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A. J. SHMIDL ET AL

2,356,704

REFINING OF MINERAL OILS

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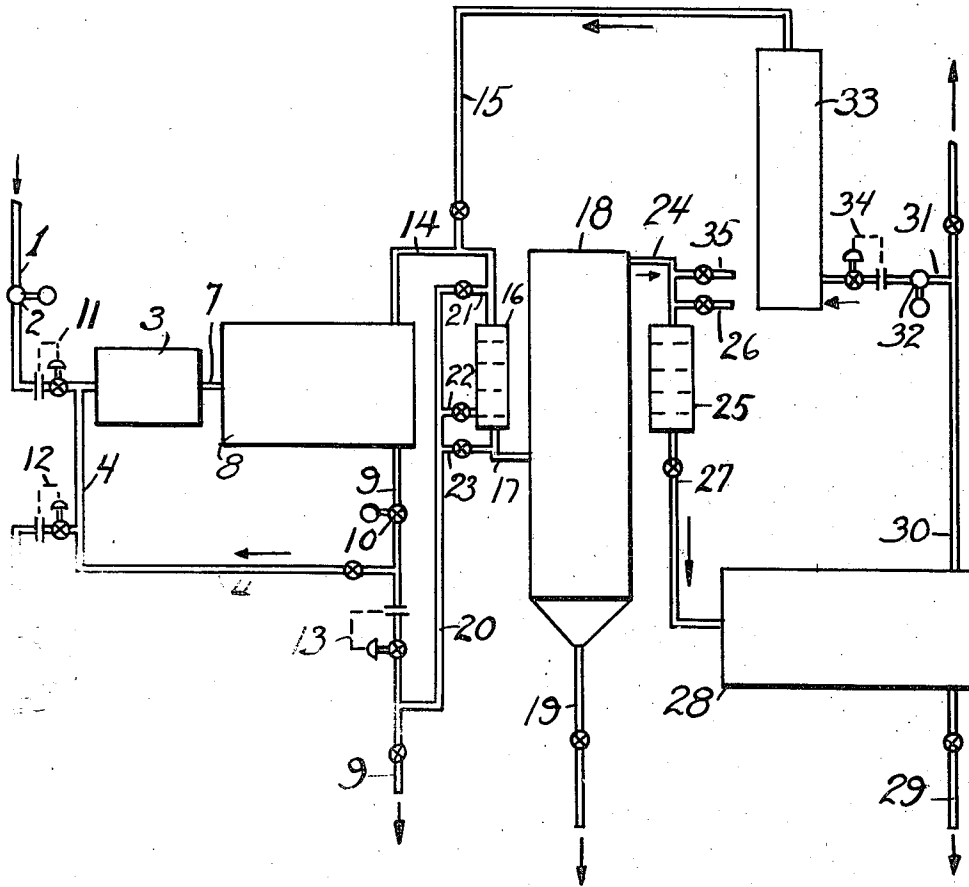


FIG.-1

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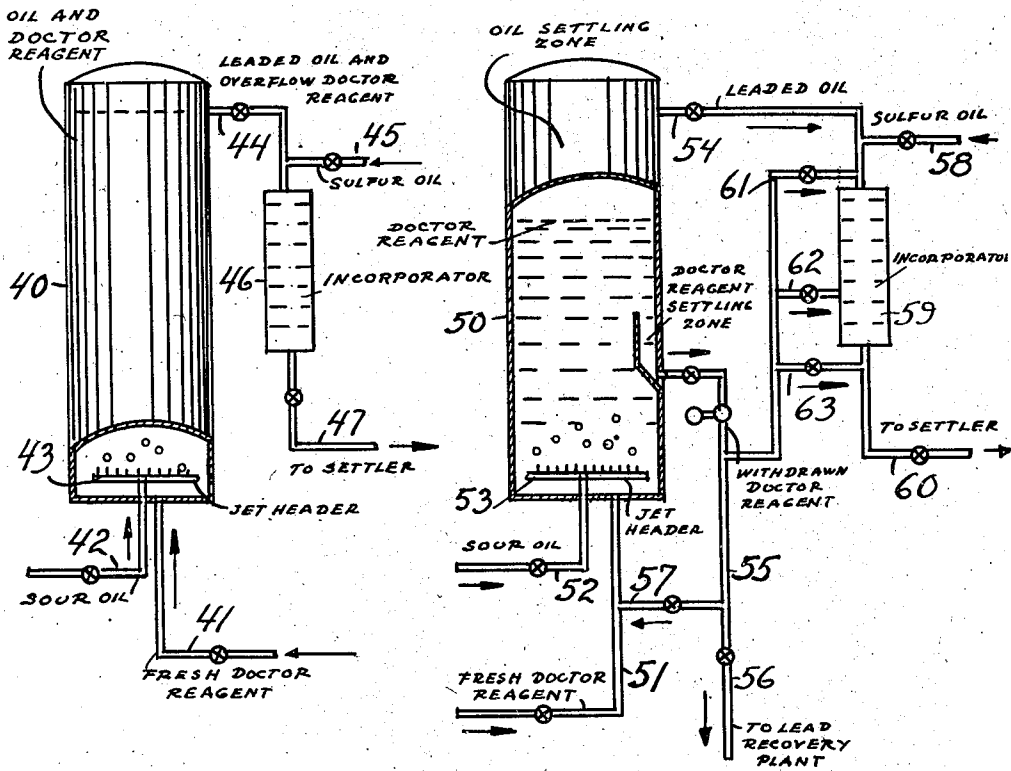
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2 Sheets-Sheet 2

