

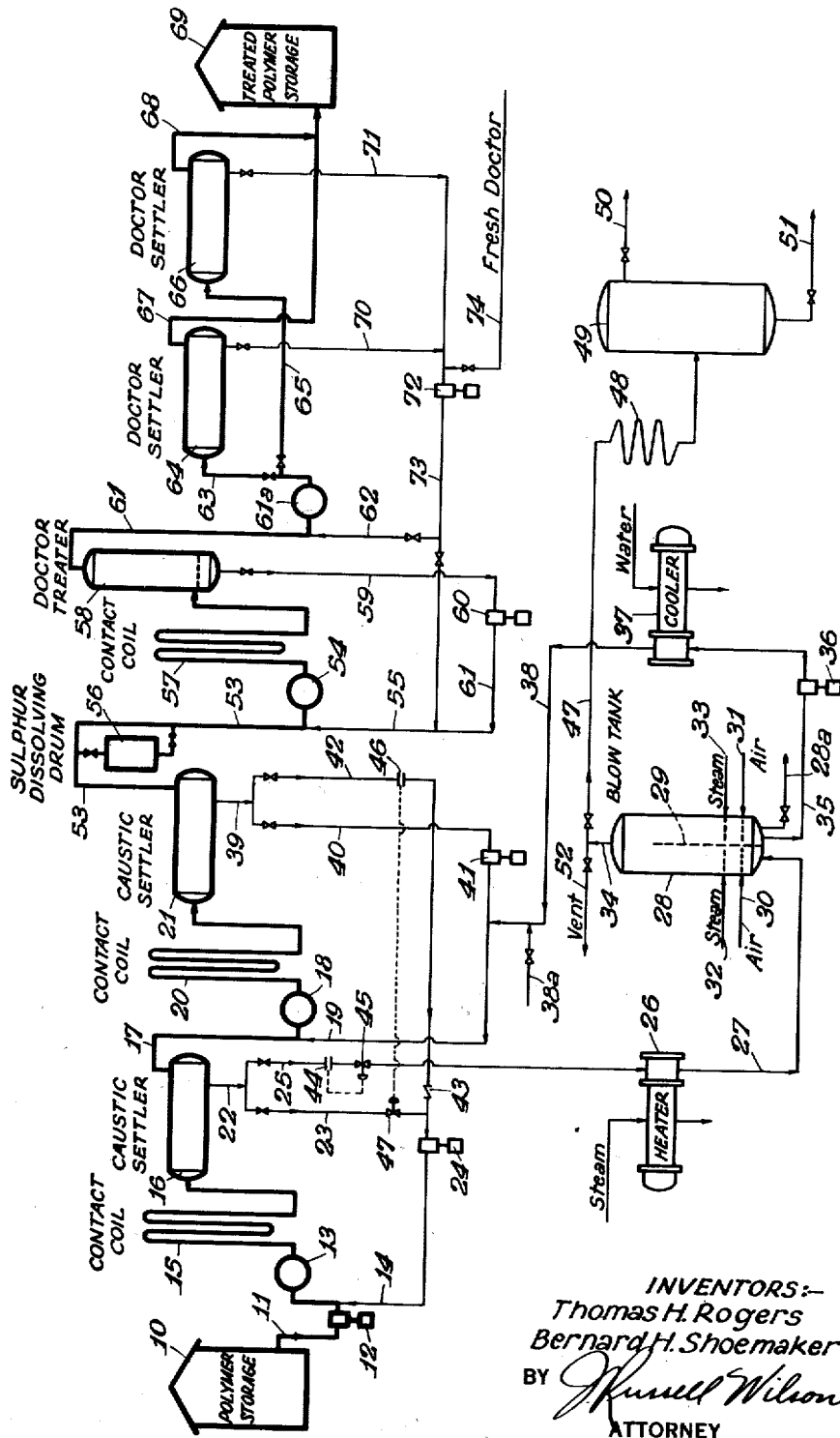
July 4, 1939.

T. H. ROGERS ET AL

2,164,665

SWEETENING HIGH-SULPHUR MOTOR FUELS

Filed May 1, 1937



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## UNITED STATES PATENT OFFICE

2,164,665

## SWEETENING HIGH-SULPHUR MOTOR FUELS

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Application May 1, 1937, Serial No. 140,106

17 Claims. (Cl. 196—32)

This invention relates to improvements in the process of sweetening petroleum naphthas, and gasolines containing relatively large amounts of sulphur in the form of mercaptans, and particularly to the treatment of polymerized gasolines containing relatively large amounts of the aforesaid sulphur compound. These gasolines and naphthas, however, are substantially free from hydrogen sulphide.

