Dec. 19, 1939. T. F. McCORMICK ET AL 2,183,968

PROCESS OF TREATING OIL

Original Filed Dec. 27, 1935 3 Sheets-Sheet 1

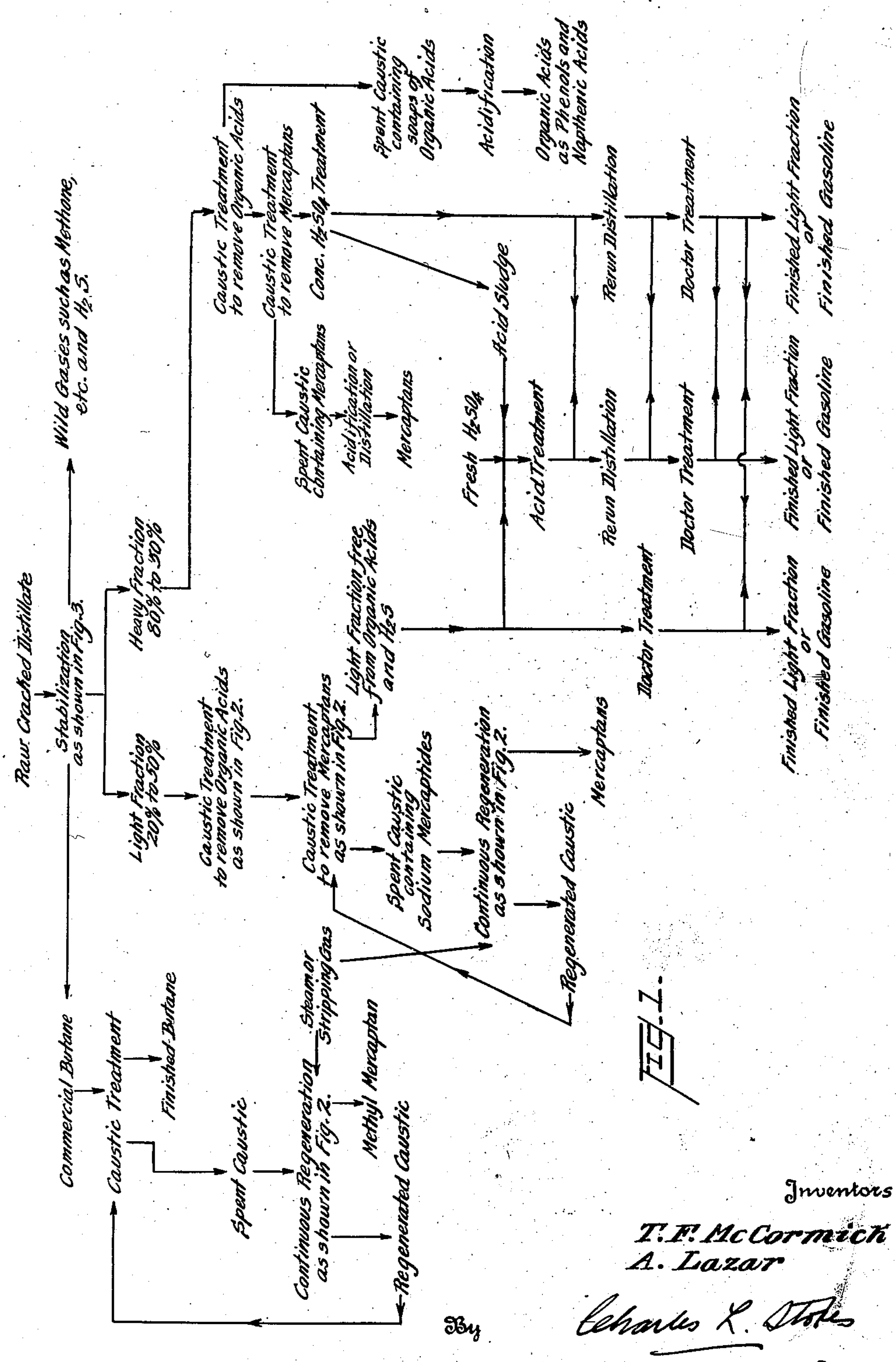

FIG. 1.

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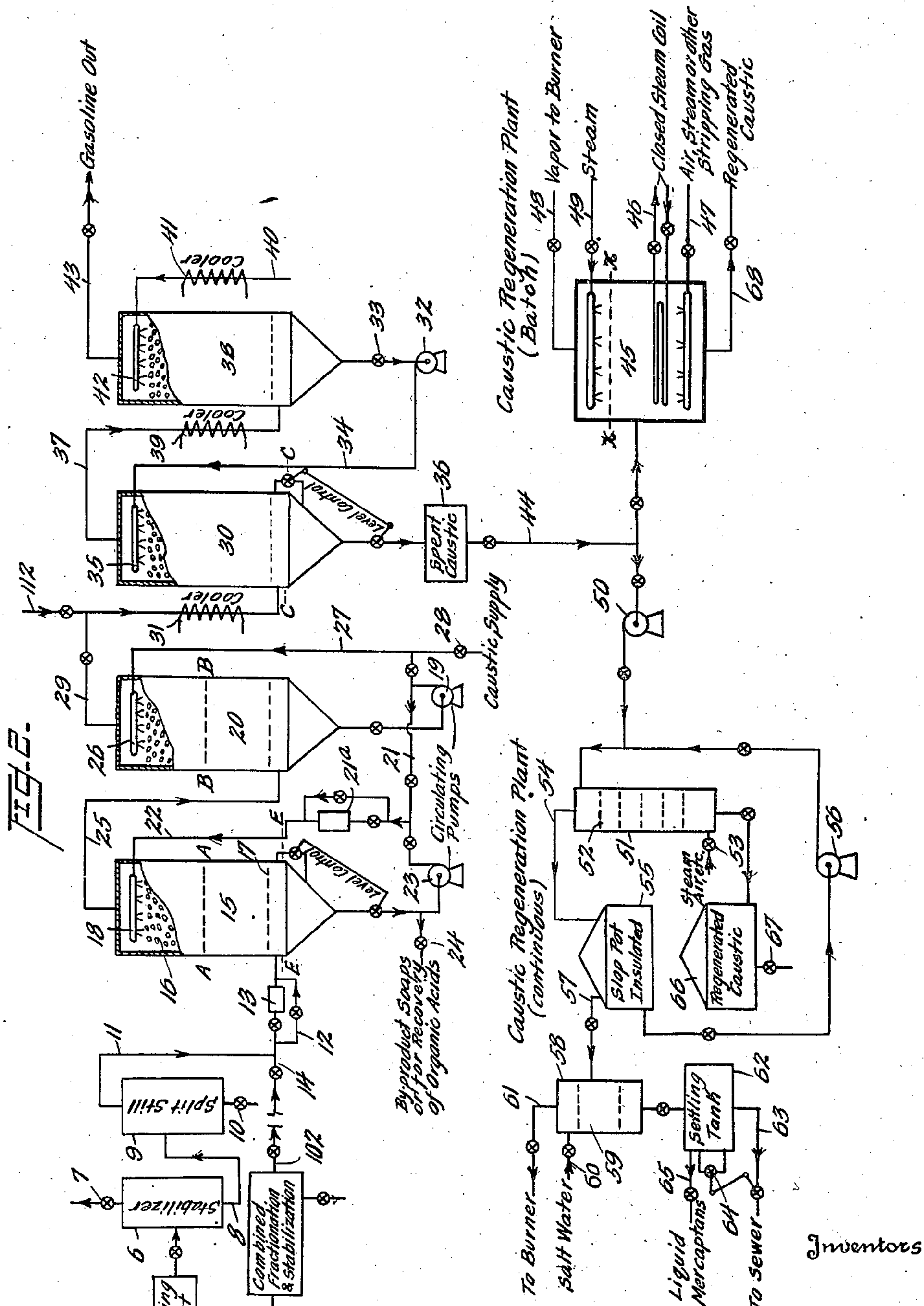