FIG.-2

FIG.-3



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REFINING OF MINERAL OILS

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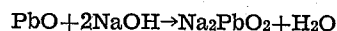
12 Claims. (Cl. 196—33)

The present invention is concerned with the refining of mineral oils. The invention more particularly relates to the removal of undesirable sulfur compounds from petroleum oils and is especially concerned with an improvement in the sweetening operation in which mercaptan compounds are converted to innocuous disulfides by treatment with an alkali metal plumbite solution and free sulfur. The invention is particularly adapted for utilization in a treating process in which the so-called "doctor solution" comprising a sodium plumbite solution is used. In accordance with the present process the treating operation is controlled in a manner that basic lead mercaptides are formed under conditions to yield a finished product of improved quality.

It is known in the art to treat mercaptan-containing mineral oils, particularly mercaptan-containing (relatively low-boiling) petroleum oils (distillates) in various processes in order to remove the mercaptan compounds or to convert them into relatively harmless disulfides. This is necessary since the mercaptan materials render the oil sour and make it undesirable for commercial use. The usual method employed in the treatment of petroleum oils, particularly in the treatment of petroleum oils boiling in the motor fuel boiling range, is to contact the oil under suitable conditions with the so-called "doctor solution" comprising a sodium plumbite solution. The sodium plumbite solution is prepared by dissolving litharge or soluble lead salts in an aqueous sodium hydroxide solution. The sodium plumbite reacts with the mercaptan to form oil-soluble lead mercaptides. These lead mercaptides are then converted to harmless oil-soluble alkyl disulfides and the lead removed from the treated oil as precipitated lead sulfides by treatment usually with free sulfur. In this operation, in order to secure a high quality product, it is very desirable that the soluble lead compounds be entirely removed. This may be readily accomplished by the addition of a slight excess of free sulfur. However, the use of free sulfur, even in relatively small amounts, is not desirable since it increases the corrosive-sulfur content of the treated motor fuel and, furthermore, impairs the susceptibility of the motor fuel toward knock-suppressing agents as, for example, tetraethyl lead. Excess free sulfur is also very undesirable in that it increases the tendency of the treated stock to form undesirable polysulfides. If this situation occurs, it is necessary to redistill the motor fuel in order to reduce its corrosiveness, to improve its anti-knocking char-

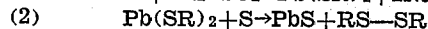
acteristics and to improve its susceptibility for knock-suppressing agents.

Fresh and regenerated sodium plumbite solutions are commonly used in commercial doctor sweetening operations. The fresh plumbite solutions are prepared from pure chemicals generally by dissolving litharge to the point of saturation in sodium hydroxide solutions having gravities in the range between about 12° and 30° Bé., preferably in the range between about 14° and 20° Bé. This procedure results in a production of plumbite reagents having soluble lead contents, expressed as pounds of lead per gallon of reagent, in the range of between about 0.08 and 0.30, preferably between about 0.1 and 0.2. The reaction is represented by the following equation:



Regenerated plumbite solution is prepared by blowing spent plumbite solution with air at a temperature of about 150° F. to about 175° F. to oxidize the lead sulfide contained therein to plumbite. Small amounts of fresh litharge and fresh sodium hydroxide are added to the regenerated plumbite solution from time to time in order to maintain an alkaline plumbite solution having a soluble lead content in the range between about 0.1 and 0.2 pound of lead per gallon of reagent.

