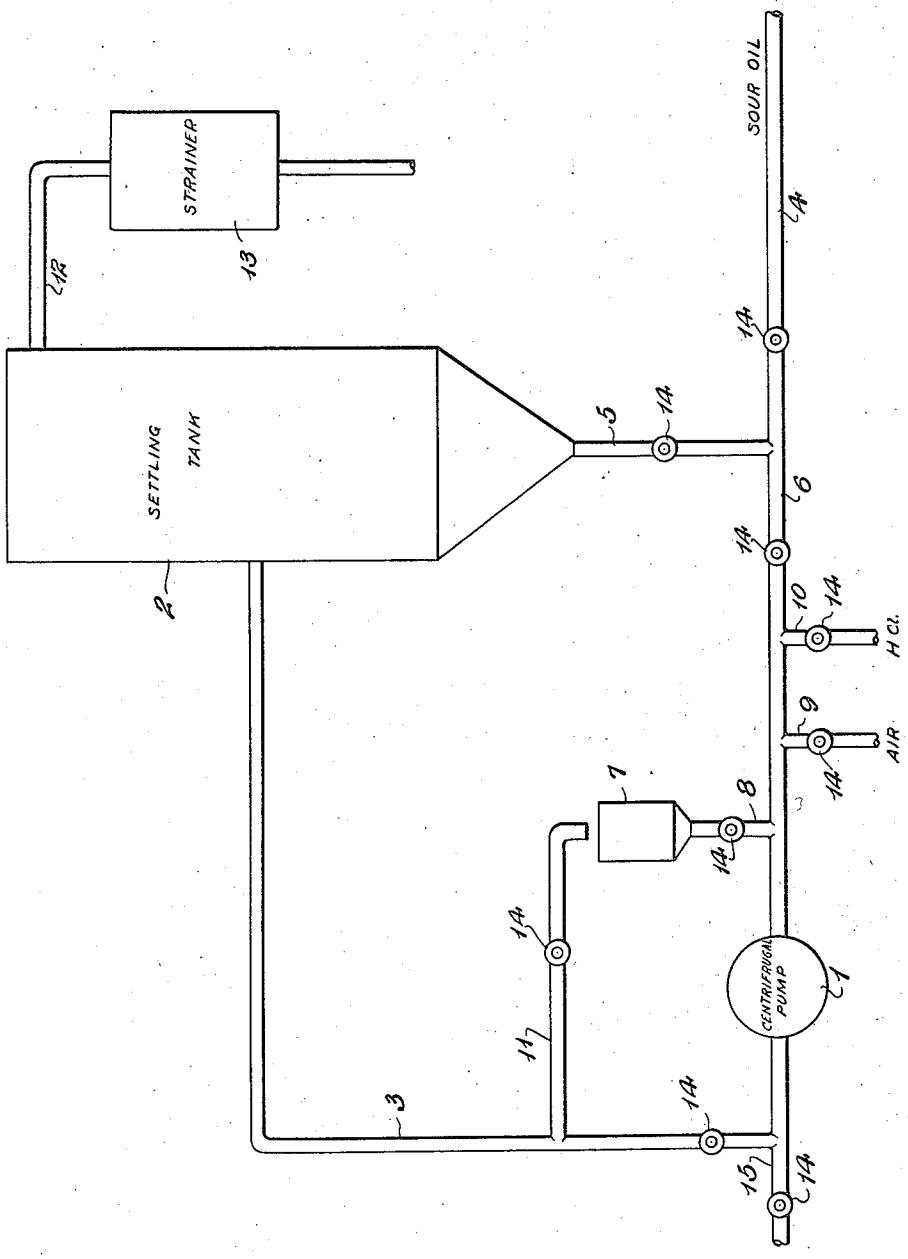
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PROCESS FOR TREATING MINERAL OILS

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PROCESS FOR TREATING MINERAL OILS

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The present invention relates to process for the treatment of mineral oils and particularly to the treatment of the relatively light mineral oil known as naphthas, gasolene, kerosene, water whites, raffinate, and the like, for removing or altering "sour compounds", namely, compounds which contain sulphur, especially the organic sulphur compounds as mercaptans as well as organic sulphur compounds which may have been formed in the oil by treatment with sulphuric acid or sulphur dioxide or other acid compounds containing sulphur.

