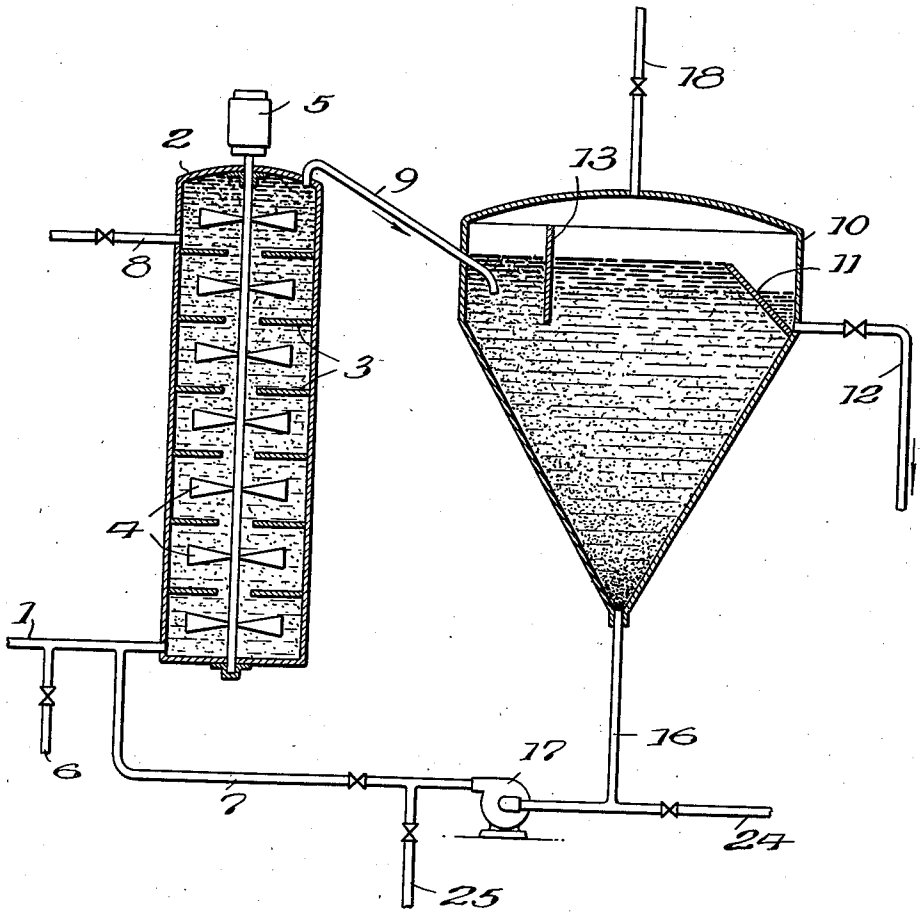
May 26, 1942. L. U. FRANKLIN 2,284,273

PROCESS FOR SWEETENING SOUR HYDROCARBON OILS

Filed July 20, 1939



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Patented May 26, 1942 2,284,273

UNITED STATES PATENT OFFICE

2,284,273

PROCESS FOR SWEETENING SOUR HYDROCARBON OILS

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Application July 20, 1939, Serial No. 285,636

3 Claims. (Cl. 196—29)

My invention relates to sweetening sour hydrocarbon oils, more particularly light petroleum distillates such as gasolines, naphthas, kerosenes, furnace oils and the like, that is to say, to a process for treating oils of the character indicated, containing "sour" and malodorous sulfur impurities such as mercaptans, to convert such impurities into sulfur compounds of less objectionable character, whereby the treated oils are rendered sweet to the "doctor" test and free from disagreeable odor.

More particularly, my invention relates to improvements in what is known in the petroleum art as "copper sweetening," i. e., a process in which sour oil to be treated is contacted with a treating agent comprising a compound or mixture of compounds capable of ionizing to form cupric and chloride ions, in the presence of a substantially inert solid carrying agent of highly advantageous character, to wit, finely divided asbestos.

There are three general types of prior art copper-sweetening processes wherein the hydrocarbon oil is treated in the liquid phase. These are the so-called "solution," "percolation" and "slurry" processes, respectively. In the so-called "solution-type" process, the oil is contacted with an aqueous solution containing the sweetening reagent. In the so-called "percolation-type" process, the oil to be sweetened is passed through a stationary mass or bed of solid treating agent in more or less dry form, usually supported upon a solid carrier.

In the so-called "slurry-type" process, to which my invention relates, the sweetening reagent is temporarily suspended in a flowing stream of oil to be sweetened. It is obvious that, in such a process, it is desirable to provide a solid sweetening agent which is easily suspended in the oil, and easily removable therefrom after sweetening has been accomplished. Provided this can be done, the slurry-type process has definite advantages over the other two types of processes mentioned hereinabove.

