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J. D. SEGUY

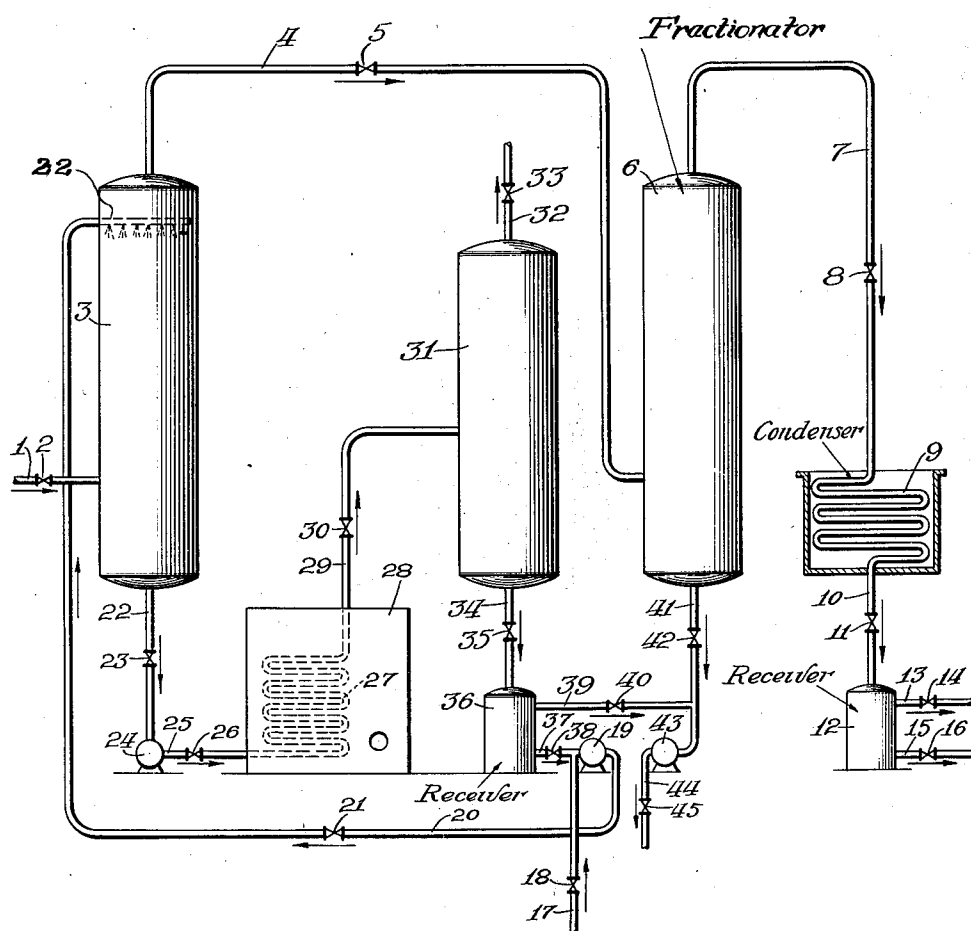
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TREATMENT OF HYDROCARBON OILS

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2 Sheets-Sheet 1

Fig.1



Inventor:

Jean Delattre Seguy

By Frank L. Belknap *Sitty.*

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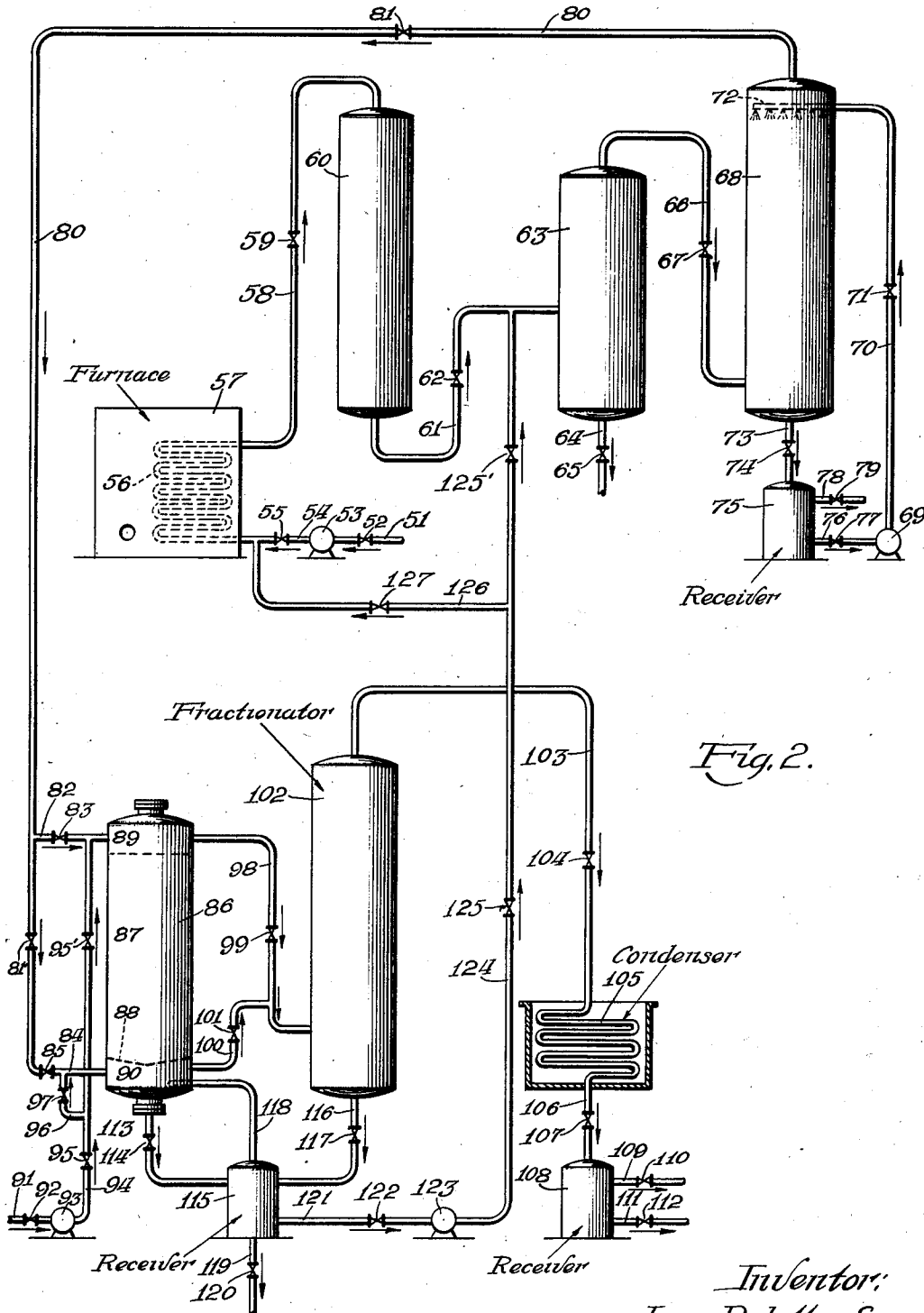
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Inventor:
Jean Delattre Seguy
By Frank L. Belknap Atty.

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TREATMENT OF HYDROCARBON OILS

Jean Delattre Seguy, Chicago, Ill., assignor to
Universal Oil Products Company, Chicago, Ill.,
a corporation of Delaware

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14 Claims. (Cl. 196—25)

This invention relates to the treatment of hydrocarbon oils and refers more particularly to the treatment of the lower boiling distillates produced in cracking operations of heavy petroleum 5 ums though similar distillates from other sources may be treated, such as those arising from straight run distilling operations upon crude petroleum or other hydrocarbon oil mixtures or those produced in the rerunning of primary distillates from different refining operations. 10

In a more specific sense the invention is concerned with the process for the removal of hydrogen sulfide and other acidic gases from the vapors of such low boiling distillates so that 15 their refining by subsequent particular vapor phase treatments is made easier, as will be developed in the succeeding more detailed discussion of the invention.