The process is especially important in the case of treating naphthas, raffinates, gasolene and kerosene and similar light fractions containing sulphur compounds existing in the form of organic sulphur compounds and is especially important in treating naphthas, raffinates, gasolene and kerosene and similar products containing organic sulphur compounds in the form of mercaptans.

Oils treated in accordance with the present invention are, after treatment, not only doctor sweet, but also exhibit a highly satisfactory corrosion test even above temperatures usually prescribed in specifications for oils. As is well known, the corrosion test for oils consists in subjecting a highly polished strip of metallic copper foil to the action of the oil to be tested at an elevated temperature for given periods of time. As the test is well known to the person skilled in the art, the details need no description here. Mineral oils, such as naphthas, treated in accordance with the present invention are not only "doctor sweet" after treatment when the "doctor test" is applied, but the naphthas after treatment also pass in a highly satisfactory manner the corrosion test at a temperature of even 210° F. for 30 minutes. That is to say, in terms of the language of the oil refiner, the oils treated in accordance with the present invention are O. K. corrosion at 210° F.

An object of the present invention is to provide a process by which the sour compounds may be removed or altered, thus making the oils or distillates sweet.

A further object of the present invention is to provide a process by which not only doctor sweet oils are obtained as a result of the practice of the process but also oils which exhibit a satisfactory or negative corrosion test.

A further object of the invention is to provide a process of the character described which will be continuous or regenerative in nature.

A further object of the present invention is the provision of a process by which mercaptans in the oils may be converted into compounds which are not sour to doctor solution without the use of "doctor" solution, that is sodium plumbite, and without the use of elemental sulphur usually employed when sodium plumbite is used to remove or decompose mercaptans.

The removal of mercaptans from oils of the character described by the use of sodium plumbite is well understood in the art and the removal is accomplished by intimately contacting the sodium plumbite or "doctor" solution with the oil from which the mercaptans are to be removed. The sodium plumbite reacts with the mercaptans to produce lead mercaptides and these are in turn decomposed by elemental sulphur added to the oil treated either before, after or during the treatment with the "doctor" or sodium plumbite solution. The elemental sulphur reacts with the lead mercaptides and produces organic disulphides and lead sulphide. The actual number of grams or pounds of sulphur in the oil combined as the mercaptans is not reduced by the treatment with plumbite, but it is changed to a form that is not sour and relatively stable, that is if R represents the organic radicals of the mercaptans the change is from two molecules of mercaptans, 2RSH, to one molecule of disulphide, R—S—S—R. The plumbite process of treating oils is objectionable in many respects requiring sulphur, large quantities of litharge and caustic alkali for the production of the sodium plumbite and is considerably expensive since the lead of the lead sulphide is lost unless it is recovered by smelting operations or converted to sulphate or oxide by some suitable process. The recovery of the lead in available form for reuse is not generally done and many refineries on account of the cost of recovering the lead in available form from the lead sulphide, find it more advantageous to purchase fresh litharge and discard the lead sulphide or sell it for whatever can be obtained.

The plumbite treatment is further objectionable in that the oils after treatment are likely to exhibit an unsatisfactory corrosion test, and usually have their sulphur content increased.

By the present invention the conversion of the mercaptans into the disulphides is obtained without the use of sulphur and litharge and without the production of lead sulphide, whereby the cost of making the oils sweet is greatly diminished. The present process also enables the oils to be treated at a rapid rate at a very nominal cost as the agent accomplishing the conversion of the mercaptans into disulphides may be easily and

quickly regenerated for further use in accomplishing the conversion.