Possibly because highly adsorbent solid contact materials, such as fuller's earth, activated chars and the like, have long been used in the form of beds, either as such or impregnated with chemicals of various kinds, prior proponents of slurry-type processes have suggested the use of such highly adsorbent materials as solid carriers for the chemical treating agents in slurry-type processes. It has also been suggested that instead of such highly adsorbent materials, pumice, calcium silicate, porous earthenware and sand (which are neither highly adsorbent nor absorbent) may be employed.

Among the objects achieved by my invention is the provision of a sweetening process of the general character indicated, that is to say, a sweetening process of the so-called "slurry-type," wherein the agent employed to carry or support the chemically sweetened material in suspension is of improved type, possessing certain marked advantages more fully set forth hereinbelow.

My invention contemplates the use of finely divided asbestos as a carrying or supporting means for the sweetening chemical or chemicals in a sweetening process of the character indicated, that is to say, a slurry-type sweetening process in which the entire sweetening agent (comprising the sweetening chemicals and asbestos) is temporarily suspended in the oil to be sweetened.

Various sweetening chemicals may be employed, although my invention is particularly useful in connection with a chemical or mixture of chemicals capable, upon ionization, of yielding chloride ions and cupric ions. Thus cupric chloride itself may be used. It is advantageous, however, to employ a mixture of cupric sulfate and sodium chloride, the reaction products of which include cupric chloride. But my invention is less concerned with the specific nature of the chemical reagent or reagents, (for many such reagents are referred to in the prior art which are capable of sweetening sour gasolines and other oils), than with the use of asbestos as a solid carrying agent for the chemical or chemicals in a process of the character indicated.

I have discovered that asbestos, when used in accordance with my process, is free from any tendency to cause polymerization of unstable, unsaturated constituents present in the hydrocarbon oils undergoing treatment. Even in the presence of copper compounds, asbestos does not exert any deleterious effect upon color-imparting and gum-forming constituents; for instance, those present in substantial amounts in most cracked gasolines.

I have also found that a mixture of asbestos with the solid chemical or chemicals used for sweetening is readily suspended in the oil under turbulent flow conditions, induced by agitation or the like. On the other hand, when the mixture of oil and solid treating agent containing asbestos is passed into a quiescent zone, the treating material settles out easily from the oil. The treated oil can therefore be freed of solid treating agent and withdrawn without difficulty, and

the use of excessively large or complicated separating apparatus is avoided.

I have also discovered that asbestos, because of its physical character, admirably performs its primary function, that is to say it represents an ideal carrying or supporting means for the sweetening chemical or chemicals. There is little or no tendency toward separation of the asbestos from the sweetening chemical or chemicals throughout the cycle of operations, and the chemical agent or agents are suitably exposed over a large surface for contact with the oil, while at the same time there is no tendency for asbestos to hold the sweetening agent or agents in such form as to render access of the regenerating gas to the chemicals difficulty or impossible, as is true when highly adsorbent bodies are used as carrying agents.

Asbestos also has a marked advantage over prior art materials in that it does not possess an abrasive character. On the contrary, I have discovered that it actually serves as a "lubricant" in the system, and that an admixture of a given solid sweetening chemical and asbestos is considerably less abrasive in effect than the chemical alone. Asbestos, instead of aggravating the tendency toward abrasion as is the case with most other materials, actually tends to reduce such abrasive effects as are possessed by solid sweetening chemicals when used alone.

Moreover, I have discovered that the substantially non-adsorbent character of asbestos makes it possible to maintain the total treating agent in a highly active condition, free from adsorbed or deposited gums. Fuller's earth and other highly adsorbent materials tend to form gums which deposit on the available surfaces of the treating material, thereby reducing the contact efficiency. This harmful effect is substantially eliminated when asbestos is used as the carrying or supporting agent.

I have also found that asbestos has a lower tendency to selectively absorb any moisture present, in contra-distinction to fuller's earth and other highly adsorbent bodies, which tend to bind any free moisture present and thereby reduce its effectiveness. As is well known, some moisture must be present, although not in amount sufficient to form an independent aqueous phase. By proceeding in accordance with my invention, using asbestos as the solid carrying or supporting agent, it is possible to maintain a desired moisture content more easily and accurately, and more effectively, than is true with respect to highly adsorbent bodies.