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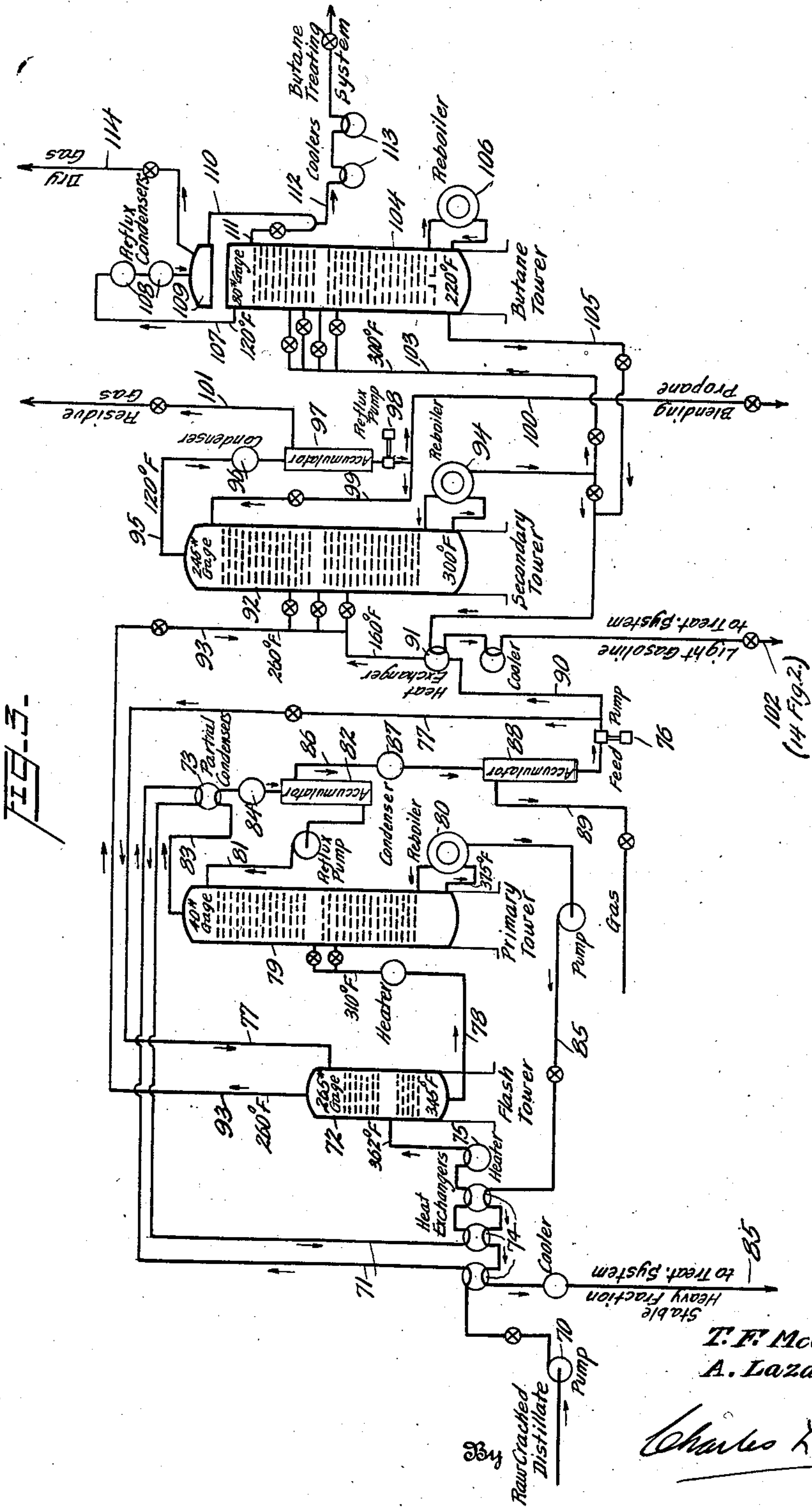

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PROCESS OF TREATING OIL

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Application December 27, 1935, Serial No. 56,398
Renewed April 13, 1939

13 Claims. (Cl. 260—609)

This invention relates to improvements in desulphurizing petroleum or its distillates and has for a particular object the removal of mercaptans from cracked distillate, especially cracked gasoline.

Another object of the invention is the reduction in, or elimination of, the usual sulphuric acid treatment used ordinarily in sulphur removal from cracked gasolines whereby the loss of valuable unsaturated hydrocarbons desired in the finished product is substantially prevented.

Another object is to increase the octane number of cracked gasoline by removal of mercaptans.

Another object is the recovery of mercaptans in purified form and the recovery of the treating agent so that a simplified process assures a minimum treating cost far below that of heretofore known processes.

Another object is the recovery of a specific mercaptan in relatively purified form.

Another object is the recovery of lower molecular weight fatty acids from a cracked distillate.

Another object is the effective removal of H_2S coupled with stabilization of the distillate by removal of wild gases such as methane etc.

Another object is to recover a commercial butane substantially free from H_2S, from cracked products.

Further objects will become apparent as the invention hereinafter is more fully disclosed.

A feature of the invention comprises the removal of certain compounds contained in cracked gasoline which have a deteterious effect on the selective removal of mercaptans whereby the mercaptans are left in a condition easily susceptible of removal by themselves.

This will be better understood by stating that when mixtures of organic compounds, such as straight run gasoline, cracked gasoline and other hydrocarbon mixtures, are treated with an alkaline reagent, such as caustic soda solution, sodium carbonate solution and the like, a reaction with certain acidic compounds dissolved in the oil takes place.

Such acidic compounds may include phenols, naphthenic acids, hydrogen sulfide gas, mercaptans, and particularly in the case of cracked distillates, fatty acids. Inasmuch as naphthenic acids, fatty acids, and H_2S are relatively strong acids and are relatively easily removed from the oil, such easy removal constitutes a base to work from leading to the selective removal of relatively less strong acidic compounds such as mercaptans.

