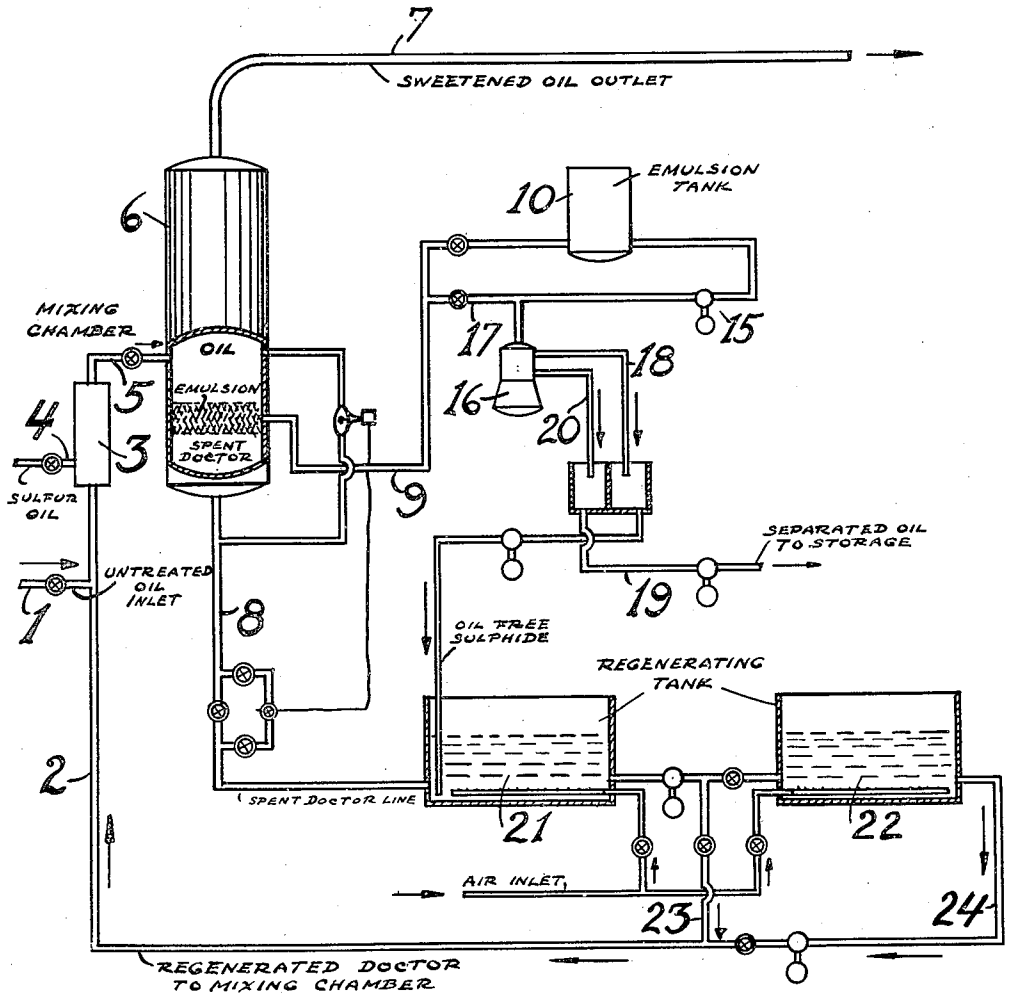
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REFINING OF MINERAL OILS

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REFINING OF MINERAL OILS

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This invention is concerned with the refining of mineral oils. The invention is more particularly concerned with the refining of petroleum oils as, for example, motor fuels and similar products and especially relates to a process and apparatus for treating sulfur-containing oils with sodium plumbite or analogous lead compounds for the purpose of removing objectionable sulfur compounds therefrom. The invention is more particularly directed to an improvement in the so-called "doctor sweetening operation" by which high quality petroleum products are secured and in which material economies in the process are effected. In accordance with the present process, the lead mercaptides are converted to disulfides and lead oxides by utilizing a novel procedure which materially improves the operation and eliminates inherent disadvantages heretofore secured due to the emulsions which form.

