

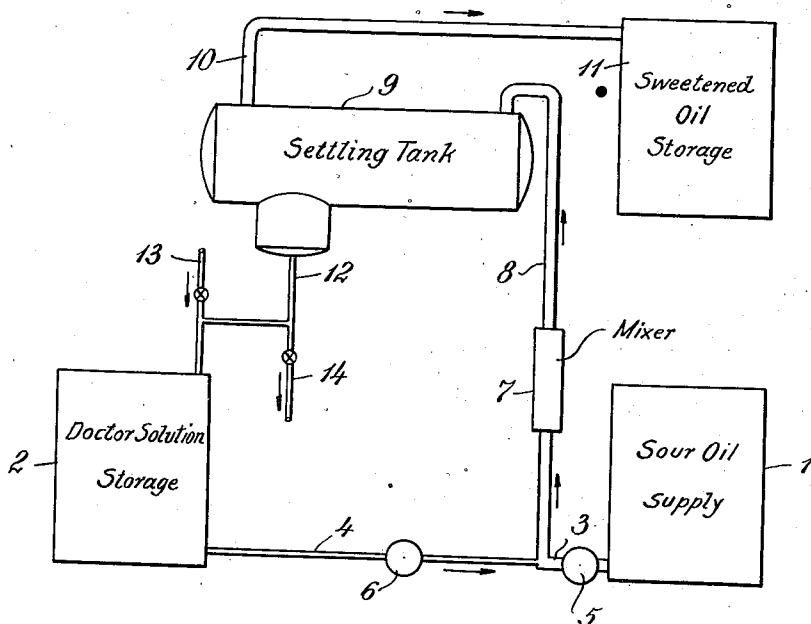
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METHOD OF SWEETENING A HYDROCARBON OIL

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METHOD OF SWEETENING A HYDRO-CARBON OIL

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10 Claims. (Cl. 196—33)

This application relates to the treatment of hydrocarbon oils such as petroleum oils and is directed particularly to an improved method for the sweetening of such oils. Petroleum oils contain considerable proportions of sulfur compounds amounting sometimes to as much as 3 or 4% or more of the oil. This sulfur usually is present in the form of hydrogen sulfide, elemental sulfur, various mercaptans, alkyl sulfides and disulfides, thiophenes, and perhaps carbon disulfide, and the sulfonic acids and alkyl sulfates.

The presence of mercaptans and hydrogen sulfide in the oil gives rise to objectionable odors. The mercaptans in the presence of elemental sulfur further render the oil corrosive to metals.

In view of the objectionable character of these sulfur compounds some treatment for their removal is ordinarily employed in the refining of petroleum containing them. The hydrogen sulfide is readily removed by treatment with an alkali, for example sodium hydroxide. The mercaptans, however, are not so readily removed and require special treatment. An oxidation with hypochlorite is sometimes employed for their removal but is objectionable for use with cracked distillates and other oils containing reactive unsaturated hydrocarbons. The treatment in general use for removing mercaptans from all types of oils consists in what is known as the "doctor treatment" employing sodium plumbite. With cracked distillates for use in internal combustion engines, especially, the doctor treatment with sodium plumbite has been the only successful method of destroying the objectionable sulfur compounds present without destroying at least to some extent the desirable character of the oil treated.

The doctor treatment generally is effected by adding sulfur to the mercaptan-containing oil in carefully limited amounts and treating the oil with a sodium hydroxide solution containing sodium plumbite, Na_2PbO_2 . Solutions having a concentration of 8 to 24% of sodium hydroxide and containing sodium plumbite corresponding to from $1\frac{1}{2}$ up to 6% of lead oxide, PbO , are usually satisfactory. Mercaptans present in the petroleum oil are converted by the sodium plumbite to lead mercaptides in accordance with the equation:



The lead mercaptides thus formed react with elemental sulfur forming disulfides in accordance with the equation



It will be noted, therefore, that the sweetening of petroleum oil by the treatment with plumbite does not result in the removal of sulfur present as mercaptans, but converts the objectionable mercap-

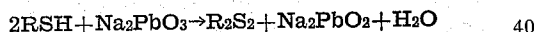
tans to less reactive products which may be retained in the petroleum oil without objectionable odor or corrosive qualities.