The low boiling hydrocarbon fractions produced as a result of the decomposition of heavy hydrocarbon oil mixtures under elevated temperature and pressure conditions differ in several definite respects from distillates of similar boiling range produced in the straight run or non-cracking distillation of crude oils. They contain relatively higher percentages of olefinic and cyclic hydrocarbons, and correspondingly lower percentages of saturated hydrocarbons, either straight chain or cyclic. When the primary 25 charging oils contain appreciable amounts of oxygen and sulphur compounds, particularly the latter, water, hydrogen sulfide and low boiling hydrocarbon derivatives containing these elements appear in admixture with the hydrocarbons. The percentage of sulphur and of highly unsaturated di and tri olefinic hydrocarbons must be reduced to a minimum value in commercial motor fuels, the former class of compounds on account of their usually foul odor and corrosive tendencies both before and after combustion and the latter on account of their polymerization to form high boiling gums and coloring matter which detract largely from the sales value and to some extent from the fuel value of the 30 gasoline. 35

Pyrolytic decomposition of sulphur-containing oils results in the formation of hydrogen sulfide as well as of hydrocarbon sulphur derivatives such as mercaptans, sulphur ethers, thiophenes, thiophanes, etc., and it is the primary object of the present invention to provide a process for the removal of hydrogen sulfide from cracked hydrocarbon vapor mixtures so that subsequent vapor phase treating steps can be more effectively accomplished. 40 45 50 55

In one specific embodiment the invention comprises treatment of hydrocarbon oil vapors, particularly cracked hydrocarbon oil vapors with specific liquid absorbents for hydrogen sulfide, the preferred absorbing liquids being certain types of organic amines. 5

The mean boiling point of hydrocarbon motor fuel mixtures under atmospheric pressure conditions varies commonly between limits of 250 to 300° F. though this range is only approximate. 10 In the case of cracked naphtha vapors arising from the fractionators of commercial cracking plants, the temperature of the vapors will be considerably higher on account of the usually high superatmospheric pressures which are employed in the cracking operations. Thus at pressures of from 100 to 300 pounds per square inch which comprises roughly the pressure range of cracking plants, the temperature of the naphtha vapors continuously evolved from the primary 20 fractionator of the plant may be anywhere from 250 to 600° F., these temperatures being somewhat lower in case the pressure is reduced at the exit of the fractionator. Ordinarily these primary vapors are condensed and treated with sulphuric acid to remove gum-forming and sulphur compounds, the treated naphtha neutralized with caustic soda or sodium plumbite and subjected to redistillation to produce a finished gasoline. Various proposed processes have 30 sought to treat the naphtha vapors so that a finished gasoline could be produced from the cracking plant without going through the steps of condensation, liquid phase treatment and redistillation but none have met with complete success to date. The use of the selective adsorbent liquids for removing hydrogen sulfide 35 from the vapors as a part of such proposed vapor phase treatments constitutes the main feature of the present invention, the nature of these adsorbent liquids and their method of application being described in succeeding parts of the specification. 40

The liquid which it is preferred to use in the present invention is triethanolamine having the chemical formula $(C_2H_4OH)_3N$, and being therefore a substituted ammonia in which the hydrogen atoms have been replaced by the ethyl alcohol or an "ethanol" residue. This material along with certain related materials which will be presently enumerated is of recognized value 50 as a selective absorbing liquid for acidic gases in gaseous mixtures at ordinary temperatures and pressures and it has been found that it can be applied to the removal of acidic gases, particu- 55

larly hydrogen sulfide at elevated temperatures and pressures, when operations are properly controlled. The use of this and related substances and the advantages to be gained thereby may be conveniently shown in connection with the attached drawings, Fig. 1 showing the essential details of a plant hookup for treating hydrocarbon oil vapors to remove hydrogen sulfide, recover the absorbent and produce gasoline and hydrogen-sulfide-free fixed gases while Fig. 2 shows a plant comprising such an absorption system interposed between a cracking plant and a subsequent vapor phase treating plant. The drawings shown in both figures are diagrammatic and make use of ordinary conventional figures, unnecessary detail having been omitted to avoid possible confusion as to the essential operations.