10 The sulphur in petroleum naphthas and gasolines occurs in many forms and due to the chemical nature of these various types of sulphur compounds it is necessary to treat the gasoline under varying conditions in order to sweeten the gasoline in an effective and economical manner. A large portion of the sulphur in gasolines is in the form of mercaptans, but since the low molecular weight mercaptans and high molecular weight mercaptans have somewhat different chemical properties the applicants have found that gasolines containing large amounts of these various types of mercaptans must be treated under special conditions in order to sweeten the gasoline in an effective and economical manner and, at the same time, lower the sulphur of the finished gasoline sufficiently so that it will not be unduly corrosive.

The object of the present invention is to sweeten gasolines which contain large amounts of sulphur, particularly in the form of mercaptans, by a series of steps which will effect the maximum sweetening with a given amount of reagent and, at the same time, provide for the recovery of the mercaptans if desired. Our process is particularly adapted for continuous operation.

A particular object of our invention is to sweeten a high sulphur polymerized gasoline which has been partly depentanized by a series of steps which will effect the maximum sweetening with a given amount of reagent and, at the same time, provide for the recovery of a fraction of mercaptans consisting mostly of isopropyl mercaptan and secondary butyl mercaptan.

45 A detailed discussion of our process will be given with the aid of the drawing which is attached to and forms a part of the specification. The high sulphur polymerized gasoline which has been rerun to the desired end-point in any conventional type of re-run tower is withdrawn from the storage tank 10 through line 11 and passed with the aid of the pump 12 to a suitable mixing device 13 where it is mixed with an aqueous solution of caustic that enters line 11 through line 14. The origin of the caustic that

enters the mixer 13 will be discussed hereinafter, but generally the concentration of alkali in this aqueous solution ranges from 5 to 35%, but preferably within the range of 10 to 30%. The admixture of caustic and naphtha (gasoline) passes from the mixer 13 through an elongated contact coil 15 where sufficient time is provided for the caustic to react with the mercaptans present in the gasoline. The products in the contact coil 15 are then passed to the caustic settler 16 where the naphtha is separated from the aqueous caustic solution by settling. The mixer 13, contact coil 15 and settler 16 may be referred to as the first treating zone.

The naphtha is withdrawn from the settler 16 through line 17 and passed to the mixer 18 where it is contacted with a second caustic solution which enters line 17 through line 19. The origin of caustic solution that enters the treater 18 through line 19 will be discussed hereinafter. Generally the concentration of the caustic in the solution introduced through line 19 is within the range of 12 to 40%, but preferably within the range of 15 to 35%. The admixture of aqueous caustic solution and naphtha is passed from the mixer 18 through the contact coil 20 where the mercaptans and other sulphur compounds in the naphtha or gasoline are permitted to react with the caustic. The products from contact coil 20 are then passed to the second caustic settler 21 where the aqueous caustic solution and dissolved sulphur compounds are permitted to settle as a bottom layer. The mixer 18, contact coil 20 and settler 21 may be referred to as the second treating zone.

For convenience, the method of circulating, proportioning and revivifying a certain part of the caustic used in the two treating zones hereinbefore described will be considered at this point in the specification. Furthermore, to illustrate this improved method of treating the sulphur-containing gasoline with caustic, reference will be made to a specific embodiment of the invention wherein 100 bbls. of gasoline per hour are treated with an equivalent volume of aqueous caustic. The end point high sulphur gasoline is passed from the storage tank 10 to the mixer 13 at the rate of 100 barrels per hour and also an aqueous caustic solution is passed through line 14 to this mixer at the rate of 100 barrels per hour. The caustic solution which settles to the bottom in settler 16 is withdrawn therefrom through line 22 at the rate of 100 barrels per hour and split into two streams. One stream of about 80 barrels per hour is passed

through valved line 23 with the aid of pump 24 and recycled through line 14 to the mixer 13. The other stream comprising about 20 barrels per hour is passed through valved conduit 25 to the heat exchanger or heating means 26 and thence through line 27 to the blow-tank 28 where it is revived by blowing with air, steam, or air and steam.

The aqueous caustic solution in the blow-tank 28 is maintained at a temperature within the range of about 180° F. to 230° F. This temperature may be maintained in part by the heat exchanger 26.