It is typical of conventional doctor sweetening processes to contact 100 volumes of naphtha distillate containing mercaptan sulfur with about 5 to about 20 volumes of sodium plumbite reagent and with an amount of free sulfur, in naphtha solution, equivalent to about 1.5 times that theoretically required to convert the lead mercaptides to the corresponding alkyl disulfides. In this manner, the oil is sweetened according to the following reactions:



where R is a hydrocarbon radical. In some operations, the oil is contacted simultaneously and concurrently with both the plumbite solution and with the free sulfur; whereas, in other operations, the oil is first contacted with the plumbite solution and then with the sulfur or sulfur solution. These conventional doctor sweetening operations are not entirely satisfactory since, in order to insure complete and rapid removal of the soluble lead compounds from the oil, it is necessary to add an excess of free sulfur over that theoretically necessary to complete

the doctor sweetening reaction which often results in the production of corrosive distillates containing excessive amounts of polysulfide sulfur. Various suggestions have been made for overcoming the inherent difficulties encountered when attempting to add just the right amount of free sulfur to the oil. However, none of these suggestions have been practical from a commercial standpoint since they are relatively cumbersome. For example, various electrolytic methods have been tried in order to accurately determine the amount of sulfur necessary to just quantitatively precipitate the lead. These methods are not desirable since the reaction, when using the quantitative amount of sulfur, is slow in reaching completion which materially decreases the throughputs and capacities of the equipment.

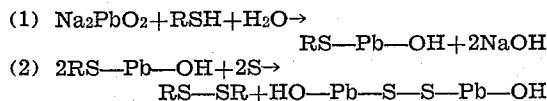
Many variations and modifications of the doctor sweetening process for treating oils containing mercaptan sulfur are in commercial use at the present time. For instance, it is known in the art to use vertical or horizontal reaction and settling vessels, to use means of mixing the reagents with oil such as passing the oil and reagents simultaneously and concurrently through a series of orifices or agitating with mechanical stirrers, to add sulfur or sulfur solution to the oil before or after it is contacted with sodium plumbite reagent, to use a continuous doctor method of sweetening, and to use one, two or three cycle operation. All the modifications of this process used heretofore have one common defect, namely that no means is provided for controlling to a minimum at all times the formation of organic polysulfide in the distillate. It is highly desirable that the polysulfide content always be kept at a minimum because of its detrimental effect on the octane number, lead susceptibility, gum inhibitor requirement, sulfur content and color stability of the distillate. We have, however, now discovered a means of controlling to a minimum at all times the formation of organic polysulfides in distillates during the process of doctor sweetening.

Our improved process of doctor sweetening comprises contacting the mercaptan-containing oil with sodium plumbite reagent of suitable strength and quantity in a manner such that substantially all the mercaptans are converted to basic lead mercaptides, (RS—Pb—OH, where R is a hydrocarbon radical), rather than to the usual neutral lead mercaptide, (RS—Pb—SR), mixing the leaded oil with a carefully controlled amount of sulfur or sulfur solution in oil which is substantially the theoretical amount required to effect a break, then settling, water washing or otherwise clarifying the sweetened oil.

Several factors which are interrelated influence or control the degree to which the mercaptans are converted to basic lead mercaptides during the plumbite treatment. The more important factors are concentration of soluble lead in the plumbite reagent, degree of contact between the oil and plumbite reagent, amount of plumbite reagent employed, and the type, that is, alkyl or aryl, of mercaptans present in the oil being treated. We have found that by intimately contacting one volume of sour oil with one or more volumes of plumbite reagent containing soluble lead in concentrations of about 0.10 to 0.20 pound of lead per gallon, preferably in concentrations of about 0.15 to 0.20 pound of lead per gallon, until the oil is thoroughly leaded before adding a carefully controlled amount of

sulfur or sulfur solution, the mercaptans are predominantly converted to the basic, rather than to the neutral, lead mercaptides. It is essential that the oil be thoroughly leaded before adding the sulfur, otherwise the sweetening reaction will proceed through the neutral lead mercaptide. Where the type of mercaptans present in the oil is responsible for some difficulty in converting substantially all the mercaptans to basic lead mercaptides, the difficulty is overcome by using somewhat longer periods of contact and larger volumes of plumbite reagent.