Referring to Fig. 1, vapors to be treated for the removal of constituents absorbed by the liquids whose use is comprised within the scope of the invention may be admitted to the absorption plant through a line 1 containing a control valve 2 and enter an absorption tower 3 to pass upwardly countercurrent to a descending stream of absorbing liquid admitted from line 20 through distributing means 22 which may be a perforated spray or arrangement of nozzles or any other effective means of producing fine streams or drops of the liquid. The absorption tower may further contain any suitable filling or baffling material for breaking up the descending stream of liquid or it may contain any arrangement of regularly spaced pans or perforated plates. The vapors may be admitted at their normal temperature and pressure conditions if these permit the economical use of the preferred absorbent or if desired they may be partly cooled so that a certain amount of condensation of heavier components takes place and only the residual vaporous components are treated, these containing in all cases the hydrogen sulfide which it is desired to remove. When further treatment of the total vapors is contemplated by methods which will be mentioned later, it will be necessary to revaporize a certain proportion of the liquids condensed at this point, this being accomplished by suitably arranged heat exchangers or by the application of further heating as may be most convenient, though such means are not included in the drawings.

The mixture of gases and vapors emergent from the treater may be passed through a line 4 containing a control valve 5 and enter a fractionator 6 adapted to separate vapors of substantially gasoline boiling range from heavier refluxes in case the latter are present. Vapors from fractionator 6 may be submitted to the ordinary steps of cooling and condensation, passing along with fixed gases through vapor line 7 containing control valve 8 through condenser 9 and continuing as condensed liquids and fixed gases through line 10 containing control valve 11 to receiver 12, this receiver having a gas release line 13 containing a control valve 14 and a liquid draw line 15 containing control valve 16. The fixed gases withdrawn through line 13 will be substantially free from hydrogen sulfide and this will also be absent from solution in the condensed liquids.

Liquid accumulating in the bottom of treater 3 will consist of either merely the specific absorbent containing a certain amount of dissolved or combined hydrogen sulfide or such liquid mixed with heavy hydrocarbon oil refluxes de-

pending upon whether the temperature and pressure conditions employed are such that substantially no condensation of hydrocarbons occurs or whether the temperature has been reduced by some means to permit partial condensation and the treatment of only a portion of the vapors. In either event the liquid accumulations may be withdrawn through a line 22 containing control valve 23 and discharged by a pump 24 through a line 25 containing control valve 26 through a coil 27 which may be either heated or cooled as certain temperatures are demanded which are best for the release of the hydrogen sulfide from solution or combination with the absorbent to permit its reuse. For example, it may be found that a slight elevation of temperature with substantially no reduction in pressure may effect sufficient release of hydrogen sulfide or that this release is best effected by lowering both temperature and pressure or any combination of temperature and pressure change. Thus coil 27 may be supported in a furnace setting 28 or may be positioned to be cooled by any suitable means.

The spent absorbent and hydrocarbons if any be present, may then be passed under the altered conditions of temperature and pressure through line 29 and control valve 30 to separator or stabilizer 31, from which the released hydrogen sulfide may be vented through line 32 containing control valve 33 and the regenerated absorbent passed through line 34 containing control valve 35 to a receiver 36. The absorbent may be subjected to cooling if necessary or advantageous to the best operation of the process and recirculated for further use by pump 19 which takes suction upon the receiver through line 37 containing control valve 38 and discharges the regenerated absorbent back to the absorbing tower through line 20 and control valve 21. To start the cycle or to introduce further quantities of absorbent, a line 17 containing control valve 18 is provided.

Since the specific gravity of the liquid absorbents is greater than that of hydrocarbon oils, the latter will appear as an upper layer in receiver 36 and be removable therefrom through a line 39 containing control valve 40 and joining with line 41 containing control valve 42 and conducting refluxes from fractionator 6 to a pump 43 having a discharge line 44 containing a control valve 45. The disposition of refluxes at this point will depend generally upon whether they are to be wholly or partly revaporized for subsequent treating steps or whether they represent refluxes of relatively heavy character suitable for further conversion treatment in the cracking process furnishing vapors for treatment.

