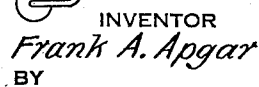


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PROCESS FOR REFINING OILS

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PROCESS FOR REFINING OILS

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6 Claims. (Cl. 196—29)

This invention relates to the refining of petroleum oils and more particularly to an improved process for the refining of petroleum distillates, such as gasoline, containing undesirable sulfur compounds, such as mercaptans.

The presence of mercaptans in gasoline was early recognized as objectionable because of their offensive odor and corrosive nature. Petroleum distillates containing such objectionable sulfur compounds are known as "sour" distillates and the process of freeing sour distillates of these sulfur compounds is known as "sweetening." The sweetening of these sour petroleum distillates has been the object of a multitude of proposed processes.

For many years, the so-called "doctor treatment" has been generally regarded as the most efficient method of sweetening such distillates. In the conventional doctor treatment, the sour distillate has been subjected to prolonged intimate contact with an aqueous solution of caustic soda and litharge (sodium plumbite), so-called "doctor solution," at or near atmospheric temperature. A typical doctor solution is one produced by admixing 125 pounds of caustic soda, 70 pounds of litharge and 125 gallons of water. The amount of this solution added to the oil is usually pre-determined by tests in which additional doses are added to a sample of the distillate until it does not further darken. Almost invariably elemental sulfur has been finally added to the distillate to complete the doctor "break." In such operation, care must be taken to avoid adding excess sulfur as the presence of sulfur renders the finished distillate corrosive.

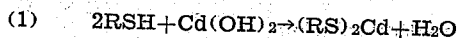
Though the doctor treatment is generally effective in sweetening sour distillates, it has been found to have disadvantages with respect to the refining of modern gasoline motor fuels. Specifically, gasoline so sweetened has been found to be impaired as to its anti-knock properties, as to its susceptibility to improvement of its anti-knock values by the addition of tetraethyl lead, hereinafter referred to as T. E. L., and as to its susceptibility to the action of oxidation inhibitors of the type frequently added to improve stability in storage. Particularly in present-day motor fuel, anti-knock properties and susceptibility to improvement thereof by the addition of T. E. L., are of major importance and it is an object of the present invention to provide a process whereby one may economically effect the sweetening of the gasoline without impairment thereof. This object and other advantages, as

subsequently appear herein, are attained by my improved process.

The process of my present invention consists primarily of two major steps or stages. In the first stage of the treatment the distillate is brought into intimate contact with an aqueous suspension of cadmium hydroxide at an elevated temperature and with rigid exclusion of air or other oxygen-containing gases. In the second stage, the distillate from the first stage, which has been separated from the major portion of the fouled treating compound, is intimately contacted, also at an elevated temperature, with an oxygen-containing gas such as air.

Advantageously, the cadmium hydroxide is supplied to the first stage of the operation as a suspension in a caustic solution. A caustic soda solution of such concentration as to have a Baumé gravity of from about 10° to about 30° and containing cadmium hydroxide in suspension is satisfactory for this purpose.

In the first stage of the operation, the mercaptans present in the distillate are caused to react with the cadmium hydroxide to form cadmium mercaptides, as indicated by the following equation:



where R represents a hydrocarbon radical.

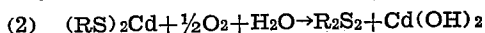
The cadmium mercaptides thus formed are substantially insoluble in hydrocarbons and may be almost completely removed therefrom as by settling.

The amount of cadmium hydroxide supplied to the first stage of my process will depend primarily upon the amount of mercaptans present in the distillate to be sweetened and may be readily calculated from the above Equation 1. An amount of cadmium hydroxide somewhat in excess of the theoretical requirement is usually desirable.

In the first stage of my process, the major portion of the sulfur present in the distillate charged thereto is separated from the partially treated distillate as cadmium mercaptides, which are substantially insoluble in hydrocarbons. However, a minor portion of the mercaptides remain in the distillate. The partially-treated distillate from the first stage of my process is not impaired as to anti-knock properties, stability or susceptibility to improvement of its anti-knock values by the addition of "T. E. L." The major portion of the sulfur has been removed but the distillate is not completely nor sufficiently sweetened, because of traces of mercaptides remain-

ing either in solution or suspended therein. To effect the desired sweetening, it is essential that the residual objectionable sulfur compounds be eliminated from the oil and this is accomplished in the second stage of my process without sacrifice of the advantages obtained by the first stage of the process with respect to other desirable properties.