According to the present invention mineral oils, for example gasolene, naphthas, raffinate, water whites, furnace oils, Diesel engine oils, transformer oils, kerosene, or heavier oils than these, containing mercaptans as a sour constituent which are to be sweetened are brought in intimate contact with a compound of a metal which may be reduced from a higher to a lower valency. This intimate contact is preferably accomplished in the presence of clay of a highly absorbent character, for example, fuller's earth or bentonite or like clays. Examples of metal compounds which may be employed are cupric oxide, cupric chloride, cupric nitrate, mercuric chloride, ferric chloride, ferric sulphate etc. Iron compounds usually give objectionable colorations to oils containing a high proportion of unsaturated hydrocarbon compounds and for that reason should not be used in treating such oils when an uncolored products is desired. Cupric chloride may advantageously be used in treating naphthas, raffinate or gasolene or other oils containing high proportions of unsaturated compounds. In addition to the clay and metal compound an oxidizing agent may be associated therewith such as alkali permanganates, as potassium permanganate or manganates, manganese dioxide or other oxidizing agent. According to the present process the metal compounds, such as cupric oxide, cupric chloride, cupric nitrate, mercuric chloride, ferric chloride or ferric sulphate is kept active or regenerated by intimately mixing with the naphtha or gasolene, or other oil to be treated, air or oxygen, or an oxygen containing gas or an oxidizing agent either solid or liquid capable of oxidizing the metal in the metal compounds from a lower to a higher valency.

Very satisfactory results may be obtained by utilizing a mixture comprising from 70 to 98 per cent clay with from 30% down to 2%, and even less, of metal compound, as for example cupric chloride. An oxidizing agent may be mixed into the mixture of clay and metal compound to the extent of about 2–15%, for example 5% of potassium permanganate. The reagents in the mixture, including the clay, preferably should be in a fine state of division, preferably completely passing through a 100 mesh screen and most of it passing through a 200 mesh screen. Very satisfactory results are produced by using a reagent mixture containing 90% of dry clay, 5% of cupric chloride and 5% of potassium permanganate. A satisfactory mixture also consists of 95% dry clay and 5% cupric chloride.

The metal compound or mixture of metal compound and clay, with or without added oxidizing agent, may be agitated in any suitable way with the "sour" oil, naphthas or gasolene and air or oxygen intimately contacted with the mass being agitated. After agitation of the naphthas, gasolene or kerosene in presence of air or oxygen and the metal compounds or metal compounds and clay, the metal compounds and clay are allowed to settle from the sweetened naphthas, gasolene or kerosene, and the said settled metal compounds, or metal compounds together with the clay associated therewith, are again agitated with "sour" naphtha, gasolene or kerosene in the presence of air or oxygen to produce sweetening of the oils.

In carrying out this use and reuse of reagents, the reagents, sour naphthas, gasolene or kerosene and air, or oxygen, may be fed to the inlet of a centrifugal pump which will produce the necessary agitation of the oils, reagents and air or oxygen. The oil will be substantially completely sweetened on passing through the centrifugal pump. The mixture may then be led to a point about midway of the height of a tall tank where the reagents and clay will separate and settle from the sweet naphthas, gasolene or kerosene. The reagents and clay with some oil may be aspirated from the bottom of the tank by the centrifugal pump and fed with further quantities of sour naphthas, gasolene or kerosene and air to the inlet of the centrifugal pump and the mixture produced by the pump discharged into the tank as above described. Sweet oil will accumulate in the upper portion of the tank free of metal compound and clay, and may be drawn off continuously or intermittently. The centrifugal pump may be operated intermittently or continuously in its aspiration of reagent and clay from the tank and in its mixing of the reagents and air with the sour oil and discharging of the mixture into the tank.

I have found it advantageous to add a small amount of an acid to the oil undergoing treatment. The acid is preferably one which contains the negative radical of the metal compound. Thus in the case of cupric chloride it would be hydrochloric acid, in the case of cupric nitrate it would be nitric acid, and sulphuric acid for sulphates. This addition of acid in many cases increases the degree and rate of regeneration. This additional acid is required in those cases where on account of the acidic character of the salt or metal compound in the presence of water or moisture acid is removed by reaction with the basic constituents of the clay employed or absorbed as acid by the clay. As understood by the person skilled in the art, the amount of acid to be added will depend upon a number of factors including the character of the clay, the degree of hydrolysis of the salt and all of which may be readily ascertainable, if not by computation, then by trial.