The materials which have been proposed for use in the prior art do not have the advantageous combination of properties referred to above. Thus, fuller's earth and similar highly adsorbent bodies have a marked tendency to cause polymerization of unstable, unsaturated constituents of hydrocarbon oils. As is well known, they are frequently used for the deliberate purpose of causing polymerization of color-forming and gum-forming bodies, the polymers being subsequently removed by distillation. In sweetening processes, however, such re-distillation must be avoided for the reason that sweet gasoline containing organic disulfides tends to become sour again when elevated to the temperatures necessary for such distillation. Consequently, prior slurry-type processes have tended to cause marked reduction in oxygen stability of the oils treated, whereas in my process, because of the use of asbestos, this tendency is avoided or reduced to a very remarkable extent.

It may be mentioned at this point that asbestos is particularly useful as a carrying or supporting means in a copper sweetening process, for the reason that copper compounds tend to promote oxidation and polymerization reactions, with resultant formation of gums and highly colored bodies. A combination of copper compounds and a highly adsorbent material such as fuller's earth is particularly offensive in this respect, whereas I have successfully "copper-sweetened" sour cracked distillates, using asbestos as the supporting body for the copper-containing chemical, without impairing the oxygen stability of the oil.

It has previously been contended that highly adsorbent bodies, such as fuller's earth and the like, are advantageous because of their tendency to hold or "grip" the treating chemicals more closely than is true of less highly adsorbent bodies. It is probably true that they do have such a tendency, but I have discovered that this very fact constitutes a definite disadvantage with respect to the use of such materials. Adsorption of the chemical in the fine pores of an adsorbent, such as fuller's earth, materially increases the difficulty of regeneration. The oxygen supplied for regeneration cannot reach all of the adsorbent chemical, and there is a tendency for a large part of the adsorbed chemical or chemicals to remain throughout the system in a rather highly "spent" condition. These disadvantages are to a considerable extent cumulative. Asbestos, on the other hand, is free from these disadvantages.

Other proposed prior art materials of less highly adsorbent character, such as pumice, finely divided firebrick and the like, are not suitable for use as carrying or supporting agents in slurry-type processes. They tend to separate from the chemical or chemicals used, they are excessively abrasive, and they are difficult to maintain in suspension. Asbestos, on the other hand, admirably serves its primary function as a supporting or carrying agent, does not tend to separate from the chemical to any substantial extent, and is not abrasive in character. It possesses an extremely large contact surface per unit of weight, without the disadvantages inherent in the use of highly adsorbent materials on the one hand, and the prior art absorbent materials on the other hand. It does not pack when allowed to settle. A slurry containing it is easily stirred and easily pumped, and at the same time easy to separate from the oil undergoing treatment. Chemicals carried on the asbestos are readily regenerated.

The asbestos employed in accordance with my invention is preferably pulverized prior to use. An especially satisfactory grade of asbestos is that sold by Johns Manville Company as "7-RF Asbestos Floats." This particular material, although finely ground, retains its fibrous nature, a large proportion of fibers having a length of from 2 to 3 millimeters being present. However, other finely divided grades of asbestos may be employed.

As has been pointed out hereinabove, various sweetening chemicals may be employed in conjunction with asbestos, but I prefer to employ a chemical or mixture of chemicals capable of reacting with mercaptans present in oils containing the same to form sweet sulfur compounds, such as organic disulfides, and also capable of being

regenerated by means of oxygen or an oxygen-containing gas. I have obtained the best results, however, by using a mixture of asbestos, cupric sulfate and sodium chloride, all finely divided in form. The following proportions have been found especially advantageous:

	Parts by weight
$CuSO_4.5H_2O$	1
NaCl	2 to 4 (preferably 3)
Asbestos	0.5 to 1.

Increasing the amount of asbestos in the mixture above about 20 per cent by weight is neither necessary nor particularly effective, for amounts of asbestos in excess of about 20 per cent by weight simply represent an unnecessary excess of asbestos above that amount necessary to serve as a proper carrying agent. On the other hand, the use of asbestos in amounts lower than about 5 per cent by weight is ordinarily to be avoided.

Where a mixture of cupric sulfate and sodium chloride is used, as aforesaid, sufficient time should be given to permit reaction with resultant formation of cupric chloride prior to use. This reaction is facilitated by the presence of moisture. After the reaction has taken place, however, the solid treating agent is preferably preconditioned down to a total moisture content of 0.5 to 1.0 per cent, as set forth in the copending application of Leslie U. Franklin, Walter H. Weeks, and Jack W. Harris, Serial No. 284,117, filed July 12, 1939. This pre-conditioning step may take place before the sweetening agent is added to the system or thereafter, as also disclosed in the application just referred to.