The foregoing description is given to indicate in a general way the cycle of operations which may be employed in removing hydrogen sulfide from cracked hydrocarbon vapors. The particular advantages to be gained by this operation will be more evident from the operation which will be described with reference to Fig. 2. Referring to Fig. 2 the elements of a commercial cracking plant are shown in combination with the process of the invention and a succeeding treating step adapted to controllably refine the cracked vapors and produce a substantially finished gasoline requiring at the most only treatments of a minor character to render it suitable for immediate use or storage over considerable periods of time without deterioration.

Line 51 containing control valve 52 is a sup-

ply line for introducing any charging stock to the cracking process, pump 53 discharging the stock thus admitted through line 54 containing control valve 55 into and through heating element 56 disposed to receive heat from furnace 57. Line 54 also receives intermediate refluxes from line 126 subsequently produced as will be later more fully described and heat is added to the combined feed during passage through the heating element to produce the necessary temperature and pressure for decomposition with economical yields of low boiling fractions, these conditions varying with the charging stock, the type of coil, the method of heating, etc., though the general conditions are well known in the cracking art. The heated and partly cracked products may be discharged through a line 58 containing control valve 59 and enter an enlarged vaporizing and reaction zone 60 wherein the reactions of conversion are allowed to progress to a desired point, the cracked products both vaporous and liquid then being discharged together through a line 61 containing control valve 62 to a vaporizer 63. Subsequent refluxes may also be admitted to line 61 from line 124 as will be presently described. Vaporizer 63 represents any fractionating equipment which may be employed to produce vapors of desired boiling point range for subsequent treatment and may comprise merely a vaporizer capable of effecting a rough separation of vapors from non-vaporized liquids or more efficient fractionating equipment. Thus the liquid drawn from vaporizer 63 through line 64 and valve 65 may comprise only heavy residual products of a tarry character or intermediate refluxes amenable to further treatment in the process though means for their return to the cracking zone is not shown.

Vapors may be passed from fractionator 63 through line 66 containing control valve 67 and subjected to the treatment of the process for the removal of hydrogen sulfide in absorbing tower 68 which may be similar to absorber 3 shown in Fig. 1, though the remainder of the absorption and regenerating equipment has been considerably simplified. A specific absorbing liquid for hydrogen sulfide may be introduced into the absorption tower from distributing means 72 which is fed by line 70 containing control valve 71, a recirculating pump 69 introducing regenerated liquid obtained from receiver 75 through line 76 and control valve 77. It is assumed in the present instance that no condensation of oils occurs in the absorber and that only spent absorbent is introduced into the receiver from line 73 containing control valve 74. Furthermore, means for controlling the temperature of the absorbent during the regeneration stage have been omitted and line 78 containing control valve 79 merely shown as a means of releasing hydrogen sulfide.

The vapors freed from hydrogen sulfide may then be passed through a line 80 containing a control valve 81 and be further treated in vapor phase by the use of hydrochloric acid in contact with solid materials of a generally metallic character contained in a treater 86 in space 87 supported upon a perforated false bottom 88, the contact mass dividing the treater into upper vapor space 89 and lower vapor space 90. Either upward or downflow over the contact mass may be practiced. In the former event the vapor mixture may be passed through control valve 81', line 84 and control valve 85 to lower vapor space 90 and in the event of downflow treatment

they may be passed to vapor space 89 by way of line 82 containing control valve 83.

Hydrochloric acid either as a substantially dry gas or an aqueous solution may be supplied to a pump 93 through a line 91 containing control valve 92 and discharged therefrom through a line 94 containing a control valve 95, this line having a branch line 96 containing control valve 97 for the admission of the acid into the vapors in line 84, and leading directly to line 82.