The primary step includes the substantially complete removal of H_2S, preferably by the use of steps involving stabilization and fractionation of the distillate under treatment, because it has been determined that the major portion of the mercaptans present in gasolines, or cracked gasolines, is contained in a fractional part thereof, such as the first 30% to 40% of the distillation range and, for instance, between 170° and 250° F. end boiling point and therefore a combined treatment is very effective for H_2S removal and stabilization for eliminating the use of chemicals.

Such fraction likewise contains a relatively high percentage of unsaturated hydrocarbons comprising olefines and aromatics which are especially desirable in the finished gasoline primarily on account of the anti-knock value of the same and also by reason of their saving from loss due in ordinary sulphuric acid treatment to sulphonation and polymerization.

In accordance with this invention, therefore, a gasoline or total cracked gasoline is split into two or more fractions, according to volatility, to yield a light fraction comprising about 20% to 50% of the cracked gasoline and a heavy fraction comprising from about 80% to 50%. This may be termed a "split treat", and the said light fraction may be treated for the removal and recovery of mercaptans so as to require a relatively light sweetening treatment thereafter.

The invention comprises alternative methods of treatment with respect to the H_2S removal, in one of which the use of chemicals is eliminated and in the other of which a reduced chemical treatment may be used, but as to certain novel steps of the invention, it is immaterial how the H_2S is previously removed although a preferred form of operation without the use of chemicals will be particularly described.

While the treatment of cracked gasolines is also particularly described, it must be understood that other forms, or cuts, of petroleum distillates, coal tar distillates, shale oil distillates, or other hydrocarbons or mixtures of the same, are included in the scope of the invention.

In the appended drawings, Fig. 1 is a descriptive flow sheet showing the treatment of both the said light and heavy fractions;

Figure 2 is a diagrammatic flow sheet specifically illustrating the treatment of the said light fraction for removal and recovery of mercaptans, and regeneration of the treating agent.

Fig. 3 is a diagrammatic flow sheet illustrating a preferred method of removing H_2S from a distillate coupled with efficient fractionation thereof to provide the desired "split" stream for the desired light and heavy fractions which are thereby also stabilized.

Figure 1 is self-explanatory and discloses the variations in treatments given the light and heavy fractions.

In Figure 2 the treatment of a light fraction is seen to comprise a general method of treating and includes the passage of total cracked distillate from any well known cracking and fractionating system **5** through a stabilizer column **6** wherein a separation of so-called "wild" vapors occurs, such as H_2S gas, methane, ethane, propane, etc., said vapors and gases being eliminated through valve **7**.

The liquid distillate, comprising a total cracked gasoline, then passes through pipe **8** into a still, or fractionator **9**, wherein a desired cut is made preferably to yield a light fraction of about 20% to 50% of the distillate and a heavy fraction of about 80% to 50%.

The heavy fraction is withdrawn from still **9** through valve **10** to be treated according to the procedure of Fig. 1, while the light fraction containing the major portion of the mercaptans is passed through pipes **11** and **12** into the lower part of a contact tower **15**, substantially filled with contact material **16** comprising Raschig rings, glass beads, broken glass, crushed gravel or other suitable contact material supported on a suitable screen **17**. At times it may be desirable in the selective removal of organic acids to add heat to the distillate, in which case a heater **13** may be used. Pipe **14** is used for the supply of stabilized and purified distillate when the method of Fig. 3 is used.

The light fraction flowing upwardly through tower **15** bubbles through a body of caustic solution maintained at a level A—A, contact being enhanced by said Raschig rings, etc., which contact is usually sufficient for the purpose of the process. However, additional contact efficiency values may be obtained by circulating caustic by means of pump **23** from the bottom of tower **15** through line **22**, and dispersing the same over the top of the tower packing **16** by means of a spray **18** which causes the caustic to flow downward by gravity countercurrent to the gasoline stream. When the free caustic value of the treating agent is reduced to a low figure, the spent solution is discharged through line **24** and represents a basic stock for the recovery of alkali soaps or free organic acids as by-products. Partially spent caustic from a second contact tower **20** is pumped by pump **19** through lines **21** and **22** to tower **15** and fresh caustic is charged through valve **28**, line **27**, and spray **26** to tower **20**. If desired to maintain a certain temperature of treating in tower **15**, above atmospheric temperatures, a heater **21a** may be cut into line **22**.

The once treated light fraction from tower **15** flows through line **25** to the second contact tower **20** (of similar construction to tower **15** and having a reagent level B—B) wherein it is contacted in similar fashion with fresher caustic solution supplied as described through valve **28**, line **27**, and spray **26**. Continuous circulation of caustic solution from the bottom of the tower **20** through spray **26** by means of pump **19** will increase the contact and efficiency of treatment and may be used. The treating agent introduced through valve **28** may comprise a caustic soda solution of about 5° to 20° Bé. gravity.

The above mentioned step countercurrent method is preferred but it is to be understood that a true countercurrent method may be employed. In such cases fresh caustic of from 3° to 20° Bé. gravity is charged continuously through valve **28**, line **27**, and spray **26** to tower **20** and flows downward by gravity countercurrent to the gasoline stream, contact taking place in the Raschig rings. In such processing no caustic level is held in tower **20**, caustic being pumped by pump **19**, with up to 100% of the gasoline charge to the treating system, through lines **21**, **22** and spray **18** to tower **15** wherein contact takes place in the Raschig rings by gravity counterflow. A caustic level E—E is maintained below the gasoline inlet to this tower **15**. The treating agent is charged through valve **28** in amounts sufficient to accomplish substantial removal of organic acids and is withdrawn continuously through line **24**. As in the preferred system the treatment may be performed hot in which heaters **13** and **21a** are employed but in general practice the treatment is performed at ordinary atmospheric temperatures.

The treatment in towers **15** and **20** is used to take advantage of the selective removal of organic acids because it has been found that these compounds along with the mercaptans go into solution in fresh strong caustic soda solution but, as the soda solution becomes increasingly spent by absorbing, or reacting, with such compounds, the stronger acids replace the mercaptans, which are thus liberated to again go into solution in the gasoline.

While it is true that some mercaptans are removed in towers **15** and **20**, the major portion of the mercaptans thus remain in solution in the light fraction and the amount of such removal is the result of an equilibrium condition in which the removal depends on the relative solubilities of mercaptans in the gasoline and caustic solution respectively. This distributional factor will be affected by the strength of the caustic solution in free alkali, the temperature, the quantity of the treating agent, and the concentration and type of mercaptan present in the gasoline, so that in providing initially a certain strength of caustic soda solution through valve **28** these facts must be borne in mind to effect minimum removal of mercaptans in towers **15** and **20** and a maximum recovery of stronger organic acids which represent a valuable by-product and which are withdrawn through line **24** when the free alkali content is reduced to a low figure. The removal of strong organic acids in one or more steps is effective in preventing or minimizing the quantity of such compounds which otherwise would be removed with the mercaptans in a later step of the process.