Mineral oil distillates, as for example, petroleum oil distillates boiling in the kerosene and motor fuel boiling range contain certain sulfur compounds which impart disagreeable odors to the oils. Various methods have been employed for the removal of these compounds or for the conversion of these disagreeable sulfur compounds to innocuous materials. However, these compounds are usually removed by agitating the oils with an alkali metal plumbite solution such as a sodium plumbite solution which is prepared by dissolving lead oxide in an excess of sodium hydroxide. The petroleum oil and plumbite solution are mixed and a chemical reaction occurs, resulting in the conversion of mercaptans to corresponding lead mercaptides. These mercaptides are then decomposed usually by the addition of free sulfur resulting in the lead being precipitated as an insoluble lead sulfide and in the formation of odorless disulfide compounds. This operation known as "sweetening" may be summarized by the following reactions:

(1) $PbO + 2NaOH \rightarrow Na_2PbO_2 + H_2O$

(2) $2RSH + Na_2PbO_2 \rightarrow Pb(RS)_2 + 2NaOH$

(3) $Pb(RS)_2 + S \rightarrow PbS + RSSR$

This operation, while entirely satisfactory for the conversion of the objectionable sulfur compounds to innocuous disulfides does have certain inherent operating difficulties. For example, the efficiency of the operation, particularly when treating certain types of feed oils, is impaired due to emulsion difficulties. The emulsion is difficult to break and requires a relatively long time period and necessitates the use of emulsion-breaking equipment. In addition, although in many cases the emulsion seems to be satisfactorily broken, the quality of the treated oil is materially impaired and in many cases necessitates a further refining step. Furthermore, the doctor solution contains oil particles which affect subsequent regeneration. Various suggestions have been made for overcoming these inherent difficulties resulting from the fact that undesirable emulsions form. The proposed methods are more or less cumbersome and are not entirely satisfactory from a commercial standpoint. For example, various electrolytic precipitation methods have been suggested which materially increase the overall costs of the operations.

We have now discovered a process by which oils may be treated in the usual manner with an alkali metal plumbite solution and the treated products readily separated from the spent solution in a continuous and efficient operation. Our invention comprises passing the oil solution and the added doctor solution, as well as the added sulfur into a settling zone, from the top of which treated oil free from undesirable sulfur constituents is withdrawn. In accordance with our process there is withdrawn from an intermediate point in the settling zone, a stream comprising the emulsion. This stream is passed through an emulsion-breaking zone and handled in a manner to completely separate the spent doctor from the separated oil. The spent doctor solution removed from this stream is combined with the total volume of spent doctor solution which is withdrawn from the bottom of the separation zone while the oil is combined with the oil removed overhead from the separation zone.

The process of our invention may be readily understood by reference to the attached drawing illustrating one modification of the same. For purposes of description, the feed oil is taken to be a mercaptan containing petroleum cracked naphtha boiling in the motor fuel boiling range. The sour feed oil containing the mercaptans is introduced into the system by means of feed line 1. An alkali metal plumbite solution, which for the purposes of description is assumed to be a sodium plumbite solution, is combined with the untreated oil by means of line 2 and the mixture passed into mixing chamber 3. An oil solution of sulfur is introduced into mixing chamber 3 by means of line 4. This mixture is withdrawn from mixing chamber 3 by means of line 5 and passed into settling zone 6 in which an oil phase forms which rises to the top of settling zone 6. A spent doctor phase forms in the bottom of settling zone 6 while the emulsion layer forms at the interface between the oil and the spent doctor. In accordance with our operation, the treated oil is withdrawn from settling zone 6 by means of line 7 and the spent doctor solution phase withdrawn by means of line 8. The emulsion phase is withdrawn from settling zone 6 by means of line 9 and passed into emulsion storage tank 10 from which it is withdrawn by means of pump 15 and passed into demulsification zone 16 which comprises any suitable de-

mulsification means. It is to be understood that the emulsion phase withdrawn by means of line 9 may be passed directly to demulsification zone 16 by means of line 17. The separated oil is removed from demulsification zone 16 by means of line 20 and withdrawn from the system by means of line 19. The separated spent doctor solution is withdrawn from demulsification zone 16 by means of line 18 and passed to doctor solution regeneration zone 21 along with the spent doctor solution removed from settling zone 6 by means of line 8. The spent doctor regeneration zone may comprise a single unit 21 or any other number and arrangement of units. For the purpose of description, it is assumed that the regeneration zone comprises units 21 and 22 which may be operated in series or parallel. The regenerated doctor solution is preferably recycled to the treating zone by means of lines 23 and 24.