If hydrogen sulfide is present during the plumbite treatment, this is converted to lead sulfide and is removed. However, it is ordinarily preferred to remove the hydrogen sulfide by means of sodium hydroxide prior to treatment with the doctor solution. The disulfides produced by reacting mercaptans present in petroleum oils with plumbite decompose at high temperatures forming mercaptans and hydrogen sulfide. A distillation of the oil subsequent to sweetening accordingly is detrimental to the sweetening treatment and may undo the beneficial results derived from the sweetening.

The usual sweetening process has been described in considerable detail because of its relation to the present process. In addition to the plumbite treatment, treatment with other aqueous salts of lead e. g., lead acetate $\text{Pb}(\text{CH}_3\text{COO})_2$ has been suggested. All of these prior processes have employed those lead compounds wherein lead is present in the divalent form.

I have now found that if an aqueous solution of a quadrivalent-lead compound is employed, superior results are obtained.

The preferred process of the present invention differs from the usual treatment of petroleum oils with sodium plumbite and sulfur primarily in that a plumbate, preferably sodium plumbate, Na_2PbO_3 , is employed as the sweetening reagent. The sodium plumbate, Na_2PbO_3 , is employed in the same manner as the usual plumbite,—that is, in a suitable alkaline solution. The reaction of the Na_2PbO_3 , however, differs from that of Na_2PbO_2 , and the following equation is given as illustrative of this difference:



It will be evident from the equation that in accordance with the present process the unobjectionable dialkyl disulfides are formed directly by the reaction of mercaptans with the sweetening reagent and the presence of sulfur to complete their formation is unnecessary. The product of the reaction between the Na_2PbO_3 and mercaptans, contains Na_2PbO_2 and unless the reaction is stopped at this point, the Na_2PbO_2 will further react with mercaptans to form lead mercaptides, which in the presence of sulfur may be converted to the dialkyl disulfides with the formation of lead sulfide as previously illustrated.

The process of the present invention is applicable generally to mercaptan-containing hydrocarbon oils of high or low molecular weight and particularly to sour petroleum oils, both to distillates, straight, cracked, or steam distillates, and to distillation residues. It is especially ap-

plicable to oils such as sour fuel or burning oils, sour kerosene, sour, straight run, or cracked gasoline, sour casing-head gasoline (natural gasoline), sour lubricating oils, and similar oils.

5 The petroleum oils may be treated with the sodium plumbate solution at ordinary temperature or above or below; the temperature may be maintained, for example, between about 30° and 120° F. Lower temperatures are usually ad-
10 visable when more volatile oils are being treated in order to avoid possible evaporation losses. In most cases the temperature of treatment should be below normal distillation temperature because maintenance of a higher temperature
15 may cause souring of the sweetened oil, and perhaps formation of organic acid compounds.

The sodium hydroxide solutions employed may contain anywhere from 5 to 30% of NaOH (which may be partly in the form of Na_2PbO_3)
20 and from 0.1% of PbO_2 up to 5 or 6% of PbO_2 , which may be present as Na_2PbO_3 . Ordinarily the maximum amount of lead in the form of sodium plumbate depends on the limit of solubility of the sodium plumbate, rather than on any
25 limitation imposed by the sweetening operation but about 2% sodium plumbate (corresponding roughly to one and a half per cent lead) is very satisfactory. The entire amount of plumbate present need not be in solution but some of it
30 may be present as a suspension or slurry. Whether the lead is actually in the form of a solution of PbO_2 in aqueous NaOH or in the form of Na_2PbO_3 , the result is believed to be the same, for both probably come to a state of substantial
35 equilibrium in the solution.

The volume ratio of "doctor" solution to oil varies depending upon the mercaptan content of the oil treated and upon whether or not it is desired to permit the reduction of plumbate completely to lead sulfide or only to sodium plumbite.
40 In general the Na_2PbO_3 should be added in a ratio of Na_2PbO_3 (mols): SH (radicals) equal to at least 1:4. But to overcome practical difficulties and obtain complete reaction, it is some-
45 times preferred to add many times this ratio.