The spent caustic solution withdrawn through line **24** contains the stronger organic acids in form of sodium salts. In order to recover these acids the solution may be acidified, whereby the organic acids are set free and subsequently can be separated into chemical individuals by fractional distillation. Another method of purification and separation of those organic acids would be a conversion of the sodium salt mixture into alkaline earth or other metal salts, followed by fractional crystallization of those salts and finally regeneration of the individual acids from the separated salts. It is also possible to accomplish separation by esterifying the organic acid mixture and fractionating the resulting esters. It is found that the organic acids thus obtained belong to the lower molecular group of monocarboxylic acids, or fatty acids. Propionic and butyric acid are predominating in quantity, but the presence of lower and higher molecular homologues of this group is indicated.

These fatty acids are very valuable raw materials for the chemical industry, where they find widespread use in the manufacture of esters, dye-stuff intermediates and pharmaceutical products.

This equilibrium reaction is especially valuable in treatment of the light fraction derived from the above described "split-treat" because it is found that not only is the major portion of the mercaptans from the total unsplit cracked gasoline concentrated in the said light fraction comprising say up to about 40% of the gasoline, but the low boiling mercaptans within the boiling range of the light fraction are the ones most soluble in caustic soda solutions.

Hence, by fractioning out the low boiling constituents of a gasoline, or cracked gasoline, up to about 40% thereof and treating this fraction separately with caustic solutions, a maximum removal of mercaptans is assured together with maximum desulphurization.

And, not only are the above factors important, but the removal of mercaptans by themselves relieves the load ordinarily thrown on the doctor treatment for sweetening wherein the mercaptans are altered to disulphides, and also the caustic solution is capable of regeneration for reuse for several cycles.

In addition to the above described treatment for selective removal of relatively strong organic acids and H_2S whereby a large percentage of the mercaptans remain dissolved in the light fraction, it is found that temperature has a marked effect on the above equilibrium condition and that as the temperature of the mercaptan containing light fraction mixed with caustic soda solution approaches the freezing point of the said solution, the solubility of the mercaptans in caustic increases in proportion.

In consequence, the treated light fraction issuing from tower **20** is passed through line **29** to a third similarly constructed contact tower **30**, being cooled by cooler **31** to a point preferably just above the freezing point of a caustic solution introduced into tower **30** by pump **32** from the bottom of a fourth similarly constructed contact tower **38** through lines **33**, **34**, and spray **35**.

The caustic solution then passes in true countercurrent flow to the light fraction through tower **30**, the spent caustic containing mercaptans being withdrawn to tank **36**, while the light fraction relieved of part of the mercaptans flows through line **37** to a fourth similarly constructed contact tower **38**, being cooled, as before, on its way by cooler **39** to a point preferably just above the freezing point of fresh strong caustic solution supplied through line **40**, cooler **41**, and spray **42**.

In tower **38**, contact of the once treated cooled light fraction is completed with fresh caustic to finally remove all mercaptans in the caustic in the form of sodium mercaptides as far as is possible under the optimum conditions of temperature and strength of soda solution.

In order to assure the most efficient contact, pump **32** provides a rate of circulation from tower **38** back to tower **30** at a rate up to about 50%, or higher, of the volume of the light fraction under treatment, which is finally withdrawn through line **43** to undergo the usual doctor treatment for sweetening and is then a finished light fraction ready for blending to yield a finished motor fuel. Some of the advantages of thus treating the light fraction may be summarized as follows:

(1) The unsaturates present in the light fraction which are highly desired for their antiknock value in finished gasolines are not attacked and lost as in sulphuric acid treatment.

(2) A re-run distillation with its accompanying losses may, in many cases, be dispensed with, due to the elimination of polymerization which takes place in ordinary acid treatment.

(3) The loss in octane number is not only minimized when compared with acid treatment followed by distillation but the octane value may be actually increased.

(4) The desulphurization by mercaptan removal is a maximum with the selective treatment of a light fraction.

(5) The maximum value may be obtained from the caustic soda solution by regeneration and re-use.

The temperature to which the reacting mixture is reduced in towers **30** and **38** may be just above the freezing point of the caustic solution used up to 60° F., and the amount of caustic soda solution used ranges from about 5% to 30% by volume of the light fraction treated and is of a strength from about 3° to 20° Bé. Preferably, the caustic strength used is between 5° and 12° Bé. and about 10% by volume and the treating temperature in towers **30** and **38** about 30° to 40° F.

In cases where a more selective removal of strong organic acids is desired, a hot caustic treat is used in tower **15** by means of heaters **13** and **21***a*. The solubility of mercaptans in the caustic solution increases as the freezing point of that solution is approached so that as the temperature rises the quantity of mercaptans extracted with the organic acids is reduced. This treatment is performed in the liquid phase and applies to both the light and heavy fractions. Temperatures up to 300° F. and pressures up to 300 pounds per square inch, absolute, may be employed and caustic strengths from 5 to 30° Bé. utilized. In general however, it is preferred to treat at normal atmospheric temperatures which range from 30° to 110° F. and use pressures up to 100 pounds per square inch, absolute, or higher, which pressures may be applied by the use of suitable valves in the system.

Referring now to Figure 1, it will be seen that the heavy fraction from still **9**, which contains a small amount of mercaptan sulphur, for example, of the order of 0.08%, may be given a caustic soda wash to remove relatively strong organic acids and mercaptans according to the steps already disclosed in treating the light fraction for the same purposes.

Although the heavy mercaptans are much less soluble in caustic soda than the lower molecular weight compounds, a partial removal is effected, thus reducing the mercaptan content of said heavy fraction. Such processing is beneficial when high acid rates are not required, for example on pressure distillates produced from selected cracking stocks which yield cracked gasolines of low sulfur content. The spent caustics derived from this mercaptan removal are solutions of the sodium mercaptides of higher boiling members of the mercaptan group and represent a further separation of selected mercaptans for by-product recovery.

The heavy fraction thus relieved of organic acids and mercaptans is then treated in countercurrent flow with concentrated sulphuric acid of say 66° Bé. to 98% strength, or higher or lower, at a preferred temperature of from 0° F. to about 50° F. to remove such sulphur compounds like thiophenes which are not removable by caustic soda solutions.

After drawing off the acid sludge, the heavy fraction is redistilled, then doctor treated to yield a finished heavy fraction ready for use as such, or for blending with the light fraction treated as above described to yield a finished gasoline, or motor fuel.

At times, it may be desirable to give the light fraction passing from tower 38 through line 43, a slight acid treatment to stabilize the gasoline for color and to remove gum forming compounds, or to further desulphurize by removing other kinds or sulphur compounds.

This may be accomplished by contacting the light fraction, after removal of mercaptans as described, with the acid sludge derived from the treatment of the heavy fraction, or with fresh acid of a suitable degree of concentration at a suitable rate.

After thus acid-treating, the light fraction may be re-run and doctor treated to be then blended with the treated heavy fraction to form a total finished gasoline.

It is apparent that, after separate acid treatments of the light and heavy fractions, the fractions may be blended and then re-run and doctor treated to obtain the finished motor fuel.