The drawing accompanying the present application shows schematically apparatus suitable for use in practicing the invention. Referring to the drawing the numeral 1 indicates a centrifugal pump. The numeral 2 indicates a settling tank. The discharge end of centrifugal pump 1 is connected with the settling tank 2 by means of a pipe 3, the pipe 3 discharging into the tank 2 about midway of its height. The numeral 4 indicates a line from which the sour oil to be treated is taken. The tank 2 is conically shaped at its bottom and discharges from its bottom into a pipe 5 which connects with a pipe 6 which leads to the inlet side of the centrifugal pump 1, the pipe 6 forming a continuation of the pipe 4. A hopper 7 is connected by means of a pipe 8 to the pipe 6 for introducing into the pipe 6 the metal compound or clay and metal compound mixtures described above. A pipe 9 connects with the pipe 6 for introducing air or oxygen into the pipe 6 leading to the inlet of the centrifugal pump 1. The air or oxygen is preferably dry. Hydrochloric acid, preferably as dry hydrochloric acid gas, is introduced into the pipe 6 by means of the pipe 10. A pipe 11 may be connected with the pipe 3 to discharge oil into the hopper 7 to facilitate the discharge of clay and reagent from the hopper 7 into the pipe 6. To the upper end of the tank 2, or near its upper end, is connected a discharge pipe 12 for the treated product. A strainer or filter 13 may be connected with

the discharge pipe 12 to remove any entrained metal compound, clay, or suspended matter in the oil treated. The numeral 14 indicates valves for suitably controlling the flow in the various pipes. A pipe 15 also connects with the discharge from the centrifugal pump 1, the purpose of said pipe 15 being to enable the system or apparatus to be emptied.

In operation the oil to be treated enters from the pipe 4 into the pipe 6 where it is mixed with hydrochloric acid and air respectively entering the pipe 6 from the pipes 10 and 9. The metal compound or mixture of metal compound and adsorbent clay enters the pipe 6 from the hopper 7 by means of the pipe 8. In this description of the operation, a mixture of 95% clay and 5% cupric chloride will be taken as illustrative of the reagents employed. The sour oil, substantially free of water (that is without admixture with water), is intimately mixed with the air, hydrochloric acid and clay-cupric chloride mixture in the centrifugal pump 1 and the mixture is discharged through the pipe 3 into the tank 2 where the clay-cupric chloride mixture settles from the oil in the conical portion of the tank 2. The settled clay-cupric chloride mixture is then redrawn into the pipe 6 through the pipe 5 under the action of the pump for treating further quantities of oil.

The treated or sweet oil is withdrawn from the tank 2 by means of the pipe 12, and, if necessary, passed through a strainer 13 to remove suspended matter. When air is introduced through the pipe 9, nitrogen will also escape with the oil passing out through 12.

For a naphtha containing 44 milligrams mercaptans per 100 cubic centimeters of naphtha and containing 0.060% total sulphur and 5.0 milligrams gums (by copper dish method) per 100 cubic centimeters oil, it has been found that 25 barrels of such an oil may be circulated in the apparatus shown with 125 pounds of a clay mixture containing 95% clay and 5% cupric chloride and the sweetened oil withdrawn at 12. The sweetening is substantially fully accomplished after the mixture of oil and reagents has passed through the centrifugal pump 11.

As the oil to be treated enters the circulating body of oil and reagents from the pipe 4, the treated oil is withdrawn by the pipe 12. The clay-cupric chloride mixture is thus continually re-circulated with oil to be treated.

The clay-cupric chloride mixture seems to be utilizable as long as it is practically possible to circulate it with the oil under treatment in the apparatus shown. The conversion of the mercaptans into doctor sweet products is accompanied by the formation of water which is taken up by the clay mixture together with water or moisture associated with the air, dry hydrochloric acid, or oil fed into the apparatus as described. It has been found that when the moisture content of the clay mixture reaches about 10 to 14 per cent, small spherical pellets are formed in the apparatus shown, the said pellets then being considerably smaller than mustard seed.