The blow-tank 28 is divided by a partition 29, and the used caustic solution, containing mercaptides, enters one side of the blow-tank through line 27 and is contacted with air, steam, or air and steam. As the caustic solution rises in one side of the blow-tank during the revivification it flows over the partition 29 into the second portion of the tank where it is further contacted with air, steam, or air and steam. If air is used in the revivification of the aqueous caustic solution it is introduced into the lower part of the blow-tank 28 through the perforated lines 30 and 31. If steam is used, it is introduced into a tank through perforated lines 32 and 33. The air may be pre-heated before introduction into the blow tank. Saturated steam and superheated steam may be used. As stated above, both air and steam may be used to revivify the used aqueous caustic solution. The volatile constituents including the sulphur compounds are withdrawn from the top of the blow-tank through line 34 and disposed of in the manner hereinafter described. The thus revived caustic solution is withdrawn from the bottom of the blow-tank through line 35 and passed by pump 36 through the water cooler 37, and thence through line 38 to line 19 where it enters the second mixer 18. A draw-off line 38a may be provided in the bottom of the blow-tank.

We have found that cold caustic solutions are more effective in reacting with the mercaptans in the gasoline being treated and consequently it is important that the regenerated caustic withdrawn through line 35 be cooled before it is returned to the second treating zone. This cold caustic solution greatly enhances the effectiveness of our process in removing substantial proportions of the mercaptans present in the gasoline being sweetened.

Caustic solution is withdrawn from the second settler 21 through line 39 at the rate of 100 barrels per hour and split into two streams. One stream consisting of about 80 barrels per hour passes through valved conduit 40 with the aid of pump 41 and is passed into line 19 which leads to the second mixer 18. The second stream of caustic solution from line 39 consisting of about 20 barrels per hour, is passed through valved line 42 and check valve 43 with the aid of pump 24 and returned to the first mixer 13.

From the foregoing specific example it will be noted that 80 barrels of caustic solution per hour is recycled from the bottom of settler 16 through lines 23 and 14 to the mixer 13 and thence through the contact coil back to the settler 16. Likewise, about 80 barrels of the caustic solution withdrawn from the second settler 21 are recycled through lines 40 and 19 to the second mixer 18 and thence through the second contact coil 20 to the second settler 21. Twenty barrels of the caustic from settler 16 are passed through lines 25 and 27 to the blow-tank 28 and thence through

lines 35, 38 and 19 to the second treating tank. Twenty barrels of caustic from the second treating tank 21 are passed through lines 42 and 14 to the first treater 13. Briefly, about 80 barrels of caustic are continuously recycled in each of the treating zones while an additional 20 barrels of caustic are withdrawn from the first settler, revived, and passed to the second treating zone while an additional 20 barrels of caustic are recycled from the settling tank of the second zone to the treater of the first zone. Fresh caustic may be added to the system through valved conduit 38a.

It should be understood that the above example, with regard to the amount of caustic solution used and recycled, illustrates one embodiment of our invention. Instead of using one part of the caustic solution in the treating zones for one part of naphtha, the ratio may be 2, 3, 4, 5 or 6 volumes of naphtha for one volume of the caustic solution. When these ratios of caustic to naphtha are used, 50 to 85 volumes of caustic solution may be continuously recycled in each of the treating zones while 50 to 15 volumes of caustic solution may be drawn from the first settling zone, revived, and passed to the second treating zone while and additional 50 to 15 volumes of caustic are recycled from the settling tank of the second zone to the treater of the first zone.

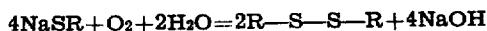
A recording flow-control device 44 which actuates valve 45 may be placed in line 25 in order to control or regulate the proportion of used caustic solution that is withdrawn from the settler 16 and passed to the revivification step. Line 42 may contain a recording flow-control device 46 which actuates valve 47 in line 23, thereby regulating or maintaining the ratio of aqueous caustic solution recycled in the first treating zone to the amount of aqueous caustic solution recycled from the second treating zone to the first treating zone.

Before describing the doctor treatment of the caustic treated naphthas, the reactions effected in the revivification step and the recovery of mercaptans will be described in more detail. The total amount of sulphur in gasolines produced by thermal and catalytic polymerization processes will vary, but in many cases the total sulphur will range from 0.2 to 0.6%, and of this total sulphur content from 50 to 75% usually is in the form of mercaptans. When a polymer gasoline has been stabilized by removing therefrom the hydrocarbons boiling below pentane and a portion of the pentane, the mercaptans remaining in the polymer gasoline will contain three or more carbon atoms each—the methyl and ethyl mercaptans being removed during the stabilization. The mercaptans in the gasolines react with caustic to form mercaptides. However, the reaction between the caustic solution and low molecular weight mercaptans proceeds to a greater degree than the reaction between the higher molecular weight mercaptans and caustic. Consequently, during the caustic treatment of the naphtha in the first zone which may consist of mixer 13, contact coil 15 and settling tank 16, a very substantial part of the low molecular weight mercaptans are converted into mercaptides before an appreciable amount of the high molecular weight mercaptans and other sulphur compounds have reacted with the caustic. Consequently, the caustic solution which is withdrawn from the bottom of the first caustic settler 16 and passed to the blow-tank 28, will contain a very substan-

