocarbons together with lighter and heavier hydrocarbons, hydrogen sulphide, mercaptans, and aliphatic acids is separated by fractional distillation to yield a fraction com-

prising predominantly C_3 and C_4 hydrocarbons together with the hydrogen sulphide, certain aliphatic acids, and low boiling mercaptans, and the hydrogen sulphide is removed from said fraction by treatment with an alkaline reagent which is regenerated and reused in the process, the method of preventing contamination of said alkaline reagent by said aliphatic acids remaining in said fraction as a result of said distillation, which comprises: first subjecting said C_3—C_4 fraction to fractional distillation to remove therefrom the C_3 hydrocarbons and the hydrogen sulphide whereby said aliphatic acids and low boiling mercaptans remain with the C_4 hydrocarbons, then treating the C_3 fraction with said alkaline reagent to remove the hydrogen sulphide, and removing the mercaptans and aliphatic acids from the C_4 hydrocarbons by treatment with further alkaline solution.

7. The process of purifying normally gaseous hydrocarbons which comprises: fractionally distilling a mixture of C_3 and C_4 hydrocarbons containing hydrogen sulphide, mercaptans, and aliphatic acids to obtain a light fraction comprising said C_3 hydrocarbons predominantly together with said hydrogen sulphide, and a heavy fraction comprising said C_4 hydrocarbons predominantly together with said mercaptans and said aliphatic acids; continuously passing a stream of the light fraction through a zone wherein the hydrogen sulphide is abstracted by contact with an alkaline reagent; continuously withdrawing the contacted alkaline reagent from said zone and removing the hydrogen sulphide therefrom; continuously returning the purified reagent to said zone; removing the mercaptans from said heavy fraction with an alkaline reagent; and blending the thus treated light and heavy fractions.

8. The process according to claim 7 in which the alkaline reagent used to remove the mercaptans from the heavy fraction is aqueous caustic soda.

9. The process of purifying normally gaseous hydrocarbons which comprises: fractionally distilling a mixture of C_3 and C_4 hydrocarbons containing hydrogen sulphide, mercaptans, and aliphatic acids to obtain a light fraction comprising said C_3 hydrocarbons predominantly together with said hydrogen sulphide, and a heavy fraction comprising said C_4 hydrocarbons predominantly together with said mercaptans and said aliphatic acids; continuously passing a stream of the light fraction through a zone wherein the hydrogen sulphide is abstracted by contact with an alkaline reagent; continuously withdrawing the contacted alkaline reagent from said zone and removing the hydrogen sulphide therefrom; continuously returning the purified reagent to said zone; removing the aliphatic acids from said heavy fraction with an alkaline reagent; continuously passing a stream of the thus purified heavy fraction through a second zone wherein the mercaptans are abstracted by contact with an alkaline reagent; continuously withdrawing the contacted alkaline reagent from said second zone and removing the mercaptans therefrom; continuously returning the thus purified reagent to said second zone; and blending the thus treated light and heavy fractions.

10. The process according to claim 9 in which the alkaline reagent used to remove the aliphatic acids from the heavy fraction is aqueous caustic soda.

11. The process according to claim 9 in which the percentage of aliphatic acids in the mixture of C_3 and C_4 hydrocarbons before treatment thereof is from 0.001% to 0.1% by weight.

12. The process of continuously obtaining a purified C_3—C_4 fraction from cracked hydrocarbon distillates which comprises: fractionating a cracked distillate containing hydrocarbons with four carbon atoms together with lighter and heavier hydrocarbons, hydrogen sulfide, aliphatic acids, and mercaptans to recover a composite fraction comprising predominantly C_3 and C_4 hydrocarbons together with the hydrogen sulfide and containing mercaptans and aliphatic acids; distilling said composite fraction to obtain a light fraction comprising said C_3 hydrocarbons predominantly together with the hydrogen sulfide, and a heavy fraction comprising said C_4 hydrocarbons predominantly together with mercaptans and aliphatic acids; contacting a continuous stream of said light fraction in a contact zone with an alkaline reagent capable of absorbing H_2S and liberating the same upon heating; removing contacted reagent from said contact zone; distilling H_2S from said contacted alkaline reagent to regenerate the same; returning regenerated alkaline reagent to said contact zone; contacting said heavy fraction with an alkali solution to remove mercaptans and aliphatic acids; removing the purified heavy fraction from the alkali solution; and blending the thus treated light and heavy fractions to obtain a purified C_3—C_4 mixture.

HERSCHEL Y. HYDE.
CLARE KENNETH VILAND.
LIONEL S. GALSTAUN.