The process of the present invention may be widely varied. Although elevated temperatures and pressures may be employed, it is preferred to contact the motor fuel and the doctor solution at ordinary temperatures and pressures. In accordance with a preferred modification of the invention, an automatic liquid level controller is maintained on the settling tower which controls the withdrawal rate of the spent doctor solution. The emulsion which forms at the interface of the oil and spent doctor solution is withdrawn continuously and passed either directly or by way of an intermediate storage tank to demulsifying zone wherein the oil and spent doctor solution are separated. The oil free of objectionable sulfur compounds and spent doctor solution is removed continuously and the separated doctor solution is removed continuously and the separated doctor solution regenerated.

In order to illustrate the invention further, the following example is given which should not be construed as limiting the same in any manner whatsoever.

Example

Various operations were conducted in which a feed oil was handled in a conventional manner and in which a similar feed oil was treated with a doctor solution in accordance with the present process. The results of these operations with respect to the inspection of the feed oil were as follows:

	Continuous withdrawal and separation	Conventional withdrawal and separation
Color	Light yellow	Deep red.
Gum—cu. dish with no inhib	26	316.
Sulfur	.15	.5.
Octane No	61.0	57.0.

From the above it is apparent that the quality of the feed oil is greatly improved over that secured when using a conventional method with respect to color, gum, stability, sulfur content and octane number.

Furthermore, when employing the present process, the capacity of the doctor settler of the continuous sweetening system is increased since the emulsion is not allowed to build up in the tower. This results in less sulfide carry-over from the settler. Furthermore, no oil reaches the doctor regeneration tanks since the spent doctor is free of oil and the oil in the emulsion is thoroughly separated. This eliminates the fire hazard present when blowing the spent doctor with air for the regeneration of the same. An improved sweetening operation is obtained since the spent doctor solution and the sulfide are withdrawn continuously to the regeneration system. This results in a constant quality regenerated doctor solution which permits a better controlled sweetening operation.

What we claim as new and wish to cover by Letters Patent is as follows:

1. Continuous process of refining petroleum oils containing mercaptans by doctor treating, which comprises continuously mixing a feed petroleum oil containing mercaptans with an alkali metal plumbite solution under conditions to convert said mercaptans into lead mercaptides, and with a sufficient amount of sulfur to convert said lead mercaptides to lead sulfide and alkyl disulfide, whereby an emulsion forms during said mixing, continuously passing the resulting mixture into a settling zone where said mixture separates continuously into three layers, an upper oil layer, a middle emulsion layer and a lower spent plumbite layer, and continuously removing each of said three layers separately directly from said settling zone.

2. Process according to claim 1 in which the removed spent plumbite solution is regenerated and recycled for further doctor treating.

3. Process according to claim 1 in which the removed emulsion layer is broken into an oil phase and a spent plumbite phase and then later is regenerated and recycled for further doctor treating.

4. Continuous process for doctor sweetening of a cracked petroleum oil of the motor fuel boiling range, which comprises continuously mixing said petroleum oil with a sodium plumbite solution under conditions to convert mercaptans to corresponding lead mercaptides, and with an amount of sulfur sufficient to convert the resulting lead mercaptide to lead sulfide and alkyl disulfide, whereupon an emulsion forms during said mixing, continuously passing the resulting mixture into a vertical tower settling zone where said mixture separates continuously into three layers, an upper cracked petroleum layer, substantially completely free of mercaptans, a middle emulsion layer containing a relatively small proportion of the original feed oil, some of the spent plumbite solution and some finely divided precipitated lead sulfide, and a lower spent sodium plumbite solution layer substantially completely free of oil constituents, continuously removing each of said three materials separately directly from said settling zone, said upper sweetened oil layer being removed overhead, said middle emulsion layer being removed from a point in the tower intermediate between the upper oil layer and the lower spent plumbite layer, said emulsion layer being de-emulsified into an oil phase and into a spent plumbite phase containing oil-free lead sulfide, and passing said de-emulsified spent plumbite phase to a plumbite regeneration zone, also removing from the bottom of the tower settling zone the lower layer consisting of spent plumbite solution, passing it also to the plumbite regeneration zone, regenerating the spent plumbite solution in said regeneration zone by airblowing and recycling the resultant regenerated sodium plumbite solution for further doctor sweetening of feed oil.

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