Although our invention is not to be limited by theory of chemical reactions involved, it is our belief that, when mercaptan-containing petroleum oils are intimately contacted in an initial stage with large quantities of sodium plumbite solution containing soluble lead in an amount greater than about 0.1 pound of lead per gallon, the mercaptans are converted substantially completely to basic lead mercaptides. The basic lead mercaptides, when treated with sulfur, are converted to oil-soluble alkyl disulfides and oil-insoluble lead polysulfides. These reactions are illustrated as follows:



From the above, it is apparent that a material improvement will result when employing our process. Sufficient sulfur may be added to rapidly and completely precipitate the soluble lead compounds without incurring the possibility of having excess free sulfur dissolved in the treated oil, since the lead polysulfides precipitated will completely remove any excess free sulfur. Thus, our process will permit the ready removal of mercaptan compounds from petroleum oils and will result in the production of higher quality products.

It has been known for several years that a small amount of basic lead mercaptide is formed in the usual processes of doctor sweetening mercaptan-bearing distillates, but, heretofore, it has not been known that the reaction can be directed to go substantially completely through the basic rather than through the neutral lead mercaptide. Neither has it been known that the basic lead mercaptide sweetening gives the oil a lower content of organic polysulfides. It is well known that the polysulfides are detrimental to naphtha and kerosene since they give these products a high sulfur content, a poor color stability and, in many cases, a bad test for copper corrosion at 212° F. The theoretical amount of sulfur required for breaking out the lead from a basic lead mercaptide is the same as that required for the neutral mercaptide containing only half as much lead, but the excess sulfur required to complete the reaction in a reasonably short time is much lower in the case of the basic lead mercaptide. Furthermore, we have discovered that where an excess of sulfur is used to effect a rapid break, more of the excess sulfur is retained in the oil probably as organic polysulfides in the case of neutral lead mercaptide sweetening than in the case of basic lead mercaptide sweetening.

The process of our invention may be readily understood by reference to the attached drawings illustrating modifications of the same. Figure 1 illustrates an overall operation, while Figures 2 and 3 illustrate preferred modifications wherein the oil is jetted into a body of doctor reagent.

Referring specifically to Figure 1, it is assumed that the mercaptan containing oil comprises a petroleum oil boiling in the motor fuel boiling range. The feed oil is introduced into mixing zone 3 by means of line 1 and pump 2 wherein it is intimately contacted with a strong doctor reagent in the ratio of 1 volume of oil to 2 volumes of reagent. The doctor reagent is introduced into mixing zone 3 by means of line 4 and consists of recycle reagent to which a small quantity of doctor reagent has been added by means of line 5 and pump 6, for the purpose of maintaining a constant concentration of lead in the reagent, and for replacing reagent discarded or lost from the system. Mixing zone 3 may comprise a turbo mixer, a centrifuge or mixing pump, an orifice or jet incorporator, or any other equivalent means of securing contact between the oil and reagent. The mixture of oil and reagent is removed from zone 3 by means of line 7 and introduced into zone 8 which may comprise a horizontal or vertical drum, wherein the oil is maintained in contact with the reagent before separation from the same. The reagent is withdrawn from zone 8 by means of line 9 and pump 10 and recycled to zone 3 by means of line 4. If desired, a portion of the reagent is withdrawn from the system and handled as desired. It is generally passed to a lead recovery plant. The quantity of spent doctor reagent passed to the lead recovery plant is proportional to the volume of oil treated and also the concentration of mercaptan sulfur in the oil. In general, this quantity is just sufficient to permit the addition of the minimum amount of fresh reagent of a given lead concentration required to maintain a treating reagent of the desired strength. Flow control arrangements 11, 12, and 13 are employed respectively as a means of carefully regulating the feed oil charged, the fresh doctor reagent charged, and the spent doctor reagent discarded.

The oil separated from the doctor solution in zone 8 is removed by means of line 14 and mixed with a carefully controlled amount of sulfur oils substantially equivalent to that theoretically required to complete the sweetening reactions. The sulfur oil is introduced into line 14 by means of line 15 and the mixture passed through incorporator 16 wherein intimate contact between the sulfur and the oil is secured. The sweetened oil discharged from incorporator 16 passes through line 17 into zone 18 wherein the lead sulfide and other insoluble materials are separated from the oil. Zone 18 may comprise either a vertical or a horizontal drum. However, we prefer a vertical type drum with a cone bottom which is better adapted for removal of the lead sulfide and other precipitated materials which are withdrawn by means of line 19.