A particular advantage of the process of the invention now becomes apparent in view of the types of solid contact material which are employed in this type of vapor phase treatment, aimed primarily at reduction in gum-forming constituents. These metallic masses comprise various finely divided metals, their alloys, salts and ores, alone or in particular combinations suitable for assisting in producing specific treating effects. For example, a particularly efficient contact material consists of brass turnings containing both copper and zinc and typifying any alloy or mechanical mixture of metals above and below hydrogen in the electrochemical series. The effect of such metallic contact masses is apparently to catalyze the polymerization of highly unsaturated di and tri olefinic compounds in the presence of hydrochloric acid so that the vapors are stabilized with respect to gum and color-forming tendencies. In many instances when such contact masses are employed and the vapors treated contain relatively large amounts of hydrogen sulfide, the contact mass rapidly deteriorates on account of the formation of relatively stable sulfides with the electronegative metals such as copper, mercury, etc. With the elimination of hydrogen sulfide from the vapor mixture according to the process of the present invention, the treatment with hydrochloric acid and metallic contact materials may continue uninterruptedly over considerably extended periods of time before a shutdown is required.

The course of the treatment following contact of the vapors and hydrochloric acid with the metallic contact mass follows generally the order of separation of heavy polymers and spent chemicals from the vapors and the fractionation of the latter to produce a finished gasoline product. Thus the heavy polymers and spent chemicals from treater 86 may be withdrawn therefrom through a line 113 containing a control valve 114 to an intermediate accumulator 115 having an open vent line 118 leading back to the treater to eliminate vapor lock and insure ready flow of liquids to the accumulator. Heavy refluxes from the succeeding fractionator 102 may be conducted therefrom through a line 116 containing control valve 117 and mingle with liquids of approximately similar character from the treater 86. The polymer accumulator 115 may have a draw line 119 containing control valve 120 at its lowermost point for the removal of chemical sludges such as, for example, chloride solutions which may result from the treatment and may have a line 121 containing control valve 122 to conduct hydrocarbon polymers to a pump 123 which returns them by way of line 124 and valves 125 and 125' to the fractionating zone of the cracking plant or through line 126 containing control valve 127 to the conversion zone thereof as already indicated.

To provide for the release of vapors from up-flow treatments, line 98 containing control valve 99 is shown and for the release of vapors from downflow treatments, a line 100 containing con-

trol valve 101, these both joining to permit entry of treated vapors to the fractionator from either type of treatment. Vapors and fixed gases from fractionator 102 may be passed through a vapor line 103 containing control valve 104 and be cooled by a condenser 105, fixed gases free from hydrogen sulfide and condensed gasoline passing together through line 106 containing control valve 107 to receiver 108, provided with the usual gas release line 109 containing control valve 110 and a liquid draw line 111 containing control valve 112.

In addition to the preferred absorbent mentioned above (triethanolamine) a number of other absorbents for hydrogen sulfide may be used within the scope of the invention though it will be recognized that the effects produced by the use of different chemical compounds or mixtures thereof will not be exactly equivalent either in degree or in kind, owing to the variations in boiling points, absorptive capacity for hydrogen sulfide, the temperature and pressure of the absorption treatment and other operating conditions. The selection of any particular compound or mixtures thereof will be determined by a consideration of these and other pertinent factors.

Besides triethanolamine other amines of suitable boiling range and absorptive capacity containing hydroxyl groups but not carbonyl nor carboxyl groups may be employed. Thus diethanolamine is applicable and also glycerolamine, benzylamine and various amines containing both aliphatic and/or aromatic hydrocarbon residues as constituent groups. However, the cyclic hydrocarbon groups which may constitute the ammonia hydrogen do not include unsaturated rings attached directly to the amino group, NH_2 . Thus aniline is not applicable.

The types of amines which may be used also include members of such groups as tertiary heterocyclic amines free from carboxyl and carbonyl groups and also tertiary heterocyclic amino alcohols.

Certain hydrazines such as, for example, ethyl or propyl hydrazine may be used and also such compounds as piperidyl ethanol.