In the second stage of my process the traces of mercaptides remaining in solution and in suspension in partially-treated distillates are converted to disulfides by intimately contacting the partially treated distillate with air, or the like, at an elevated temperature. The reaction by which the mercaptides are converted to disulfides may be represented by the following equation:



The disulfides formed by this reaction have substantially the same effect upon the octane number of the oil as the mercaptides from which they are formed and thus the improvement in T. E. L. susceptibility obtained by the first stage is retained.

An essential characteristic of my improved process is that each of the operations be carried out at an elevated temperature and under a pressure sufficient to maintain the distillate in the liquid phase. The pressure employed will depend upon the characteristics of the oil being treated and the operating temperature. The temperature of the operation may be varied somewhat but, in order to effect the reaction within a reasonable period of time and to obtain maximum benefits, it is desirable to maintain the temperature of each stage of the treatment within a range of about 180°-260° F.

The use of cadmium hydroxide in the sweetening of sour distillate has previously been proposed in an operation carried out at atmospheric temperatures and pressures and without recognition of the effects of air upon the results obtained. So far as I am aware, such previous proposals have had no commercial significance. Serious difficulties previously encountered included the adequate separation of the mercaptides from the treated distillate and the regeneration of the fouled treating solution.

The process of my present invention is distinguished from such previously proposed operations by a sequence of correlated steps carried out under the herein-described conditions. The desired sweetening of the distillate in conjunction with the desired improvements in anti-knock characteristics, susceptibility to T. E. L. and improvements in gun stability will not result from either of these process steps alone, but these advantages are readily obtained by the correlation of the steps of my process when carried out under the conditions herein described.

I have found that these advantages are not obtained when air, or other oxygen-containing gases, is present in the first stage of the treatment. Accordingly, a further essential of my improved process is the rigid exclusion of air from the first stage of the operation.

A further aspect of my present invention is the regeneration of the fouled treating solution or suspension separated from the first stage of the operation. Cadmium hydroxide is relatively expensive and, accordingly, from a practical aspect, it is essential that it be recovered for repeated use. My present invention provides a unitary process whereby the cadmium in the form of mercaptides, precipitated from the first stage of

the operation, is readily and economically reconverted to cadmium hydroxide which may be returned to the first stage of the operation. The regeneration of the cadmium hydroxide is effected by blowing the fouled treating solution, separated from the first stage of the operation, with air, while maintained at the boiling temperature of the solution. This regeneration may with advantage be carried out at about atmospheric pressure.

The invention further provides an improved process which may with advantage be carried on continuously by the continuous supply of the sour distillate and cadmium hydroxide to the first stage of the operation with the exclusion of air, separation and continuous withdrawal of the partially-treated distillate and fouled treating solution on the first stage, continuously subjecting the partially-treated distillate to treatment with air in the second stage of the operation and the continuous regeneration of the fouled treating solution and return of regenerated cadmium hydroxide to the first stage of the operation.

The invention will be further described and illustrated by reference to the accompanying flow diagram which represents an advantageous method by which the process may be continuously carried on. In this method of operation the raw distillate, which for instance, may be stabilizer or debutanizer bottoms devoid of air and having its temperatures adjusted to about 180°-260° F., is passed to the system through the line 1. Caustic soda solution having cadmium hydroxide suspended therein, and advantageously at approximately the temperature of the distillate, is introduced into the system through the lines 2a and 2, is combined with the raw distillate in line 1 and passes together therewith through the mixer, conventionally indicated at 3. The mixer may with advantage consist of a series of orifice plate mixers whereby the distillate and treating solution are intimately admixed. From the mixer the admixed distillate and treating solution pass through line 4 into the chamber 5 which, on the flow sheet, is designated "1st stage treating tower."