tial proportion of the low molecular weight mercaptides. In particular, the mercaptides in the used caustic solution withdrawn from settler 16 through line 25 are mostly sodium isopropyl mercaptide ( $C_3H_7SNa$ ) and sodium secondary butyl mercaptide ( $C_4H_9SNa$ ). Small amounts of other sodium alkyl mercaptides are also present, namely, the mercaptides having 2, 3, 4, and 5 carbon atoms each.

By treating the used caustic solution with steam and maintaining the temperature of the caustic solution undergoing revivification at approximately 215–235° F. the mercaptides are converted into mercaptans and the caustic solution is thereby regenerated. The reaction effected with steam may be represented by the following equation:  $RSNa + H_2O = RSH + NaOH$ . The uncondensed steam and mercaptans withdrawn from the top of the blow-tank 28 through line 34 and valved line 47, pass to the condenser 48 and then are introduced into the settling tank or separator 49. The mercaptans may then be drawn off from the top part of the separator through valved conduit 50 and the water is withdrawn through valved conduit 51. In the treatment of a partly depentanized polymerized end-point gasoline, produced by catalytic polymerization of unsaturated normally gaseous hydrocarbons, the mercaptans recovered through line 50 were about 70% iso-propyl mercaptan and 17% secondary butyl mercaptan.

When air is used to revivify the used caustic solution in blow-tank 28, at temperatures ranging from 195 to 212° F. the mercaptans are partially oxidized to di-sulphides as represented by the following reaction.



A part of the low molecular weight di-sulphides are vaporized during the regeneration step and may be vented through valved conduit 52 or recovered in the settling tank 49 as described above in connection with the mercaptans. The di-sulphides that remain in the revivified caustic will be picked up by the naphtha undergoing treatment when the revivified caustic is returned to the second treating zone. To avoid this result, we prefer to place a settler in line 38 for the removal of the di-sulphides. Since the high molecular weight di-sulphides are insoluble in caustic, we prefer to use a horizontal settler having an inlet near the middle, an outlet at the bottom and a valved outlet at the top to draw off the di-sulphides.

When steam alone is used to regenerate the used caustic solution, precaution should be taken to keep dissolved air out of the gasoline so that the mercaptides will not be oxidized to di-sulphides.

The caustic treated gasoline in the second settler 21 is withdrawn through line 53 and passed to the mixer 54 where it is contacted with doctor solution that enters the mixer 54 through line 55. A small part of the naphtha in line 53 may be by-passed through sulphur pot 56. The mixture of naphtha and doctor solution in mixer 54 is passed through the contact coils 57 to the doctor treater 58. The doctor solution that settles to the bottom of treater 58 is withdrawn through valved conduit 59 and forced by pump 60 through line 61 to the inlet side of mixer 54. The thus treated naphtha is withdrawn from the top of treater 58 through line 61 and passed to the mixer 61a where it is contacted with an additional amount of doctor introduced therein through

valved line 62. The admixture of naphtha and doctor solution withdrawn from the second mixer 61a is divided into two streams, and one is passed through valved conduit 63 to the settling tank 64 and the second portion is passed through valved conduit 65 to the settling tank 66. The sweetened gasoline or naphtha is withdrawn from the two settling tanks through lines 67 and 68 respectively, and passed to the storage tank 69. If desired, the sweetened naphtha in tank 69 may be re-run to any desired end-point.

The doctor solution withdrawn from the bottom of settling tanks 64 and 66 are withdrawn through valved conduits 70 and 71 respectively and recycled by pump 72 through line 73 to either the mixer 61a or the mixer 54. If desired, a portion of the doctor solution in line 73 may be recycled to mixer 61a and the remainder recycled to mixer 54. Fresh doctor solution is added to the system through valve conduit 74.

The doctor solution used to sweeten the caustic treated naphtha is an aqueous solution of sodium plumbite. Usually, this doctor solution is prepared by dissolving from 4 to 8% of litharge in a 10 to 20% aqueous solution of sodium hydroxide.