Any of the types of compounds mentioned above may be employed as such or in either aqueous or hydrocarbon oil solution as circumstances warrant and beneficial results are obtained. For example, triethanolamine may be employed as an absorbent in aqueous solution or in solution in tetrahydronaphthalene.

The description of operations given in connection with Fig. 2 above has indicated the advantage to be gained in using the process prior to a particular type of vapor phase treatment in which the contact mass was sensitive to hydrogen sulfide. The process may be employed similarly as a preliminary treatment in other cases such as, for example, cases involving the use of metallic salts with or without hydrochloric acid either as solids or in solution and is particularly advantageous when used preceding vapor phase catalytic processes such as hydrogenation processes wherein the catalyst is poisoned by free hydrogen sulfide.

As a particular example of the results obtainable by improved vapor phase refining made possible by the use of the process of the invention, those obtained in connection with the cracking of a California residuum to produce gasoline may be cited. Charging stock may contain approximately 1% of sulphur and the fixed gases from the process when vapor phase treat-

ments are not employed may contain as high as 0.5% hydrogen sulfide. This corresponds to a volume percentage of approximately 0.25% hydrogen sulfide in the naphtha vapors of approximate gasoline boiling range emergent from the fractionator of the plant. This percentage of hydrogen sulfide is the largest contributing factor to the inefficiency of vapor phase treatments aimed at the removal of gum-forming and sulphur compounds prior to condensation of the gasoline fractions. Attempts to utilize the hydrochloric acid-metal treatment to remove polymerizable hydrocarbons results in rapid deterioration of the metallic contact mass.

The hydrogen sulfide in such a gas-vapor mixture may be substantially completely removed at a temperature of approximately 450°F . and a pressure of 200 pounds per square inch by the use of triethanolamine, the absorbed hydrogen sulfide being continuously removed by lowering the pressure to approximately 50 pounds per square inch in the regeneration step. Somewhat larger amounts of the absorbing liquid will be needed for this purpose than in the absorption of similar percentages of hydrogen sulfide contained in relatively cold gas mixtures at ordinary pressures, the hydrogen sulfide content of the saturated absorbent being considerably lower than that corresponding to the normal triethanolamine sulfide. However, this relatively low absorptive capacity as compared with cold absorption processes may be compensated for by the use of relatively larger amounts of absorbent.

By absorbing the hydrogen sulfide from the gas-vapor mixture in this manner, it is possible to apply the polymerizing treatment for the removal of di and tri olefins from the hydrocarbon vapors without perceptible diminution in the activity of the metallic contact mass for long periods of time, such as, for example, three to four weeks. Thus the commercial advantage of the present process is shown in the case in question.

The foregoing specification defining the nature of the invention and including the description of characteristic operations and results obtainable therefrom is given for illustrative purposes and is not to be considered as imposing any undue limitations upon the generally broad scope of the invention.

I claim as my invention:

1. A process for removing hydrogen sulphide and other acidic gases from hydrocarbon vapors which comprises contacting the vapors at a temperature of from 250°F . to 600°F . and under substantial superatmospheric pressure with and absorbing acidic gases therefrom in an absorbent including an amine containing a hydroxyl group and free of carbonyl and carboxyl groups and which is a relatively stable liquid under the conditions of contact, whereby the amine is heated to a temperature at which it may be regenerated by pressure reduction and without further application of substantial quantities of heat thereto.

2. A process for removing hydrogen sulphide and other acidic gases from hydrocarbon vapors which comprises contacting the vapors at a temperature of from 250°F . to 600°F . and under substantial superatmospheric pressure with and absorbing acidic gases therefrom in an absorbent including an amine containing a hydroxyl group and free of carbonyl and carboxyl groups and which is a relatively stable liquid under the conditions of contact, and subsequent-

ly regenerating the amine out of contact with the vapors by lowering the pressure thereon whereby absorbed hydrogen sulphide is liberated therefrom.

under the conditions of contact, and subsequently regenerating the amine out of contact with the vapors by lowering the pressure thereon whereby absorbed hydrogen sulphide is liberated therefrom.