In the acid treatments of the light and heavy fractions as described above, it is preferred to use as the most efficient and economical method the processes described in a co-pending application S. N. 50,206 filed Nov. 16, 1935, and in the co-pending application of Edwards and Stark, S. N. 532,000, filed April 22, 1931, which show the true countercurrent contacting desired, but it should be understood that the herein described invention is not limited to any particular type of contacting with acid, or caustic, or to the degree of concentration of either, or to any particular kind of hydrocarbons to be treated, as the disclosure comprehends the treatment of any kind of hydrocarbon containing mercaptans in accordance with the described steps, preferred forms only being illustrated herein. Caustic soda solution may be replaced by caustic potash, as is well known.

The efficiency of the process as a whole, while not dependent thereon, is materially increased by the regeneration and reuse of the spent caustic solution from tower 30, and the regeneration may be accomplished by either batch or continuous operation. While batch regeneration is effective, continuous regeneration is to be preferred in order to conform with the continuous operation of the preceding steps set forth.

In the batch regeneration, by reference to Fig. 2, it will be seen that the spent caustic containing sodium mercaptides is drawn from tank 36 through line 44 to tank 45 containing a closed steam coil 46 and an open line 47 for the introduction of air, steam, or an inert gas for stripping.

A solution level X—X gives head room for the removal of the low boiling mercaptans in vapor form through pipe 48, the same being derived by the splitting up of the sodium mercaptides under the influence of heat supplied through coil 46 to bring the solution to or near, the boiling point.

Alternative methods of applying open steam, air, etc. may be used. If steam alone be passed through the mixture, the mercaptan sulphur may be reduced from say 50 grams per liter to as low as 2 grams per liter. If the velocity of the steam through the mixture is great enough to cause foaming, additional steam may be passed through spray line 49 to break the foam.

Alternatively and preferably, continuous regeneration is effected by passing the spent caustic solution from tank 36 through line 44 and pump 50 to the top of a contact tower 51 containing a plurality of bubble plates 52, the caustic solution flowing down countercurrent to the heating and stripping steam or gas supplied through line 53.

In such a contact tower 51, when insulated and being 4′ in diameter and 32′ high, using 1.8 pounds of steam for 5 pounds of caustic solution charged, it is found that with seven plates the mercaptan sulphur content will be reduced from 40 grams per liter to 6.00 grams per liter. Using a higher ratio of steam to caustic the mercaptan content may be still further reduced, or the number of plates may be increased to provide an additional reduction in mercaptan sulphur.

The mercaptans are taken as overhead through line 54 to an insulated slop pot 55, wherein a separation of vapors from any caustic in the form of foam takes place, and the mercaptan vapors then pass through line 57 to a contact tower 58 containing suitable contact material 59 in which the vapors are scrubbed with water applied through pipe 60 to condense the mercaptans at a predetermined temperature and pressure.

Vapors are tapped off through line 61 and are composed largely of the more volatile mercaptans as methyl and ethyl mercaptan. These mercaptans may be recovered by suitable absorption agents or may be liquified by means of a refrigeration or compression in the well known manner. Mercaptans condensed by the water pass to a settling tank 62 wherein the water separates by gravity to be withdrawn through pipe 63 controlled by an automatic liquid level regulator 64. The desired liquid mercaptans are drawn off through pipe 65.

Any caustic solution passed over from tower 51 and trapped out in the slop pot 55 may be returned by pump 56 for restripping in tower 51.

The regenerated caustic solution flows continuously from tower 51 into tank 66 whence it may be withdrawn through line 67 to be used as charging caustic through line 40. In similar fashion, the regenerated caustic solution from the batch treatment (when used) may be passed through line 68 to line 40.

The life of the regenerated caustic solution is not necessarily indefinite as there may be a gradual accumulation of impurities in the same which are not responsive to regenerative separation, but it may be used effectively in towers 38 and 30 for at least three cycles which gives great economy in caustic consumption.

Referring to Fig. 3, a preferred method of removing H_2S from a raw cracked distillate, while stabilizing the same during fractionation to obtain the before described light and heavy fractions is shown.

In these steps, which are preferably used in place of the stabilizer column 6 and still 9 of Fig. 2, the flow sheet and data represent actual refinery operations during the production of finished cracked gasoline from a stabilized raw cracked distillate having the following characteristics:

Gravity	58.2
Sulphur ... per cent	0.75
Octane No. (C. F. R. Motor method)	70
Initial B. point	90
5%	112
10	124
20	160
30	191
40	227
50	257
60	283
70	309
80	343
90	366
95	394
End point	399
Recovery	95.0
Residue	1.0
Loss	4.0

The raw cracked distillate from the cracking stills is forced by pump **70** through line **71** into a flash tower **72**, absorbing heat during its passage from partial condenser **73**, heat exchangers **74** and heater **75** so that the distillate is discharged into flash tower **72** at about 362° F., or at a temperature sufficient to release H_2S, wild gases and certain desired low boiling fractions.

Flash tower **72** operates successfully and efficiently in the present invention with nine plates, but any desired number can be used, and with a suitable reflux liquid, which may conveniently be supplied from another part of the system by pump **76** and line **77**, to separate up to say 25% of low boiling constituents together with the greater portion of the H_2S.

Operating flash tower **72** with entering distillate at 362° F. and under a pressure of 265 pounds per square inch, gage, the desired light fraction is taken off as overhead with the H_2S which latter will then be found to be reduced from 0.30 gram per liter of the raw distillate down to 0.09 gram per liter in the bottoms which are withdrawn through line **78** and passed into a primary tower **79**. Said bottoms are injected into primary tower **79** at a temperature of about 310° F. for rectification by removal of the remaining H_2S and light ends of the boiling range of the desired light fraction.

To this end, primary tower **79** may be a 30 plate tower, fitted with a reboiler **80** wherein the bottoms are heated to about 375° F., operated under a pressure of about 40 pounds per square inch, gage, and supplied with suitable reflux liquid through line **81** which may conveniently be supplied from an accumulator **82** wherein is collected part of the overhead from primary tower **79** which passes thereto by way of line **83** and partial condensers **73** and **84**.

In primary tower **79**, operating under the above described conditions, the H_2S will be reduced from 0.09 gram per liter of the entering stock to a trace in the rectified heavy fraction passing out through line **85** to the treating system described, while the overhead (comprising constituents of the desired light fraction) passes from accumulator **82** through line **86** and condenser **87** to be collected in accumulator **88** in liquid form, incondensible gases being taken off through line **89** for recompression, absorption, or other uses.

The condensed overhead is picked up by pump **76** and passed through line **90** and heat exchanger **91** at a temperature of about 160° F. into a 34 plate secondary tower **92**, being joined therein and in its passage by the vapor overhead brought from flash tower **72** through line **93**.

Secondary tower **92** is provided for the purpose of stabilizing the desired light fraction by the elimination of undesired wild gases such as methane, ethane, etc., during which operation all H_2S is separated. To this end, tower **92** is provided with a reboiler **94** adapted to heat the bottoms to a temperature of about 300° F. thereby giving a temperature gradient through the column and yield an overhead having a temperature of about 120° F. at the outlet pipe **95** while operating under a pressure of about 245 pounds per square inch, gage.