By using the two caustic treating steps in combination with the revivification of part of the caustic solution, before treating with doctor solution, we effect a substantial saving in the amount of doctor solution that normally would be required to sweeten high sulphur gasolines or naphthas. Our particular process of treating the gasoline or naphtha with caustic coupled with the regeneration of a part of the caustic solution results in the removal of a substantial amount of the sulphur in the naphtha without the loss of appreciable amounts of caustic. In carrying out our processes with one end-point polymerized gasoline having a copper number of about 125, it was found that the copper number of the naphtha leaving settler 16 was about 35, and that the copper number of the gasoline leaving settler 21 was about 20. In general, if the copper number of the naphtha entering the sweetening plant through line 11 is within the range of 120–225, the naphtha leaving the settler at 16 will have a copper number within the range of 25–50 and the naphtha leaving the settler 21 will have a copper number within the range of 15–30. The copper number represents the milligrams of mercaptan sulphur per 100 cc. of gasoline. The multi-stage caustic treating steps make it possible to maintain a maximum sodium ion concentration during the caustic treatment and thereby greatly enhance the effectiveness and efficiency of our process.

Although our preferred process utilizes two caustic treating zones in series, three or more such zones may be employed. For example, a third intermediate treating zone consisting of a mixer, contact coil, and settler similar to those hereinbefore described may be inserted between the first and second treating zones. In this case, a portion of the caustic solution from settler 21 of the second treating zone will be introduced into the naphtha entering the intermediate treating zone, a portion of the caustic solution from the settler of the intermediate zone will be recycled to the same point, and the remaining portion of the caustic solution from the intermediate zone will be introduced into the naphtha entering the first treating zone together with the recycled caustic solution passing through line 23.

Other forms of caustic treating zones than that previously described may be employed. For ex-

ample, each treating zone may consist of a conventional countercurrent tower having a settling zone at the top from which treated naphtha is removed, and a settling zone at the bottom from which caustic solution containing mercaptides is withdrawn.

As herein stated, we prefer to caustic wash and sweeten  $H_2S$ -free end-point gasoline. However, we may first caustic wash and sweeten a naphtha and then rerun it to any desired end-point. When a naphtha has been rerun before treatment by our process, practically no  $H_2S$  will be present in the naphtha because it is generally removed during the rerunning operation. If  $H_2S$  is present in the naphtha or gasoline to be treated by our process, it may be first given an extraction with caustic or sodium carbonate in order to remove the hydrogen sulphide.

By using an  $H_2S$  free gasoline or naphtha which has been partly depentanized, we can recover a fraction of mercaptans from the overhead from blow tank 29 which consists almost entirely of iso propyl mercaptan and secondary butyl mercaptan.

The foregoing is a full and complete description of our invention, but it should be understood that we are not limited to the specific examples described therein except as defined by the following claims.

We claim:

1. In the process of refining a petroleum naphtha containing substantial quantities of mercaptans but substantially no hydrogen sulphide by contacting with aqueous caustic solution in a series of treating zones, the steps comprising removing the caustic solution from each treating zone, returning a portion of said caustic solution to the treating zone from which it was removed, introducing the remaining portion of said caustic solution from the second and succeeding treating zones into the treating zone preceding that from which it was removed, revivifying the remaining portion of said caustic solution from the first treating zone, and introducing the revived caustic solution into the last treating zone.

2. In the process of refining a petroleum naphtha containing substantial quantities of mercaptans but substantially no hydrogen sulphide by contacting with aqueous caustic solution in a series of treating zones, the steps comprising removing the caustic solution from each treating zone, returning a relatively large portion of said caustic solution to the treating zone from which it was removed, introducing the remaining relatively small portion of said caustic solution from the second and succeeding treating zones into the treating zone preceding that from which it was removed, revivifying the remaining relatively small portion of said caustic solution from the first treating zone, and introducing the revived caustic solution into the last treating zone.

3. In the process of refining a petroleum naphtha containing substantial quantities of mercaptans but substantially no hydrogen sulphide by contacting with aqueous caustic solution in a series of treating zones, the steps comprising removing the caustic solution from each treating zone, returning from 50 to 85 per cent of said caustic solution to the treating zone from which it was removed, introducing the remaining 50 to 15 percent of said caustic solution from the second and succeeding treating zones into the treating zone preceding that from which it was removed, revivifying the remaining 50 to 15 per-

cent of said caustic solution from the first treating zone, and introducing the revived caustic solution into the last treating zone.