5 3. In the cracking of hydrocarbon oils wherein the cracked vapors are fractionated under superatmospheric pressure to condense and separate insufficiently cracked fractions from the gasoline vapors, the method of removing hydrogen sulphide and the like from the fractionated vapors which comprises contacting the same at substantially the temperature and pressure of
10 issuance from the fractionating step with and absorbing hydrogen sulphide therefrom in an absorbent including an amine containing a hydroxyl group and free of carbonyl and carboxyl groups and which is a relatively stable liquid under the conditions of contact, whereby the amine is heated to a temperature at which it
15 may be regenerated by pressure reduction and without further application of substantial quantities of heat thereto.

7. A process for removing hydrogen sulphide and other acidic gases from hydrocarbon vapors which comprises contacting the vapors at a temperature of from 250° F. to 600° F. and under substantial superatmospheric pressure with and
10 absorbing acidic gases therefrom in triethanolamine.

8. The process as defined in, claim 2 further characterized in that said amine comprises triethanolamine.

9. In the cracking of hydrocarbon oils wherein the cracked vapors are fractionated under superatmospheric pressure to condense and separate insufficiently cracked fractions from the gasoline vapors, the method of removing hydrogen sulphide and the like from the fractionated vapors which comprises contacting the same at substantially the temperature and pressure of
15 issuance from the fractionating step with and absorbing acidic gases therefrom in triethanolamine.

10. The process as defined in claim 4, further characterized in that said amine comprises triethanolamine.

11. The process of removing acidic gases from cracked hydrocarbon vapors which comprises contacting the vapors at a temperature of from 250° F. to 600° F. and under a pressure of from 100 to 300 pounds per square inch with triethanolamine.

12. The process as defined in claim 6, further characterized in that said amine comprises triethanolamine.

13. A process for removing hydrogen sulphide and other acidic gases from hydrocarbon vapors which comprises contacting the vapors at a temperature between 250° F. and 600° F. with and absorbing acidic gases therefrom in an absorbent including an amine containing a hydroxyl but no carbonyl and carboxyl groups and which is a relatively stable liquid under the conditions of contact, whereby sufficient heat is imparted to the amine during the contact to effect its subsequent regeneration out of contact with the vapors.

14. A process for removing hydrogen sulphide and other acidic gases from hydrocarbon vapors which comprises contacting the vapors at a temperature between 250° F. and 600° F. with and absorbing acidic gases therefrom in an absorbent in liquid form including triethanolamine, whereby sufficient heat is imparted to the amine during the contact to effect its subsequent regeneration out of contact with the vapors.

4. In the cracking of hydrocarbon oils wherein the cracked vapors are fractionated under superatmospheric pressure to condense and separate insufficiently cracked fractions from the gasoline vapors, the method of removing hydrogen sulphide and the like from the fractionated vapors which comprises contacting the same at substantially the temperature and pressure of
25 issuance from the fractionating step with and absorbing hydrogen sulphides therefrom in an absorbent including an amine containing a hydroxyl group and free of carbonyl and carboxyl groups and which is a relatively stable liquid under the conditions of contact, and subsequently regenerating the amine out of contact with the vapors by lowering the pressure thereon whereby absorbed hydrogen sulphide is liberated
30 therefrom.

5. The process of removing acidic gases from cracked hydrocarbon vapors which comprises contacting the vapors at a temperature of from 250° F. to 600° F. and under a pressure of from
35 100 to 300 pounds per square inch with an absorbent including an amine containing a hydroxyl group and free of carbonyl and carboxyl groups and which is a relatively stable liquid under the conditions of contact, whereby the amine is heated to a temperature at which it may be regenerated by pressure reduction and without further application of substantial quantities of heat thereto.

6. The process of removing acidic gases from cracked hydrocarbon vapors which comprises contacting the vapors at a temperature of from 250° F. to 600° F. and under a pressure of from 100 to 300 pounds per square inch with an absorbent including an amine containing a hydroxyl group and free of carbonyl and carboxyl groups and which is a relatively stable liquid
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JEAN DELATTRE SEGUY.