The overhead from secondary tower **92** is taken through line **95** and condenser **96** to provide condensate in accumulator **97** which is forced by pump **98** through line **99** as reflux in the upper part of the tower. Excess condensate may be taken through line **100** to be used as blending propane, or for other purposes, while the incondensible wild gases and H_2S are withdrawn through line **101**.

Depending on the use desired for the light fraction as to boiling range, etc., it may be withdrawn as is for the described caustic treatment through line **102**, or may be passed at a temperature of about 300° F. through line **103** into a 24 plate butane tower **104** wherein a cut of commercial butane is taken as overhead, the bottoms comprising the desired light fraction within the gasoline boiling range being withdrawn through lines **105** and **102** for the described caustic treatment.

When a cut comprising susbtantially butanes and hydrocarbons of similar boiling range is desired with, for example, an absolute vapor pressure of about 25 to 75 pounds per square inch at 70° F., tower **104** may be provided with a reboiler **106** giving a bottom temperature of about 220° F. and a temperature at outlet line **107** of about 120° F. while operating under a pressure of about 80 pounds per square inch, gage.

The overhead passing through line **107**, reflux condensers **108** and head condenser **109**, will flow as a liquid through line **110**, part being used as reflux through line **111** and the remainder flowing through line **112** and coolers **113** to a treating system for the recovery of methyl mercaptan in substantially pure form. The incondensible gases are withdrawn through line **114**.

It is found that by thus running a raw cracked distillate, as described, when a butane cut is taken mercaptans are present up to about 0.35% by weight mercaptan sulphur and that the mercaptan sulphur is derived from the specific mercaptan, methyl mercaptan CH_3SH, which is removed by caustic soda solutions as follows:

$$NaOH+CH_3SH=NaSCH_3+H_2O$$

In consequence, the butane cut from tower **104** through line **112** may be treated with caustic soda solution according to the steps outlined with respect to the operation of towers **30** and **38** in Fig. 2.

Depending on the use desired for the light fraction as to boiling range, etc., it may be withdrawn as is for the described caustic treatment through line **102**, or may be passed at a temperature of about 300° F. through line **103** into a 24 plate butane tower **104** wherein a cut of commercial butane is taken as overhead, the bottoms comprising the desired light fraction within the gasoline boiling range being withdrawn through lines 105 and 102 for the described caustic treatment.

When a cut comprising substantially butanes and hydrocarbons of similar boiling range is desired with, for example, an absolute vapor pressure of about 25 to 75 pounds per square inch at 70° F., tower 104 may be provided with a reboiler 106 giving a bottom temperature of about 220° F. and a temperature at outlet line 107 of about 120° F. while operating under a pressure of about 80 pounds per square inch, gage.

The overhead passing through line 107, reflux condensers 108 and head condenser 109, will flow as a liquid through line 110, part being used as reflux through line 111 and the remainder flowing through line 112 and coolers 113 to a treating system for the recovery of methyl mercaptan in susbtantially pure form. The incondensible gases are withdrawn through line 114.

It is found that by thus running a raw cracked distillate, as described, when a butane cut is taken mercaptans are present up to about 0.35% by weight mercaptan sulphur and that the mercaptan sulphur is derived from the specific mercaptan, methyl mercaptan CH_3SH, which is removed by caustic soda solutions according to the following equation:

$$NaOH + CH_3SH = CH_3SNa + H_2O$$

In consequence, the butane cut from tower 104 through line 112 may be treated with caustic soda solution according to the steps outlined with respect to the operation of towers 30 and 38 in Fig. 2. In this case, towers 30 and 38 will be supplied with cooled caustic soda solution of about 5° to 12° Baumé strength and the cooled butane will flow countercurrent to the caustic with efficient contacting due to the structure of the towers, the reaction being conducted at about 30 to 40° F.

The spent caustic may then pass, as described in connection with Fig. 2, from tower 30 to the described continuous regeneration plant when pure methyl mercaptan may be recovered from line 65.

More simply, the methyl mercaptan may be removed from the spent caustic by boiling the latter and condensing the distillated mercaptan, or by passing steam, air, or other inert stripping gas through the hot caustic solution and condensing the distilled mercaptan.

The preferred system, above outlined, for obtaining desired light and heavy fractions for separate treatments in the removal of impurities has many advantages.

It provides for the complete removal of H_2S without recourse to the chemical treatment usually necessary.

It gives improved fractionation for the desired split wherein gaps of over 20° F. between the A. S. T. M. Engler end point of the light fraction and the Engler initial boiling point of the heavy fraction can be obtained, which is important when a concentration of mercaptans has been determined in a given percentage of the raw distillate and thus limits the low boiling sulphur compounds to the light fraction.

It gives by improved fractionation a light fraction of a desired boiling range which is largely uncontaminated with higher boiling and more refractory types of sulphur compounds or with compounds which may impair color stability.

It gives a light fraction free from H_2S of such character that the first treatment thereof with warm or hot caustic solution permits the selective removal of organic, or fatty, acids uncontaminated with H_2S reaction products.

It minimizes the use and cost of chemicals while yielding relatively pure valuable by-products.

It gives a commercial butane free from H_2S.

It yields a specific mercaptan in relatively pure form.

It provides ultimately for a purified cracked gasoline of superior qualities of octane rating and color stability. Combined with these is the recovery of impurities in a valuable commercial form and a high reduction in treating costs.

It must be understood that the preferred method of Fig. 3 has been applied to the treatment of a cracked gasoline specifically for the purpose of illustration and not of limitation, inasmuch as variations in temperature, pressure, tower construction and the like are permissible depending on the required split in the boiling ranges of the raw cracked distillate, the character of the cracked gasoline and many other variables well known in the art.

For instance, in the removal of H_2S alone, the operation of flash tower 72 is not as important as its chief function which is the stripping of the lightest hydrocarbons from the raw distillate so that the load on the primary tower 79 is reduced and thus permits condensation of overhead vapors therefrom at ordinary cooling water temperatures and comparatively low pressures. This permits the use of a less costly primary tower 79 and cuts down the use and cost of steam used in reboiler 80 and the cost of condensing the overhead vapors with cooling mediums other than water.

Again, while correct control and adjustment of the operations in primary tower 79 and secondary tower 92 are important for the removal of H_2S the figures given for a particular cracked distillate may be varied to suit conditions. For instance, if it is desired to operate these towers at higher pressures, the top and bottom temperatures must be raised or, vice versa, if the pressure is reduced, the temperatures should be reduced.

A great many of such variables follow physical laws, the operation of which is well known to those skilled in the art, and the practice of the invention requires no other instructions to permit its use beyond those given. Ordinary laboratory controls to determine characteristics of a particular distillate will govern correct refinery control of the process.

The increase in octane number is another result of the invention.