4. The process of refining a petroleum naphtha containing substantial quantities of mercaptans but substantially no hydrogen sulphide comprising contacting said naphtha with aqueous caustic solution in a series of treating zones, removing the caustic solution containing mercaptides from each treating zone, returning a portion of said caustic solution to the treating zone from which it was removed, introducing the remaining portion of said caustic solution from the second and succeeding treating zones into the treating zone preceding that from which it was removed, treating the remaining portion of said caustic solution from the first treating zone to decompose the mercaptides therein, introducing the substantially mercaptide-free caustic solution into the last treating zone, and sweetening the treated naphtha from the last treating zone by contacting with doctor solution.

5. The process of refining a petroleum naphtha containing substantial quantities of mercaptans but substantially no hydrogen sulphide comprising contacting said naphtha with aqueous caustic solution in two serially operated treating zones, removing the caustic solution from each treating zone, returning a portion of said caustic solution to the treating zone from which it was removed, introducing the remaining portion of said caustic solution from the second treating zone into the first treating zone, revivifying the remaining portion of said caustic solution from the first treating zone, and introducing the revived caustic solution into the second treating zone.

6. The process of refining a petroleum naphtha containing substantial quantities of mercaptans but substantially no hydrogen sulphide comprising contacting said naphtha with aqueous caustic solution in two serially operated treating zones, removing the caustic solution from each treating zone, returning a relatively large portion of said caustic solution to the treating zone from which it was removed, introducing the remaining relatively small portion of said caustic solution from the second treating zone into the first treating zone, revivifying the remaining relatively small portion of the caustic solution from the first treating zone, and introducing the revived caustic solution into the second treating zone.

7. The process of refining a petroleum naphtha containing substantial quantities of mercaptans but substantially no hydrogen sulphide comprising contacting said naphtha with aqueous caustic solution in two serially operated treating zones, removing the caustic solution from each treating zone, returning from 50 to 85 percent of said caustic solution to the treating zone from which it was removed, introducing the remaining 50 to 15 percent of said caustic solution from the second treating zone into the first treating zone, revivifying the remaining 50 to 15 percent of said caustic solution from the first treating zone, and introducing the revived caustic solution into the second treating zone.

8. The process of refining a petroleum naphtha containing substantial quantities of mercaptans but substantially no hydrogen sulphide comprising contacting said naphtha with aqueous caustic solution in two serially operated treating zones, removing the caustic solution from each treating zone, returning a relatively large

portion of said caustic solution to the treating zone from which it was removed, introducing the remaining relatively small portion of said caustic solution from the second treating zone into the first treating zone, revivifying the remaining relatively small portion of said caustic solution from the first treating zone, introducing the revivified caustic solution into the second treating zone, and sweetening the treated naphtha from the second treating zone by contacting with doctor solution.

9. The process of refining a polymerized gasoline containing substantial quantities of mercaptans but substantially no hydrogen sulphide comprising contacting said gasoline with aqueous caustic solution in two serially operated treating zones, removing caustic solution containing mercaptides from each treating zone, returning a relatively large portion of said caustic solution to the treating zone from which it was removed, introducing the remaining relatively small portion of said caustic solution from the second treating zone into the first treating zone, blowing the remaining relatively small portion of said caustic solution from the first treating zone at an elevated temperature with air to decompose the mercaptides therein, introducing the substantially mercaptide-free caustic solution into the second treating zone, and sweetening the treated gasoline from the second treating zone by contacting with doctor solution.

10. The process of refining a polymerized gasoline containing substantial quantities of mercaptans but substantially no hydrogen sulphide comprising contacting said gasoline with aqueous caustic solution in two serially operated treating zones, removing caustic solution containing mercaptides from each treating zone, returning a relatively large portion of said caustic solution to the treating zone from which it was removed, introducing the remaining relatively small portion of said caustic solution from the second treating zone into the first treating zone, contacting the remaining relatively small portion of said caustic solution from the first treating zone at an elevated temperature with steam to convert the mercaptides therein into mercaptans and caustic and simultaneously remove the mercaptans from the caustic solution, introducing the revivified caustic solution into the second treating zone, and sweetening the treated gasoline from the second treating zone by contacting with doctor solution.