The mixture is preferably introduced into the lower part of the tower at a point spaced from the bottom so as to provide a relatively quiescent zone at the bottom of the tower to facilitate the separation of the distillate from the fouled treating solution. The mixture may be introduced into the tower as indicated or with advantage through a spray head, not shown. Within this tower the distillate is separated from the treating solution by gravity and passes from the top of the tower through the line 6.

In the operation of the first stage treating tower, as just described, the admixed treating solution and sour distillate flow generally concurrently through the tower, the spent treating solution settling out in the bottom of the tower. An alternative arrangement which may be used with advantage is to pass the raw distillate, unmixed with the treating solution, directly into the lower portion of the tower and introduce the treating solution into the upper portion of the tower so that they pass through the tower in intimate contact in a generally countercurrent direction.

This alternative method of operation may be carried out in the apparatus diagrammatically represented in the drawing by closing the valve in line 2 nearest the juncture with line 1 and

passing the treating solution directly into the upper part of the tower through line 2'. With this arrangement, the raw distillate may be bypassed around the mixer 3, through line 4', by the proper adjustment of the valves shown, and from thence directly into the lower portion of the tower through line 4 without previous mixing with the treating solution.

It is desirable to maintain a considerable volume and depth of treating solution within the tower as to insure sufficiently prolonged contact between the treating solution and the distillate passing therethrough. The level of the treating solution may be maintained by means of an automatic level control conventionally indicated on the drawing at 7, the liquid level preferably being maintained near the upper end of the chamber as indicated.

The fouled treating solution, separated from the distillate in the chamber 5, is withdrawn therefrom through line 8 to a regenerating system subsequently described herein.

The above-described treatment of the raw distillate with the cadmium hydroxide suspension constitutes the first stage of my process. Raw distillate passing to this first stage of the process is free from air or oxygen and no air or oxygen is permitted to come in contact with distillate during this stage of the operation. Pressure is maintained on the system sufficient to maintain the distillate in liquid phase and the temperature, concentration of treating solution and ratio of cadmium hydroxide to distillate are maintained as previously indicated. The distillate passing from the upper end of the chamber 5 through line 6 is only partially sweetened and usually contains a minor, though undesirable portion, of mercaptides, particularly cadmium mercaptides.

As this partially-sweetened distillate passes under pressure from the first stage of the operation through line 6 to the second stage of the operation, air is injected into it through line 9. The mixture of distillate and air then passes through the mixer 10, which may with advantage be of the type previously described, and into chamber 11 which, on the flow sheet, is designated "2nd stage settler." The air entering this second stage of the operation will, of course, be under pressure and may be supplied from any convenient source.

As previously noted, the cadmium mercaptides react with the air in the second stage of the operation forming cadmium hydroxide and disulfides. The cadmium hydroxide thus formed and any treating solution entrained from the tower 5 are permitted to settle out from the distillate in the chamber 11 and are discharged therefrom through line 12, controlled by valve 13, and line 14 to the regenerating system subsequently to be described.

The settler 11 is with advantage of such size and shape as to permit adequate settling and separation of the cadmium hydroxide, formed by action of the air, and any entrained treating solution from the distillate, and for this reason it is desirable to maintain a considerable volume of distillate in the settler. In the apparatus represented, the liquid level in the chamber 11 may be observed by means of the gauge glass 15. By observing these precautions, a sweet and substantially clarified distillate may be discharged from the upper portion of the settler 11 through line 16. The distillate thus obtained is doctor sweet, having improved anti-

knock characteristics and susceptibility to T. E. L. and improved stability with respect to gum formation.

As previously indicated, a particularly desirable aspect of the invention is an operation which includes the regeneration of the cadmium hydroxide and its repeated use. In such operation the fouled treating solution withdrawn from the treating tower through lines 8 and 14, and advantageously also the material settled from the distillate in the chamber 11, are passed to a pre-heater 17 wherein the cadmium mercaptide-containing material is heated to its boiling point, as by means of the steam coil shown, and from thence passes through line 18 into the upper portion of the tower 19.