A preferred modification of our process is to utilize as an aid in the separation of the lead sulfide at least a portion of the spent doctor reagent which is withdrawn from zone 8 by means of line 9. When operating in this manner, a portion of the spent doctor solution is preferably introduced into line 14 by means of line 21. However, a portion of the spent doctor solution under certain circumstances may be introduced into incorporator 16 by means of line 22 or into line 17 by means of line 23. The sweetened oil is removed from zone 18 by means of line 24 and washed with water which is introduced by means of line 26. The mixture of oil and water is passed through incorporator 25 and introduced into settling zone 28 by means of line 27. The water

separated from the oil is removed from zone 28 by means of line 29, while the sweetened and water washed oil is removed from zone 28 by means of line 30 and passed to finished oil storage. A portion of the oil, however, is segregated by means of line 31 and pump 32 and passed through sulfur tower 33 wherein the same dissolves an amount of sulfur. The sulfur oil is introduced into line 14 by means of line 15 as hereinbefore described. The rate of flow is controlled by flow control means 34. The method of ascertaining that the correct amount of sulfur solution is being added by means of line 15 comprises withdrawing a sample of the treated oil from the system at a point subsequent to zone 18, such as by means of line 35, and testing it for the presence of mercaptans or free sulfur.

Referring specifically to Figure 2, a preferred method of operating is described. When operating in this manner the doctor solution is introduced into zone 40 by means of line 41. The mercaptan-containing oil is jetted into the bottom of zone 40 into a body of doctor solution by means of line 42 and jet header 43. The solution of doctor and leaded oil is removed from zone 40 by means of line 44 and combined with sulfur oil which is introduced by means of line 45. The mixture is passed through incorporator 46, withdrawn by means of line 47, and passed to settling zone 28 as described with respect to Figure 1.

A further adaptation of the invention in which the mercaptan-containing oil is jetted into a body of doctor and the treated oil and spent doctor withdrawn as separate streams is illustrated in Figure 3. Referring specifically to Figure 3, the doctor reagent is introduced into zone 50 by means of line 51, while the mercaptan-containing oil is jetted into the body of doctor by means of line 52 and jet header 53. The treated oil is removed from zone 50 by means of line 54 while the spent doctor is removed by means of line 55. The spent doctor may be withdrawn from the system by means of line 56 or recycled by means of line 57. The leaded oil withdrawn by means of line 54 is combined with sulfur which is introduced by means of line 58 and the same passed through incorporator 59, withdrawn by means of line 60, passed to settling zone 28, and handled as described with respect to Figure 1. In accordance with a further preferred adaptation of our invention a portion of the doctor solution withdrawn from an intermediate point in zone 50 is combined with the leaded oil withdrawn from the top of zone 50 by means of line 61. If desired, the doctor solution may be introduced into the leaded oil by means of line 62 or 63.

The process of our invention may be widely varied. The invention essentially comprises controlling three critical factors in an initial stage when treating a mercaptan-containing oil with an alkali metal plumbite solution so that substantially all the mercaptides are present as basic lead mercaptides rather than as neutral lead mercaptides. The three critical factors controlled are concentrations of lead oxide dissolved in the doctor solution, the degree of contact between the doctor solution and the oil, the amount of reagent used with respect to the character of the mercaptan composition present. These factors are controlled in a manner that at least 75%, preferably at least 90% of the mercaptides present in the doctor treated oil are present as

basic mercaptides rather than as neutral mercaptides.

In general it is essential that the doctor solution employed should have a lead content in the range above 0.1, preferably in the range from about 0.2 to 0.3 pound of lead per gallon of reagent. When employing a solution of this character, it is desirable to use at least one, preferably two volumes of reagent per volume of oil treated. A very desirable operation comprises treating one volume of oil with at least two volumes of doctor solution, which solution is characterized by having 0.2 to 0.3 pound of lead per gallon of reagent. The time of contact will vary considerably depending upon the above related factors. However, in general, it is preferred that the time of contact be in the range from about 2 to about 10 minutes, preferably about 4 to 6 minutes.

In order to illustrate the invention further, the following examples are given which should not be construed as limiting the same in any manner whatsoever:

EXAMPLE 1

To a sample of rerun gasoline which was sweet and contained 0.033% sulfur, enough amyl mercaptan was added to give the gasoline a 66 copper number and a sulfur content of 0.113%. The 0.08% increase in sulfur content, as determined by the lamp method, is equivalent to a 60 copper number for the gasoline.