In the usual sulfuric acid treatment of cracked distillates for the removal of sulfur compounds and other impurities it is possible to accomplish complete mercaptan removal with acid but due to resultant large losses such treatment is usually uneconomical. Just sufficient acid is therefore added to accomplish the desired degree of total sulfur removal and the mercaptans which remain after such treatment are often from 10 to 50% of those present in the original stock. These compounds must be converted to disulfides by a sweetening process such as plumbite treating, in order to improve the odor of the product and meet specifications.

By such usual treatments there is often a drop in octane value (as determined by the C. F. R. Motor method) as high as 4 to 5 octane numbers under the original stock with a corresponding derogatory effect on the lead susceptibility of the gasoline. While such drop, or loss, is partly due to the formation of disulphides during doctor treatment, yet octane number losses occur in such treatment over and above what is expected by the complete conversion of mercaptans to disulphides.

In consequence, it is highly desirable to not only eliminate sulphuric acid treatment with its high sulphonation, polymerization and volatility losses, but to eliminate or minimize the conversion of mercaptans by doctor treatment with its attendant octane losses.

This is accomplished largely in the present invention wherein by selective isolation of given types of mercaptans, substantially complete removal of such mercaptans can be acocmplished by the use of caustic solutions.

The conditions governing such removal include the proper distillation range, fractionation, quantity and strength of caustic solution, contact methods, and temperature.

While it is true in average commercial use of the process, not warranting the ultimate purity of complete mercaptan removal, that a small percentage of mercaptan remains in the gasoline after caustic treatment and provision is made for economically reducing this, yet the harmful effect of the remainder is markedly less than that in other known types of mercaptan removal processes.

This is more particularly shown in the present invention wherein the light fraction, which contained 0.35% of mercaptan sulphur before the described caustic treatment, contained but 0.04% of sulphur after caustic treatment.

At the same time, the removal of mercaptan sulphur, as described, increased the octane number of the light fraction from 71.0 to 72.5, before and after caustic treatment respectively.

Thus, compared with the usual sulphuric acid treatment an increase in octane number is secured instead of a loss.

The use of doctor solution herein is principally for a safety factor because any slight traces of mercaptans might be corrosive. Further, the malodorous mercaptans are highly offensive in commercial fuels.

Hence, while the mercaptans may not be eliminated to an ultimate degree in the system without doctor treatment, the use of a doctor treatment on largely mercaptan free distillate assures a minimum conversion of mercaptans to disulphides with accompanying loss of octane rating, while effecting removal of the main body of corrosive and bad smelling compounds.

The entire process, as described, as a whole comprises a number of steps which, both alone and in combination in one form or another, give maximum results in desulphurization, minimum losses of valuable hydrocarbons, high economy in treating costs, and improved recovery of valuable by-products.

These steps may be summarized as follows:

Step No. 1

Comprises the fractionation, or separation, combined with stabilization of a raw total cracked distillate to yield a light fraction up to about 40% of the volume of the raw distillate. The advantages of separately treating the light fraction are:

(*a*) The concentration of sulphur compounds in the form of mercaptans in the light fraction.

(*b*) The thus concentrated mercaptans are the low boiling range mercaptans, or low molecular weight mercaptans, which are most soluble in caustic solutions.

(*c*) With this concentration of mercaptans in the light fraction, when the percentage of other remaining sulphur compounds is relatively low, with fairly complete mercaptan removal the oil is desulphurized to a very low figure.

(*d*) The low boiling mercaptans in the light fraction may be readily distilled from caustic solutions and the remaining caustic solution is available for continued use.

(*e*) The low boiling point of the fraction yields organic acids of the fatty acid type, like propionic and butyric acids with a minimum contamination with phenols and naphthenic acids, which latter boil at a much higher range.

Step No. 2

Comprises the selective removal of H_2S and relatively strong organic acids from the light fractions prior to selective mercaptan removal. This is important because

(*a*) It prepares the light fraction for selective mercaptan removal by the elimination of acidic compounds which would prevent such selective removal.

(*b*) The elimination of strong organic acids reduces the foaming tendency of the spent caustic solutions derived during this selective mercaptan removal step, during regeneration.

(*c*) The strong organic acids removed represent a source of valuable by-products.

Step No. 3

Comprises the cooling of the light fraction to a temperature just above the freezing point of the caustic solution. Under average circumstances however, we prefer to treat at temperatures of 30–40° F. This step has the advantage of

(*a*) Giving the greatest rate of mercaptan removal with a minimum rate of caustic supply of a given concentration.

(*b*) Increases the rate of mercaptan removal when compared with higher temperatures.

Step No. 4

Comprises the continuous countercurrent treatment of the light fraction with caustic solution in a packed tower, which assures

(*a*) Maximum removal of mercaptans with consequent greater desulphurization in such manner that the sulphur percentage is reduced to a figure unattainable with sulphuric acid treatment without excessive losses.

Step No. 5

Comprises the regeneration of used caustic solution which is possible due to the selective removal of H_2S and strong organic acids and gives the advantages of

(*a*) Recovery of substantially pure mercaptans.

(*b*) Recovery of regenerated caustic solution suitable for re-use.

Step No. 6

Comprises the optional treatment of the light fraction after mercaptan removal with sulphuric acid and the separate treatment of the heavy fraction with sulphuric acid. The advantages are

(*a*) The finishing acid treatment of the light fraction is optional and is only necessary in certain cases to obtain additional treatment but in general a heavy acid treatment with large losses is eliminated.

(b) The separate acid treatment of the heavy fraction avoids treating the light fraction in many cases at all with acid.

Step No. 7

Comprises the re-run distillation of both the light fraction and the heavy fraction separately, or together, when both have been acid treated to remove compounds polymerized by the acid. If the light fraction has not been acid treated the re-run distillation may be eliminated with consequent saving.

Step No. 8

Comprises doctor, or other, sweetening when necessary. This step may be eliminated when certain stocks are treated in which the mercaptan removal by the above described steps is such that the sour sulphur content is low.

The definition of the term "total cracked distillate" used herein indicates a distillate derived from cracking various stocks and is usually a distillate cut to an end point by A. S. T. M. distillation similar to normal motor fuel marketed. However, the total cracked gasoline may have an end point from 250° F. to 500° F., or higher, depending entirely on the particular fractionating process and/or equipment used.

As a rule, the end point on total cracked gasoline is cut with modern methods and equipment to somewhere between 350° F. and 437° F., but variations from this range are permissible within the scope of the invention and may include distillates from other sources such, for instance, as those made by polymerization of hydrocarbon gases as well as sulphur bearing distillates from other sources.

Among outstanding features of the invention are included two stages of caustic treatment, the first comprising caustic treatment at atmospheric or more elevated temperatures for the recovery of organic acids, the second comprising caustic treatment at reduced temperatures below atmospheric, or at effective low temperatures, for the removal of mercaptans.

In order to obtain these by-products in the most purified form, hydrogen sulphide should be first removed as described so that the selective removal of the other impurities may be readily accomplished.