In passing downwardly through the tower, which is advantageously baffled, as shown, the heated fouled solution is intimately contacted with air introduced into the bottom of the tower through line 20. To insure adequate contact between the fouled solution and the air, a substantial body of the liquid is maintained in the tower, the tower being flooded with the fouled solution to a level above that of the entry of line 18 into the tower. This level may be maintained by means of an automatic level control conventionally indicated at 21.

In passing downwardly through the tower in contact with the air, the cadmium mercaptides react with the oxygen of the air to form cadmium hydroxide and disulfides. The disulfides, water vapor and air pass out from the upper end of the tower, as shown in the diagram, and the solution containing the cadmium hydroxide is withdrawn from the bottom of the tower through line 22 to the mixing vessel 23, wherein the cadmium hydroxide is maintained in suspension by agitation with air or the like introduced through line 24, and from which the regenerated treating solution is withdrawn through line 25 and returned to the first stage of the operation by means of pump 26 and lines 27 and 2. Such operation may be carried on continuously with a minimum of attention and only a minor loss of cadmium compounds. Water or caustic solution and cadmium hydroxide, in amounts sufficient to maintain the treating suspension at the desired concentration, may be charged to the mixing vessel 23, continuously or as required, by conventional means not shown on the diagram.

The benefits derived from my improved process will be illustrated by the following specific examples of results of an operation carried out at an operating temperature of 220° F. For comparison, the characteristics of the oil prior to treatment and of the same oil after treatment, in accordance with my present invention, are given. For further comparison, the characteristics of the same oil treated with a sufficient quantity of a standard silver nitrate solution to remove all mercaptans as silver mercaptides are given.

In the following tabulation, the characteristics of the untreated oil are set forth in column 1. In column 2 there are set forth the characteristics of the same oil treated with silver nitrate in the presence of air for a period of 0.25 hour under atmospheric temperature and pressure. In the third column, there are set forth characteristics of the oil after treatment in accordance with my present invention for the same period of time under a pressure of 40 pounds per square inch at a temperature of 220° F., an atmosphere of nitrogen having been used in the first stage of the operation. In the latter operation, the sour

distillate and treating solution were used in proportions of 3:1 by volume. The treating solution was prepared by admixing cadmium chloride with a 25 degree Baumé caustic soda solution in proportions of 5 pounds of CdCl_2 per barrel of solution.

Table I

	1	2	3
Gravity.....°A. P. I.	55.2	55.0	54.9
Reid vapor pressure.....	5.6	5.5	5.5
Mercaptan sulfur.....percent	16.0	0.0	0.0
Sulfur.....do	0.060	0.04	0.043
Iodine value.....	101.0	101.0	101.0
Stability.....minutes	160	190	190
Octane value (Motor method):			
Neat.....	67.9	67.6	67.0
+1 c. c. T. E. L.....	73.5	74.0	73.7
+2 c. c. T. E. L.....	75.7	76.1	76.2
+3 c. c. T. E. L.....	77.1	77.8	78.1
A. S. T. M. distillation:			
I. B. P.....°F.	110	113	108
10% off.....°F.	157	158	154
50% off.....°F.	284	287	284
90% off.....°F.	372	374	373
End point.....	411	408	412
Loss.....percent	2.0	1.5	2.0

In a further test, a sour distillate was treated in accordance with my present invention under conditions identical with those just described except that the operating pressure was 44 pounds per square inch. The characteristics of this distillate before and after treatment are set forth in the following tabulation:

Table II

	Before treatment	After treatment
Gravity.....°A. P. I.	56.3	55.8
Reid vapor pressure.....	6.4	6.1
Mercaptan sulfur.....percent	13.5	0.0
Sulfur.....do	0.057	0.045
Iodine value.....	101.9	101.9
Stability.....minutes		
Octane value (Motor method):		
Neat.....	66.1	67.4
+1 c. c. T. E. L.....	73.7	73.9
+2 c. c. T. E. L.....	76.0	76.5
+3 c. c. T. E. L.....		
A. S. T. M. distillation:		
I. B. P.....°F.	98	96
10% off.....°F.	147	150
50% off.....°F.	279	280
90% off.....°F.	354	352
End point.....	392	390
Loss.....percent	0.3	0.4

The proportion of air used in the second stage of my process may be varied over a considerable range. Sufficient air should be used to convert all of the residual mercaptan sulfur present in the distillate to disulfides. The optimum proportion of air will vary somewhat with other operating conditions but may readily be determined by simple tests. It is usually desirable to use an amount of air considerably in excess of the theoretical requirement but, since there is a tendency for the volatile constituents of the distillate to be carried off by the air, it is desirable to avoid the use of an amount of air in excess of that found necessary for maximum conversion of the mercaptides.