11. The process of refining a partly depentanized polymerized gasoline containing substantial quantities of mercaptans but substantially no hydrogen sulphide comprising contacting said gasoline with aqueous caustic solution in two serially operated treating zones, removing caustic solution containing mercaptides from each treating zone, returning a relatively large portion of said caustic solution to the treating zone from which it was removed, introducing the remaining relatively small portion of said caustic solution from the second treating zone into the first treating zone, contacting the remaining relatively small portion of said caustic solution from the first treating zone at an elevated temperature with steam to convert the mercaptides therein into mercaptans and caustic and simultaneously to vaporize the mercaptans formed, recovering from the resulting vapors a mixture of mercaptans consisting substantially of isopropyl and secondary butyl mercaptans, introducing the revivified caustic solution into the second treating zone, and

sweetening the treated gasoline from the second treating zone by contacting with doctor solution.

12. The process of refining a partly depentanized polymerized gasoline which contains substantial quantities of mercaptans but substantially no hydrogen sulphide comprising contacting said gasoline with an aqueous caustic solution having a caustic concentration of 10 percent to 30 percent in a first treating zone and then with an aqueous caustic solution having a caustic concentration of 15 percent to 35 percent in a second treating zone, removing caustic solution containing mercaptides from each treating zone, returning approximately 80 percent of said caustic solution to the treating zone from which it was removed, introducing approximately 20 percent of said caustic solution from the second treating zone into the first treating zone, contacting approximately 20 percent of said caustic solution from the first treating zone at a temperature of 215° to 235° F. with steam to convert the mercaptides therein into mercaptans and caustic and simultaneously to vaporize the mercaptans formed, condensing the resulting vapors, recovering from the condensate a mixture consisting substantially of isopropyl and secondary butyl mercaptans, introducing the revivified caustic solution into the second treating zone, and sweetening the treated gasoline from the second treating zone by contacting with doctor solution.

13. In the process of refining a petroleum naphtha containing substantial quantities of mercaptans but substantially no hydrogen sulphide, the steps comprising contacting said naphtha with an aqueous caustic solution in two serially operated treating zones, removing caustic solution containing mercaptides from each treating zone, returning a relatively large portion of said caustic solution to the treating zone from which it was removed, introducing the remaining relatively small portion of said caustic solution from the second treating zone into the first treating zone, contacting the remaining relatively small portion of said caustic solution from the first treating zone at an elevated temperature with steam and air to convert the mercaptides therein into alkyl disulphides and caustic and simultaneously vaporize the alkyl disulphides thus formed, recovering from the resulting vapors an admixture of alkyl disulphides, and introducing the revivified caustic solution to the second treating zone in an amount which corresponds to the portion of caustic solution passed from the second treating zone into the first treating zone.

14. In the process of refining petroleum naphtha containing substantial quantities of mercaptans but substantially no hydrogen sulphide, the steps comprising contacting the naphtha and aqueous caustic solution in a plurality of serially operated treating zones, passing both the treated naphtha and aqueous caustic solution from each treating zone into separate settling zones wherein the used aqueous caustic solution is separated from the naphtha, returning a portion of said used aqueous caustic solution to the treating zone from which it was removed, introducing the remaining portion of said used aqueous caustic solution in the second and each succeeding settling zone into the treating zone preceding that from which it was removed, revivifying the remaining portion of said used aqueous caustic solution from the first settling zone, and introducing the revivified aqueous caustic solution into the last treating zone.

15. In a concurrent-countercurrent process of refining petroleum naphtha containing substantial quantities of mercaptans but substantially no hydrogen sulphide, the steps comprising concurrently contacting said naphtha and aqueous caustic solution in two serially operated treating zones, passing both the treated naphtha and aqueous caustic solution from each treating zone into separate settling zones wherein the used aqueous caustic solution is separated from the treated naphtha, returning a substantial portion of the used aqueous caustic solution in each separating zone to the treating zone from which it was removed, introducing the remaining portion of the used aqueous caustic solution from the second settling zone into the first treating zone, revivifying the remaining portion of the used aqueous caustic solution from the first settling zone, and introducing the revivified aqueous caustic solution into the second treating zone for further treatment of the naphtha therein.

16. In a concurrent-countercurrent process of refining petroleum naphtha containing substantial quantities of mercaptans but substantially no hydrogen sulphide, the steps comprising concurrently contacting said naphtha and aqueous caustic solution in a plurality of serially operated treating zones, passing both the treated naphtha and aqueous caustic solution from each treating zone into separate settling zones wherein the used aqueous caustic solution is separated from the treated naphtha, returning a portion of said used aqueous caustic solution to the treating zone from which it was removed, introducing the remaining portion of said used aqueous caustic solution in the second and each succeeding settling zone into the treating zone preceding that from

which it was removed, revivifying the remaining portion of said used aqueous caustic solution from the first settling zone, and introducing the revivified aqueous caustic solution into the last treating zone.