The period of treatment of course will vary depending upon the type of oil treated,—for example, whether it is a light distillate or a heavy residue and whether it is high in mercaptans or
50 low in mercaptans. It also will depend upon the concentration of the plumbate solution employed, the volume ratio of plumbate solution to oil, and the efficiency of the mixing devices used. Any effective agitator may be employed whether
55 of a turbulent flow type, such as an orifice and mixing pipe, a mechanical agitator type, or a type employing a gas or vapor to effect the agitation. With efficient agitation only a relatively short period of time is necessary for effecting a
60 substantially complete conversion of mercaptans to hydrocarbon disulfides. For example, only a few minutes may be necessary or even less. The reaction may be continued, however, for a longer period,—up to several hours, although such ex-
65 tensive treatment ordinarily would not be practicable.

During the treatment of petroleum oil with plumbate, air may be passed through the solution to serve to agitate the mixture and also
70 minimize the reduction of plumbate that occurs.

Although the present process has been exemplified by equation as an oxidation-reduction reaction, it is probable that the lead in the form of plumbate is more than a mere oxidant and cata-
75 lytically or in some other manner assists the re-

action. Whatever the nature of its effect, I desire not to be limited to the particular reaction illustrated but intend that my invention shall embody treatment of sour petroleum oils and
5 other similar oils containing mercaptans, with sodium plumbate or other metal plumbates for the purpose of sweetening these oils without regard to the chemistry involved.

The drawing represents schematically apparatus for sweetening sour gasoline and similar
10 oils by the process of the present invention. In the drawing numeral 1 indicates a storage container for sour gasoline; numeral 2 indicates a storage container for sodium plumbate "doctor" solution. Pipes 3 and 4, and pumps 5 and 6 are
15 provided for supplying sour gasoline and "doctor" solution from supplies 1 and 2 to a mixer 7. The mixer 7 may be any conventional type of mixer such as those now in use for mixing
20 plumbite doctor solution with gasoline; e. g. an orifice and mixing pipe. A pipe 8 is provided for conveying the mixture of doctor solution and gasoline to a settling tank 9 wherein gravity
25 separation of the treated gasoline and doctor solution is effected. The sweetened gasoline is withdrawn through a pipe 10 to a storage tank 11 and the used doctor solution is returned by means of pipe 12 to the doctor storage tank.
30 A pipe 13 is provided for the introduction of additional plumbate solution to supply losses during treatment and an outlet 14 also is provided for removal of spent plumbate solution.

The following example is illustrative of the operation of this apparatus. To effect the sweet-
35 ening of a sour gasoline containing 0.03% of mercaptans expressed as SH group, the gasoline is introduced continuously from tank 1 through pipe 3 into the mixer 7. For treating this gasoline a 20° Bé. aqueous sodium plumbate "doctor" solution is made up from an Na_2PbO_3 —NaOH
40 mixture containing 7.6% by weight of lead or in other words about 11% of Na_2PbO_3 . The doctor solution thus prepared contains, by weight, about 14% NaOH, 1.8% Na_2PbO_3 , and 84.2% water. This doctor solution is pumped through
45 pipe 4 to the juncture of pipe 3 where it intermingles with sour gasoline from supply tank 1 and together the gasoline and doctor solution pass to mixer 7. Rates of flow may be regulated so that between 25 and 200 parts by volume of
50 the doctor solution are introduced for each 100 parts of gasoline. The gasoline and sodium plumbate solution are thoroughly mixed in their passage through mixer 7 and the mixture then
55 passes by means of pipe 8 to settling tank 9 where the sodium plumbate solution settles to the bottom and the sweetened gasoline rises to the top. The gasoline is then withdrawn through pipe 10 to storage tank 11 and the sodium plumbate is returned to storage tank 2 by means of
60 pipe 12. Under these conditions the sodium plumbate solution is only partly spent by the treatment of the gasoline and hence may be recirculated a number of times. A portion of the partly spent plumbate may be withdrawn at 14
65 and treated for reconversion of reduced compounds back to plumbate, which then may be introduced by means of pipe 13 into the storage tank 2. Additional plumbate also may be added
70 continuously or intermittently to the system to replace losses from treatment or withdrawal.