I claim:

1. A process for the treatment of light petroleum distillate containing undesirable sulfur compounds to eliminate the sulfur compounds therefrom comprising intimately contacting the distillate at an elevated temperature and in the absence of oxygen with an aqueous suspension of cadmium hydroxide, separating the distillate from the aqueous suspension and intimately contacting the separated distillate with air while at an elevated temperature, each of said operations

being under sufficient pressure to maintain the distillate in the liquid phase.

2. A process for the treatment of light petroleum distillates containing undesirable sulfur compounds to eliminate said sulfur compounds therefrom comprising intimately contacting the distillate at a temperature of about 180° to 260° F., and in the absence of oxygen with an aqueous suspension of cadmium hydroxide, separating the distillate from the aqueous suspension and intimately contacting the separated distillate with air while at a temperature of about 180° to 260° F., each of said operations being under sufficient pressure to maintain the distillate in the liquid phase.

3. A process for the treatment of light petroleum distillate containing undesirable sulfur compounds to eliminate the sulfur compounds therefrom comprising intimately contacting the distillate at an elevated temperature and in the absence of oxygen with an alkaline aqueous suspension of cadmium hydroxide, separating the distillate from the aqueous suspension and intimately contacting the separated distillate with air while at an elevated temperature, each of said operations being under sufficient pressure to maintain the distillate in the liquid phase.

4. A process for the treatment of light petroleum distillates containing undesirable sulfur compounds to eliminate said sulfur compounds therefrom comprising intimately contacting the distillate at an elevated temperature and in the absence of oxygen with cadmium hydroxide suspended in an aqueous solution of caustic soda of about 10° to 30° Baumé, separating the distillate from the aqueous suspension and intimately contacting the separated distillate with oxygen while at an elevated temperature, each of said operations being under sufficient pressure to maintain the distillate in the liquid phase.

5. A two-stage process for the treatment of light petroleum distillate containing undesirable sulfur compounds to eliminate said sulfur compounds therefrom, comprising, as the first stage, intimately contacting the distillate, at an elevated temperature and in the absence of oxygen, with an aqueous suspension of cadmium hydroxide, separating the partially treated distillate from the fouled aqueous suspension and, as the second stage, intimately contacting the separated distillate from the first stage with air while at an elevated temperature, each of said operations being under sufficient pressure to maintain the distillate in the liquid phase, regenerating the fouled aqueous suspension from the first stage of the operation by blowing with air while being maintained at a temperature approximating its boiling point, whereby cadmium mercaptides formed in the first stage of the operation are reconverted to cadmium hydroxide, and returning the regenerated cadmium hydroxide in aqueous suspension to the first stage of the process.

6. A continuous two-stage process for the treatment of light petroleum distillate containing undesirable sulfur compounds to eliminate said sulfur compounds therefrom comprising, as the first stage, continuously admixing the distillate, at an elevated temperature and in the absence of oxygen, with an aqueous suspension of cadmium hydroxide, continuously separating the partially treated distillate from the fouled aqueous suspension and, as the second stage, continuously and intimately contacting the separated distillate from the first stage, with air while at an ele-

vated temperature, settling the distillate and continuously withdrawing the treated distillate from the settling zone, each of said stages being under sufficient pressure to maintain the distillate in the liquid phase, continuously withdrawing fouled aqueous suspension from the first stage of the operation and passing it to a regenerating zone wherein it is blown with air while being maintained at a temperature approximating its

5 boiling point, whereby cadmium mercaptides formed in the first stage of the operation are reconverted to cadmium hydroxide, and continuously returning the regenerated cadmium hydroxide in aqueous suspension to the first stage of the process and intimately admixed it therein with the distillate charge.

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