We claim:

1. A process of recovering mercaptans from hydrocarbon distillates which comprises treating a hydrocarbon distillate containing mercaptans, H_2S, and other acidic compounds with a caustic soda solution at a temperature between the freezing point of the solution and 300° F. sufficiently high to selectively remove substantially all said acidic compounds of a greater acidity than said mercaptans so that said mercaptans remain dissolved in said distillate, treating the distillate with further caustic soda solution while at a lower temperature between the freezing point of the solution and about 60° F. sufficiently low for said solution to absorb the greater portion of said mercaptans, then freeing said mercaptans from said solution.

2. A process of recovering products from petroleum oils which comprises: treating a hydrocarbon distillate containing aliphatic monocarboxylic acids and mercaptans with a caustic alkali solution while at a temperature between the freezing point of the solution and 300° F. sufficiently high to selectively absorb substantially all compounds having a greater acidity than said mercaptans and to leave said mercaptans dissolved in said distillate, recovering such alkaline solution, further treating the distillate with caustic alkali solution while at a temperature between just above the freezing point of the solution and about 60° F. sufficient to absorb the greater portion of said mercaptans, then freeing said mercaptans from said solution.

3. A process of recovering products from petroleum oils which comprises: treating a hydrocarbon distillate containing aliphatic monocarboxylic acids and mercaptans with a caustic alkali solution while at a temperature between the freezing point of the solution and 300° F. sufficiently high to selectively absorb substantially all compounds having a greater acidity than said mercaptans and to leave said mercaptains dissolved in said distillate, recovering such alkaline solution, further treating the distillate with caustic alkali solution while at a temperature between just above the freezing point of the solution and about 60° F. sufficient to absorb the greater portion of said mercaptans, then freeing said mercaptans from said solution, and returning said solution freed from mercaptans to contact further mercaptan containing distillate.

4. A process of recovering products from petroleum oils which comprises: treating a hydrocarbon distillate containing aliphatic monocarboxylic acids and mercaptans with a caustic alkali solution while at a temperature between the freezing point of the solution and 300° F. sufficiently high to selectively absorb substantially all compounds having a greater acidity than said mercaptans and to leave said mercaptans dissolved in said distillate, recovering such alkaline solution, further treating the distillate with caustic alkali solution while at a lower temperature between just above the freezing point of the solution and about 60° F. sufficient to absorb the greater portion of said mercaptans, then freeing said mercaptans from said solution.

5. A process of recovering products from petroleum oils which comprises: treating a hydrocarbon distillate containing aliphatic monocarboxylic acids and mercaptans with a caustic alkali solution while at a temperature between the freezing point of the solution and 300° F. sufficiently high to selectively absorb substantially all compounds having a greater acidity than said mercaptans and to leave said mercaptans dissolved in said distillate, recovering such alkaline solution, further treating the distillate with caustic alkali solution while at a temperature between just above the freezing point of the solution and about 60° F. sufficient to absorb the greater portion of said mercaptans, then freeing said mercaptans from said solution, and maintaining a superatmospheric pressure during said treatment sufficient to hold said distillate in liquid form.

6. A process of recovering products from petroleum oils which comprises: treating a cracked gasoline containing aliphatic monocarboxylic acids and mercaptans with a caustic alkali solution while at a temperature between the freezing point of the solution and 300° F. sufficiently high to selectively absorb substantially all compounds having a greater acidity than said mercaptans and to leave said mercaptans dissolved in said distillate, recovering such alkali solution, further treating the distillate with caustic alkali solution while at a temperature between just above the freezing point of the solution and about 60° F. sufficient to absorb the greater portion of

said mercaptans, then freeing said mercaptans from said solution.

7. In a continuous process of recovering products from cracked gasoline distillates in which a continuously flowing stream of the distillate containing aliphatic monocarboxylic acids and mercaptans is contacted in a plurality of steps with caustic alkali solution to successively selectively remove first the monocarboxylic acids at a temperature between just above the freezing point of the solution and 300° F. and then the mercaptans at a lower temperature between just above the freezing point of the solution and about 60° F., and said solution is independently removed from the distillate after each treating step, that combination of steps which comprises: continuously removing said mercaptans from the mercaptans containing solution and returning the mercaptan free solution back to the mercaptan treating step.

8. A process of recovering mercaptans from hydrocarbon distillates which comprises: removing H_2S from a hydrocarbon distillate then treating said distillate, substantially freed from H_2S but containing mercaptans and other acidic compounds, with a caustic soda solution at a temperature between the freezing point of the solution and 300° F. sufficiently high to selectively remove substantially all said acidic compounds of a greater acidity than said mercaptans so that said mercaptans remain dissolved in said distillate, treating the distillate with further caustic soda solution while at a lower temperature between the freezing point of the solution and about 60° F. sufficiently low for said solution to absorb the greater portion of said mercaptans, then freeing said mercaptans from said solution.

9. The process according to claim 8 in which the H_2S is removed from the hydrocarbon distillate by fractional distillation.

10. A process of recovering mercaptans from hydrocarbon distillates which comprises: treating a hydrocarbon distillate, substantially free from H_2S but containing mercaptans and other acidic compounds, with a caustic soda solution at a temperature between the freezing point of the solution and 300° F. sufficiently high to selectively remove substantially all said acidic compounds of a greater acidity than said mercaptans so that said mercaptans remain dissolved in said distillate, treating the distillate with further caustic soda solution while at a lower temperature between the freezing point of the solution and about 60° F. sufficiently low for said solution to absorb the greater portion of said mercaptans, then freeing said mercaptans from said solution.

11. A process of recovering mercaptans from hydrocarbon distillates which comprises: treating a hydrocarbon distillate containing mercaptans and other acidic compounds with a caustic soda solution at a temperature between the freezing point of the solution and 300° F. sufficiently high to selectively remove substantially all said acidic compounds of a greater acidity than said mercaptans so that said mercaptans remain dissolved in said distillate, treating the distillate with further caustic soda solution while at a lower temperature between the freezing point of the solution and about 60° F. sufficiently low for said solution to absorb the greater portion of said mercaptans, then freeing said mercaptans from said solution.

12. In a process of recovering products from petroleum oils the combination of steps which comprises: treating a hydrocarbon distillate containing aliphatic monocarboxylic acids and mercaptans with a caustic alkali solution while at a temperature between the freezing point of the solution and 300° F. sufficiently high to selectively absorb compounds having a greater acidity than said mercaptans and to leave said mercaptans dissolved in said distillate and separating such alkaline solution from said distillate.

13. In a process of recovering mercaptans from petroleum oils in which a hydrocarbon distillate containing aliphatic monocarboxylic acids and mercaptans is treated with an alkali solution to absorb said mercaptans and said alkali solution is then subjected to distillation to recover said mercaptans and to regenerate said alkali solution, the method of preventing the accumulation of alkali salts of said aliphatic monocarboxylic acids in the regenerated alkali solution which comprises: first treating said distillate with a caustic alkali solution while at a temperature between the freezing point of the solution and 300° F., sufficiently high to selectively absorb compounds having a greater acidity than said mercaptans and to leave said mercaptans dissolved in said distillate, and separating the thus spent caustic alkali solution from said distillate.

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