Before this stage of pellet formation is reached, for example when the moisture or water content of the clay is about 9 per cent, the settled clay mixture in the tank 2 may be withdrawn by pumping it out through the pipe 15, and the so withdrawn clay mixture, which is in the form of a slurry with oil, is subjected to a drying operation in order to reduce the moisture or water content, whereupon the clay mixture may be used again for treating further quantities of oil until the water concentration builds up again to an objectionable degree, after which the clay mixture may be again freed of water by drying and used over again.

The drying of the clay mixture slurry may be accomplished by spreading the slurry out in thin layers and permitting the oil and moisture to evaporate, either with or without the application of heat. When treating raffinates, the slurry of raffinate and clay mixture is advantageously dried by distillation under reduced pressure at a temperature preferably not exceeding 200° F. The vacuum employed with this temperature is 28 inches or an absolute pressure of 1.92 inches.

In order to render the oil treated in accordance with the present process O. K. corrosion, in addition to doctor sweet, mercurous chloride is added to the metal compounds above described or to the mixture of such metal compounds with the clays described. For illustration, in the specific example described above in connection with the treatment of naphtha, 5 pounds of mercurous chloride are added to the 125 pounds of clay-cupric chloride mixture. When such a mixture of oil, clay, cupric chloride, mercurous chloride, air and hydrochloric acid are mixed in the centrifugal pump 1 the oil product passing out of the centrifugal pump is doctor sweet, and also O. K. corrosion at 210° F. for 30 minutes. The manner of operating the apparatus is the same as when using the clay-cupric chloride mixture without the addition of the mercurous chloride, and the formation of pellets may be prevented by drying the clay-mixture slurry from the tank 2 as previously described, and the dried clay mixture thereby rendered suitable for re-use.

Suitable mixtures for rendering naphthas, water whites, raffinates and other oils even heavier than these doctor sweet and O. K. corrosion comprise an intimate mixture of finely divided clay, cupric chloride and mercurous chloride in the following proportions: mercurous chloride 1–8%; cupric chloride 1 to 30%, and the remainder of the 100% being clay.

In the above described processes of treating mineral oils finely divided kieselguhr, pumice, calcium silicate, porous earthenware, and other non adsorbent materials may be substituted in whole or in part for the clays above described.

The gasoline or other oils containing mercaptans or other organic sour constituents are sweetened by treatment according to the present process. The mercaptans which are the principal sour constituents are changed into organic disulphides of the type R—S—S—R in the sweet gasolene. As a result of this conversion of mercaptans into disulphides, acid (as hydrochloric acid when using cupric chloride) appears to arise which would otherwise be found present in the treated gasolene or other oil were it not for the presence of the clay which appears to retain the acid and prevents it from contaminating the sweetened material. The clay has the further action of retaining the acid so that it may be present in contact or in association with the metal compound so that the oxygen or air used to accomplish the regeneration may accomplish its function.

The amount of air or oxygen introduced into the pipe 6 through the pipe 9 must be sufficient to accomplish the regeneration of the reagents employed. Roughly it might be said that the quantity required must be sufficient to keep the metal compounds used in their higher valency

condition. An excess of air or oxygen appears to be without harmful influence on the treatments of the oils. For example, in the case of cupric chloride, enough air or oxygen must be used to keep the cupric chloride in the cupric condition. The dry hydrochloric acid gas added through the pipe 10 is added in sufficient quantity to make up any loss of hydrochloric acid from the cupric chloride. In the specific examples given above the hydrochloric acid gas added may amount to about 0.01 cubic foot dry hydrochloric acid gas per barrel of oil treated, although the amount of acid may exceed this amount. The excess of acid seems to be taken up by the clay mixtures used, permitting the treated oils to escape through the pipe 12 free of hydrochloric acid.

In place of mercurous chloride may be employed equivalent amounts of cuprous chloride, cobaltous chloride, and cadmium chloride.