A portion of the oil containing the added amyl mercaptan was shaken with an equal volume of strong doctor solution. After settling and withdrawing this batch of reagent, the portion of oil was again shaken with a second equal portion of doctor reagent to yield an oil hereinafter designated as leaded oil "A." After withdrawing the second doctor wash, some of the original sour oil was added back to small portions of leaded oil "A" until a sample broken out with excess sulfur was no longer sweet. By this method, it was found that 48 parts of sour oil and 52 parts of the leaded oil "A" would be sweet but a 50-50 mixture was very sour. A large blend was then made for further experimental work using 48 parts of the sour oil and 52 parts of leaded oil "A." This blend is hereinafter referred to as leaded oil "B."

The lead present in leaded oil "A" was substantially completely in the form of the basic mercaptide (RS-Pb-OH); whereas in leaded oil "B" it was present almost entirely as the neutral mercaptide (RS-Pb-SR). This is indicated to be true by the fact that the leaded oil "A" is capable of thoroughly leading an almost equal volume of sour oil when mixed with the latter. It is further substantiated by lead contents determined on a sample of leaded oil "A" and also on a sample of leaded oil "B" by precipitating and weighing the lead as PbS. The data are as follows:

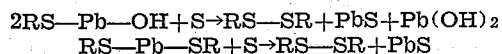
	Grams of Pb per 100 cc. of oil				
	Determined	Theoretical for RS-Pb-OH		Theoretical for RS-Pb-SR	
		66 Cu No.	60 Cu No.	66 Cu No.	60 Cu No.
Leaded oil "A".....	0.384	0.427	0.388	-----	-----
Leaded oil "B".....	0.203	-----	-----	0.214	0.194

Approximately 90 to 96% of the mercaptans

present in the sour oil were converted to basic lead mercaptides in the case of leaded oil "A"; whereas, they were converted almost entirely to neutral lead mercaptides in the case of leaded oil "B."

EXAMPLE 2

The theoretical amount of sulfur required to break out the lead in a leaded oil is the same for both the basic and the neutral lead mercaptides, as indicated by the following reactions:



Actually, a slight excess over the theoretical of sulfur is required to effect a rapid "break" in both cases. However, a finished oil of lower sulfur content is obtained by the basic lead mercaptide sweetening reaction than is obtained by the neutral lead mercaptide sweetening reaction when using the same amount of excess sulfur. This was shown to be true by the following experiment.

To separate samples of leaded oil "A" obtained in the experiment described under Example 1, sulfur was added in quantities equivalent to 1 and 3 times the theoretical amount required to break out the lead as calculated from the copper number of the oil. (The copper number of an oil represents the number of milligrams of mercaptan sulfur present in 100 cc. of the sour oil). Likewise, to separate samples of leaded oil "B" obtained in the experiment described under Example 1, sulfur was added in quantities equivalent to 1 and 3 times the theoretical amount required to effect a break. After effecting a break and clarifying the oil, the samples of oil thus treated were tested for sulfur content and copper corrosion at 212° F. The data are as follows:

Product	Sulfur content	Copper corrosion at 212° F.
Sour oil.....	Percent 0.113	
Oil sweetened by basic lead mercaptide reaction using:		
1×theoretical S for break.....	0.113	Pass.
3×theoretical S for break.....	0.139	Do.
Oil sweetened by neutral lead mercaptide reaction using:		
1×theoretical S for break.....	0.114	Do.
3×theoretical S for break.....	0.158	Did not pass.

Since as little as 0.004% free sulfur will cause this oil to be corrosive to copper at 212° F., it is evident that the additional sulfur which the oil acquired during the basic mercaptide sweetening with excess sulfur must have been largely in the form of polysulfide sulfur. On the other hand, the additional sulfur acquired by the oil during the neutral mercaptide sweetening with excess sulfur must have been in the form of free as well as polysulfide sulfur.