With conditions of agitation and settling approximating those of the usual doctor treatment, the plumbate-sweetened gasoline reacts "nega- 75

tive" to the doctor test of the Federal Specifications Board.

When it is desired to operate so that the sodium plumbate is reduced completely to lead sulfide, this advantageously may be done using a process involving two stages;—the first, a mixing as above described to form the plumbite, and the second, a treatment of the plumbite-oil mixture with sulfur to complete the reaction as previously explained in connection with the usual doctor treatment.

It has been proposed to treat petroleum oils with water-free alkaline dioxides or peroxides at elevated temperatures, i. e. distillation temperature of the oil, so as to oxidize the sulfur compounds present to organic acids and organic acid salts. My process is to be distinguished from such processes in that I employ milder conditions of treatment, for example, I prefer to employ an aqueous solution of sodium plumbate instead of the anhydrous compound, and I prefer to carry out the treatment at ordinary temperatures, temperatures below the normal distillation temperature of the hydrocarbon, rather than at highly elevated temperatures. Under these conditions the oxidation of sulfur compounds does not result in the formation of organic acids to any appreciable extent but results in the formation of alkyl disulfides. The former are objectionable in oils for many uses in that they tend to cause gum formation. The latter on the other hand are quite unobjectionable in this respect.

In general I prefer to have present in my process a relatively high ratio of NaOH to quadrivalent lead, above about 100 to 18, by weight, thereby further reducing any tendency of the doctor solution to effect overoxidation of the oil. This is of especial importance in the treatment of gasolines obtained by cracking processes. These gasolines, unlike ordinary crude petroleum or straight-run products, are relatively high in olefines, which are more sensitive to oxidation than the other hydrocarbon constituents of petroleum products, and therefore require more mild conditions of sweetening to avoid oxidation and polymerization.

I claim:

1. The method of sweetening a petroleum oil which comprises mixing the oil with an aqueous

alkaline plumbate solution at a temperature below about 120° F.

2. The method of sweetening a petroleum oil containing mercaptans which method comprises treating the oil with an aqueous solution of sodium plumbate.

3. The method of sweetening a mercaptan-containing petroleum distillate oil which comprises treating the oil with an aqueous sodium hydroxide solution containing sodium plumbate.

4. The method of sweetening a mercaptan-containing petroleum distillate oil which comprises treating the oil with an aqueous sodium hydroxide solution containing sodium plumbate, at a temperature below the normal distillation temperature of the oil.

5. The method of sweetening a mercaptan-containing gasoline which comprises treating the gasoline at a temperature below 120° F. with an aqueous solution containing NaOH and Na₂PbO₃.

6. The method of sweetening a mercaptan-containing gasoline which comprises intimately mixing the gasoline at a temperature between about 30° F. and about 120° F. with an aqueous solution containing NaOH and Na₂PbO₃.

7. The method of sweetening a mercaptan-containing gasoline which comprises intimately mixing the gasoline at a temperature between about 30° F. and about 120° F. with an aqueous solution containing about 14% NaOH and about 2% Na₂PbO₃, and mechanically separating gasoline from solution.

8. The method of sweetening a mercaptan-containing petroleum oil containing a substantial amount of olefines, which comprises treating the oil with an aqueous solution of sodium plumbate and sodium hydroxide in a ratio of not more than 18 parts lead for each 100 parts of sodium hydroxide at a temperature below the distillation temperature of the oil.

9. The method of sweetening a cracked gasoline which comprises treating the gasoline with an aqueous solution of sodium plumbate and sodium hydroxide in a ratio of not more than 18 parts lead for each 100 parts of sodium hydroxide at a temperature below the distillation temperature of the gasoline.

10. The method of sweetening a hydrocarbon oil, which comprises treating the oil with an aqueous alkaline plumbate solution.

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