In cases where the oil or material to be treated contains considerable amounts of hydrogen sulphide in addition to the mercaptans it is preferable to intimately contact the material with an aqueous caustic soda solution for the purpose of removing the hydrogen sulphide as sodium sulphide. In the case of treating naphthas, gasolenes or kerosenes as now prepared by refineries it is not usually necessary to employ this caustic alkali treatment as a preliminary step to the process of the present invention, for the reason that the naphtha, gasolene or kerosene is usually during its preparation or manufacture by the refineries intimately contacted with a water solution of sodium hydroxide which would remove hydrogen sulphide and compounds of a kindred nature.

The terms "oxygen" or "gaseous oxygen" as used herein and in the appended claims are intended to include, wherever the context permits, pure oxygen, gases rich in oxygen, and gases containing oxygen in admixture with other gases, an example of the latter being atmospheric air which is a mixture comprising about twenty-one per cent oxygen by volume.

I claim:

1. The process of treating sour hydrocarbon oil which exhibits a positive corrosion test to sweeten same and to render the same less corrosive which comprises contacting said oil, at substantially an atmospheric temperature, in the presence of gaseous oxygen added thereto, with a substantially dry mixture comprising an adsorbent material, a compound of copper which reacts with mercaptans to form mercaptides and a material selected from the group consisting of mercurous chloride, cobaltous chloride and cadmium chloride, all of said salts being present in said mixture in solid condition.

2. The process of treating sour hydrocarbon oil which exhibits a positive corrosion test to sweeten same and to render the same less corrosive which comprises contacting said oil, at substantially an atmospheric temperature in the presence of gaseous oxygen added thereto, with a substantially dry mixture comprising a chloride of copper, an adsorbent material, and a material selected from the group consisting of mercurous chloride, cobaltous chloride and cadmium chloride, all of said chlorides being present in said mixture in solid condition.

3. The process of treating sour hydrocarbon oil which exhibits a positive corrosion test to sweeten same and to render the same less corrosive, which comprises subjecting said oil, in the presence of added gaseous oxygen, to the action of solid treating agents comprising a compound of a metal forming organic sulphur metal compounds with substances in the oil imparting sourness thereto and which metal compound is maintained active by said oxygen, an adsorbent material, and a compound of a metal which reduces the corrosiveness of the oil.

4. In the treatment of sour hydrocarbon oil which exhibits a positive corrosion test to sweeten same and to render the same less corrosive, the process which comprises contacting said oil, after the removal of hydrogen sulphide therefrom, with solid treating agents comprising a compound of a metal forming organic sulphur metal compounds with substances in the oil imparting sourness thereto and which metal compound is maintained active in the presence of oxygen, an adsorbent material and a compound of a metal which reduces the corrosiveness of the oil, the said contacting step being conducted in the presence of an added gaseous oxidizing agent.

5. The process of treating sour hydrocarbon oil which exhibits a positive corrosion test to sweeten same and to render the same less corrosive, which comprises incorporating an oxygen containing gas in the said oil and subjecting the resulting mixture to the action of (1) a solid salt of a metal which reacts with sour constituents in the oil to form organic sulphur metal compounds, and which is maintained active in the presence of oxygen, (2) an adsorbent material, and (3) another solid salt of a metal which reduces corrosiveness of the oil.

6. The process of treating sour hydrocarbon oil which exhibits a positive corrosion test to sweeten same and to render the same less corrosive, which comprises subjecting said oil, incorporated with gaseous oxygen, to the action of (1) a solid salt of a metal which reacts with sour constituents in the oil to form organic sulphur metal compounds and which is maintained active in the presence of gaseous oxygen (2) an adsorbent material and (3) another solid salt selected from the group consisting of mercurous chloride, cuprous chloride, cobaltous chloride and cadmium chloride.

7. The process of treating sour hydrocarbon oil which exhibits a positive corrosion test to sweeten same and to render the same less corrosive, which comprises contacting the said oil with a mixture comprising an adsorbent material, a solid compound which reduces corrosiveness of the oil, and a solid compound of a metal forming organic sulphur metal compounds with compounds in the oil imparting sourness thereto and which is maintained active in the presence of oxygen, the said contacting step being conducted in the presence of added oxygen.

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