EXAMPLE 3

A sample of gasoline containing mercaptan sulfur equivalent to a 35 copper number was contacted with an equal volume of doctor reagent in a separatory funnel until the mercaptans were converted substantially completely to basic lead mercaptides. A blanket of methane gas was employed in the separatory funnel during the shaking to prevent excessive oxidation of the mercaptans to disulfides and, at the same time, to assimilate as nearly as possible plant conditions where a closed system is usually employed. Even though this precaution was taken, it was

found that 10% of the mercaptans originally present in the oil were oxidized to disulfides. Consequently the mercaptides remaining in the leaded oil were theoretically equivalent to an oil having about a 30+ copper number. It was determined, furthermore, that 90% of the mercaptide sulfur present in the leaded oil was in the form of the basic mercaptide while the other 10% was in the form of the neutral mercaptide. Separate portions of this leaded oil were sweetened by addition of 1.0, 1.5, and 2.0 times the theoretical amount of sulfur required to produce a break in the case of a 30 copper number stock. Data were obtained on the time required to effect a break and the amount of free and polysulfide sulfur acquired by the oil when sweetening this leaded oil with varying amounts of sulfur. These data are given in Table I below.

For purpose of comparison, samples of the sour gasoline were also sweetened through the neutral mercaptide reaction. In one case, the oil was contacted with 10% by volume of doctor reagent for just sufficient time to convert the mercaptans present in the oil to neutral lead mercaptides. Separate portions of this oil were then sweetened by adding 1.0, 1.5, and 2.0 times the theoretical amount of sulfur required for a 35 copper number stock. In another case, the sulfur used to effect the break during the sweetening reaction was added to the oil before it was contacted with the doctor reagent. Sulfur in the amount of 1.5 times the theoretical for sweetening a 35 copper number stock was added to a separate portion of the sour gasoline; this portion of gasoline was then contacted with 10% by volume of doctor solution until it was sweet. Data obtained on these neutral lead mercaptide sweetened oils are also given in Table I below.

for breaking out the lead and gives a product of lower free and polysulfide sulfur content than does neutral lead mercaptide sweetening. Furthermore, the data indicate that adding sulfur to a sour oil prior to its leading is a very undesirable doctor sweetening procedure because of the large amount of polysulfides formed in the oil thus treated.

EXAMPLE 4

The following operations show the effectiveness of jetting sour oil into a body of doctor reagent as a means of converting the mercaptans present in the oil to basic lead mercaptides. They also indicate the necessity of maintaining a relatively high lead concentration in the doctor reagent if a high conversion of the mercaptan to the basic mercaptide is to be obtained.

In the first operation, a sour naphtha of 32 copper number was pumped under a pressure of 40 pounds per square inch through a 1/2 millimeter diameter glass jet into the bottom of a 2-inch glass column filled to a depth of 5 feet with doctor solution having a 15° Baumé gravity and a soluble lead content (expressed as Pb) of 0.18 pound per gallon. A good dispersion of the oil into the doctor solution was obtained at a jet velocity of 20 feet per second; this was evidenced by the leading of 95% of the mercaptans to the basic lead mercaptide.

In order to determine the extent to which the doctor solution could be used before becoming ineffective for basic mercaptide formation, other operations similar to the one described above were made in which the reagent employed com-

Table I

Product	Time required for break, minutes		Free sulfur plus polysulfide sulfur present in treated naphtha (mg./100 cc.)	Excess sulfur added mg./100 cc.
	Cloud	Coagulation of PbS		
<i>Basic mercaptide sweetened oil</i>				
Sulfur added after leading:				
1.0×theoretical for break	20	45	0	9.4
1.5×theoretical for break	(1)	13	0	9.4
2.0×theoretical for break	(1)	1	0.5	15.0
<i>Neutral mercaptide sweetened oil</i>				
Sulfur added after leading:				
1.0×theoretical for break	120	17	0.75	8.7
1.5×theoretical for break	6.5	1	3.5	17.5
2.0×theoretical for break	(1)			
<i>Neutral mercaptide sweetened oil</i>				
Sulfur added before leading: 1.5× theoretical for break		14.0	3.0	8.6

¹ Immediate.

² Shaking time, 10 minutes; settling time, 4 minutes.

It will be noted from these data that basic lead mercaptide sweetening requires a shorter time

prised doctor solution diluted with caustic of the same Baumé gravity.

The data obtained in these experiments are tabulated below:

*Formation of basic mercaptides in column
2-inches in diameter*

Soluble lead content of doctor solution, lbs. Pb/gal.	Rate naphtha was leaded, gals./hr.	Per cent conversion of mercaptan sulfur to basic mercaptide sulfur	Degree oil leaded, per cent minimum complete leading ¹
0.18	2.0	95	195
0.12	1.0	82	182
0.12	3.0	75	175
0.06	1.5	32	132
0.06	3.0	32	132
0.018	2.0	0	94

¹ Minimum complete leading (100%) occurs when all mercaptan sulfur is converted to the neutral lead mercaptide.