17. In a concurrent-countercurrent process of treating petroleum naphtha containing substantial quantities of mercaptans but substantially no hydrogen sulphide, the steps comprising concurrently contacting the naphtha and aqueous caustic solution in two serially operated treating zones, passing both the treated naphtha and aqueous caustic solution containing mercaptides from each treating zone into separate settling zones wherein the used aqueous caustic solution containing mercaptides is separated from the treated naphtha, returning from 50 to 85% of said used aqueous caustic solution in each separating zone to the treating zone from which it was removed, introducing the remaining 50 to 15% of said used aqueous caustic solution from the second settling zone into the first treating zone, contacting the remaining 50 to 15% of used aqueous caustic solution containing mercaptides from the first settling zone at an elevated temperature with steam and air sufficient to convert the mercaptides therein into alkyl disulphides and caustic and simultaneously vaporizing the alkyl disulphides thus formed, recovering from the resulting vapors an admixture of alkyl disulphides, and introducing revivified caustic solution to the second treating zone in an amount which corresponds to the portion of used aqueous caustic solution passed from the second settling zone to the first treating zone.

THOMAS HUNTON ROGERS.  
BERNARD HARVEY SHOEMAKER.

# CERTIFICATE OF CORRECTION.

Patent No. 2,164,665.

July 4, 1939.

THOMAS HUNTON ROGERS, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 27, for "and" read an; page 3, first column, line 30, for "70%" read 79%; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 8th day of August, A. D. 1939.

(Seal)

Leslie Frazer,  
Acting Commissioner of Patents.

15. In a concurrent-countercurrent process of refining petroleum naphtha containing substantial quantities of mercaptans but substantially no hydrogen sulphide, the steps comprising concurrently contacting said naphtha and aqueous caustic solution in two serially operated treating zones, passing both the treated naphtha and aqueous caustic solution from each treating zone into separate settling zones wherein the used aqueous caustic solution is separated from the treated naphtha, returning a substantial portion of the used aqueous caustic solution in each separating zone to the treating zone from which it was removed, introducing the remaining portion of the used aqueous caustic solution from the second settling zone into the first treating zone, revivifying the remaining portion of the used aqueous caustic solution from the first settling zone, and introducing the revivified aqueous caustic solution into the second treating zone for further treatment of the naphtha therein.

16. In a concurrent-countercurrent process of refining petroleum naphtha containing substantial quantities of mercaptans but substantially no hydrogen sulphide, the steps comprising concurrently contacting said naphtha and aqueous caustic solution in a plurality of serially operated treating zones, passing both the treated naphtha and aqueous caustic solution from each treating zone into separate settling zones wherein the used aqueous caustic solution is separated from the treated naphtha, returning a portion of said used aqueous caustic solution to the treating zone from which it was removed, introducing the remaining portion of said used aqueous caustic solution in the second and each succeeding settling zone into the treating zone preceding that from

which it was removed, revivifying the remaining portion of said used aqueous caustic solution from the first settling zone, and introducing the revivified aqueous caustic solution into the last treating zone.

17. In a concurrent-countercurrent process of treating petroleum naphtha containing substantial quantities of mercaptans but substantially no hydrogen sulphide, the steps comprising concurrently contacting the naphtha and aqueous caustic solution in two serially operated treating zones, passing both the treated naphtha and aqueous caustic solution containing mercaptides from each treating zone into separate settling zones wherein the used aqueous caustic solution containing mercaptides is separated from the treated naphtha, returning from 50 to 85% of said used aqueous caustic solution in each separating zone to the treating zone from which it was removed, introducing the remaining 50 to 15% of said used aqueous caustic solution from the second settling zone into the first treating zone, contacting the remaining 50 to 15% of used aqueous caustic solution containing mercaptides from the first settling zone at an elevated temperature with steam and air sufficient to convert the mercaptides therein into alkyl disulphides and caustic and simultaneously vaporizing the alkyl disulphides thus formed, recovering from the resulting vapors an admixture of alkyl disulphides, and introducing revivified caustic solution to the second treating zone in an amount which corresponds to the portion of used aqueous caustic solution passed from the second settling zone to the first treating zone.

THOMAS HUNTON ROGERS.  
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# CERTIFICATE OF CORRECTION.

Patent No. 2,164,665.

July 4, 1939.

THOMAS HUNTON ROGERS, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 27, for "and" read an; page 3, first column, line 30, for "70%" read 79%; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 8th day of August, A. D. 1939.

(Seal)

Leslie Frazer,  
Acting Commissioner of Patents.