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

1. In a doctor sweetening process wherein mercaptan-bearing oil is treated with alkaline sodium plumbite solution and sulfur to convert the mercaptans to organic disulphides, the improvement which comprises in sequence the steps of intimately contacting one volume of the mercaptan-bearing oil with more than one-half volume of alkaline sodium plumbite reagent containing soluble lead in excess of 0.08 pound Pb per gallon to convert the mercaptans predominantly to basic lead mercaptides, separating the sodium plumbite reagent from the leaded oil, intimately mixing the leaded oil with a carefully controlled amount of sulfur slightly in excess of that theoretically required to precipitate lead sulfide and convert the lead mercaptides to organic disulfides, and separating the sweetened oil from the lead sulfide.

2. Process as defined by claim 1 wherein the sulfur is added as a solution in sweetened oil.

3. In a doctor sweetening process wherein mercaptan-bearing oil is treated with alkaline sodium plumbite solution and sulfur to convert the mercaptans to organic disulfides, the improvement which comprises in sequence the steps of intimately contacting one volume of the mercaptan-bearing oil with more than one-half volume of alkaline sodium plumbite reagent containing soluble lead in excess of 0.08 pound Pb per gallon to convert the mercaptans predominantly to basic lead mercaptides, separating a part of the sodium plumbite reagent from the leaded oil, intimately mixing the leaded oil and remaining sodium plumbite reagent with a carefully controlled amount of sulfur slightly in excess of that theoretically required to precipitate lead sulfide and convert the lead mercaptides to organic disulfides, and separating the sweetened oil from the lead sulfide and sodium plumbite reagent.

4. In a doctor sweetening process wherein mercaptan-bearing oil is treated with alkaline sodium plumbite solution and sulfur to convert the mer-

captans to organic disulfides, the improvement which comprises in sequence the steps of intimately contacting one volume of the mercaptan-bearing oil with more than one-half volume of alkaline sodium plumbite reagent containing soluble lead in excess of 0.08 pound Pb per gallon to convert the mercaptans predominantly to basic lead mercaptides, intimately mixing the leaded oil and sodium plumbite reagent with a carefully controlled amount of sulfur slightly in excess of that theoretically required to precipitate lead sulfide and convert the lead mercaptides to organic disulfides, and separating the sweetened oil from the lead sulfide and sodium plumbite reagent.

5. Process as defined by claim 4 wherein the sulfur is added as a solution in oil.

6. Process for the removal of mercaptan compounds from petroleum oils, which comprises contacting the same with at least one volume of an alkali metal plumbite solution, which is characterized by having a lead concentration in the range from about 0.2 to about 0.3 pound of lead per gallon of reagent, whereby at least 75% of the alkyl sulfides are present as basic sulfides, separating the treated oil, and contacting the same with an amount of sulfur substantially equivalent to the theoretical amount of sulfur necessary to precipitate the lead.

7. Process as defined by claim 6, in which at least two volumes of alkali metal plumbite solution are employed per volume of oil treated.

8. Process as defined by claim 6, in which the oil is jetted into the doctor solution.

9. Process as defined by claim 6, in which the oil is jetted into the doctor solution at a jet velocity of at least 20 feet per second.

10. Improved process for the removal of mercaptan compounds from petroleum oils, which comprises jetting the mercaptan containing oil into the bottom of a reaction zone containing doctor reagent, which doctor reagent is characterized by having a lead content from 0.1 to 0.3 pound of lead per gallon of reagent, whereby at least 75% of the mercaptides formed are basic lead mercaptides, withdrawing treated oil from the top of the reaction zone, withdrawing spent doctor from an intermediate point of the reaction zone, treating said oil withdrawn from the top of said reaction zone with an amount of sulfur substantially equivalent to the theoretical amount necessary to precipitate the lead, under conditions to remove the lead from the oil.

11. Process as defined by claim 10, in which the oil is jetted into the body of doctor solution at a jet velocity of at least 20 feet per second.

12. Process as defined by claim 10, in which a portion of the spent doctor withdrawn from said intermediate point of said reaction zone is combined with the leaded oil withdrawn from the top of said reaction zone.

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