In employing the improved sweetening agent in accordance with my process, a suitable quantity of the treating agent is suspended in a flowing stream of sour oil, such as sour gasoline or the like, and the mixture is caused to flow through a reaction zone under turbulent conditions, enough agitation being supplied to maintain the solid treating agent in good suspension in the oil throughout this zone. Oxygen, air or other oxygen-containing gas is added, as necessary, to effect regeneration of the sweetening agent, and moisture and HCl may also be added when and as necessary to replace losses of these materials from the system. In many cases, however, it is unnecessary to add moisture or HCl. In any event, the moisture content should be so controlled, in accordance with the disclosure contained in the aforesaid application Serial No. 284,117, as to maintain the utmost uniformity and to hold the moisture content of the treating agent between 0.5 and 7 per cent by weight. The presence of enough moisture to form an independent solution phase is undesirable and should be avoided. On the other hand, excessive dryness is also undesirable.

The mixture leaving the reaction zone is then transferred to a separating zone where quiescent flow conditions are maintained. Sweetened oil, free from solid treating agent, is withdrawn from this zone. The solid treating agent settles to the bottom of the separating zone in the form of a relatively highly concentrated slurry in sweetened oil, which is then continuously pumped back into the original reaction zone. By maintaining the moisture content of the total solid treating agent within appropriate limits, as disclosed in the aforesaid application of Franklin, Weeks, and Harris, Serial No. 284,117, filed July 12, 1939, it is possible, when asbestos is employed as the solid supporting or carrying agent in accordance with my present invention, to maintain the total treating agent in the form of a highly efficient flocculent or semi-flocculent suspension and this is facilitated by grinding the solid treating agent at some point in the cycle. Grinding is, however, much less effective with respect to the use of carrying and supporting materials other than asbestos.

In the drawing accompanying and forming part of this specification, there is illustrated a simple form of apparatus useful in carrying out the process of my invention, using my improved sweetening agent. In this drawing,

The single figure is a more or less diagrammatic vertical sectional view of apparatus for the purpose indicated.

Referring now to the drawing, sour oil to be sweetened enters the system through a pipe 1 communicating with the lower portion of a treating vessel 2, the interior of which is preferably provided with a plurality of baffles 3 and agitating means 4 driven by a motor 5. Oxygen, air or other oxygen-containing gas is introduced at some point early in the system, as for example by means of a valved pipe 6. Maintaining a moderate super-atmospheric pressure on the system assists in maintaining the added oxygen in solution in the oil.

Solid sweetening agent, comprising a reacted mixture of cupric sulfate, sodium chloride and asbestos, is also introduced into the lower portion of the treating vessel 2 by means of a pipe 7 which, as in the instance illustrated, preferably communicates with the pipe 1 through which sour gasoline is supplied to the treating vessel 2.

The mixture of oil, oxygen-containing gas and solid treating agent passes upwardly through the treating vessel 2 under turbulent flow conditions induced by the agitating means 4. Sweetening of the oil is rapidly effected and regeneration of the sweetening agent also takes place in the vessel 2. Moisture may be added to the system through the valved pipe 8, preferably in the form of a finely divided suspension in oil, and if desired, HCl may be added at the same or any other convenient point.

The mixture of sweetened oil and treating agent upon reaching the top of the vessel 2 passes through a pipe 9 into a separator 10. The separator 10, as shown, is preferably of larger internal diameter than the treating vessel 2 and is constructed substantially in the form of an inverted cone, in order to facilitate settling of the solid treating agent. A weir 11 is provided for maintaining a definite level of liquid within the vessel 10, oil flowing over the top of this weir being withdrawn from the vessel 10 through an outlet 12. A baffle plate 13 is advantageously provided between the inlet pipe 9 and the weir 11 in order to prevent any of the solid treating agent from passing directly across the upper surface of the liquid.

In the separating vessel 10, under the influence of the substantially quiescent flow conditions maintained therein, the solid treating agent is caused to settle out. The oil flowing over the weir 11 and out through the pipe 12 is free or substantially free from solid treating agent. The separated solid treating agent, in the form of a relatively concentrated slurry in sweetened oil, is withdrawn from the bottom of the separating vessel 10 through a pipe 16 and is returned by means of a pump 17 and line 7 to the treating vessel 2.

A valved vent pipe 18 is provided at the top of the vessel 10, its purpose being to aid in maintaining a constant pressure within the system, and to prevent accumulation of undue quantities of air or hydrocarbon vapors in the system.

Fresh quantities of sweetening agent may be added through a line 24 communicating with the suction side of the pipe 17, while a valved line 25 is provided for removing treating agent from the system whenever desired. In actual practice, occasional removal of the sweetening agent is sometimes desirable, but it is ordinarily advantageous to add relatively small amounts of fresh sweetening agent to the system from time to time. This may cause the total amount of the solid treating agent in the system to build up to some extent during extended operating periods, but this is not disadvantageous so long as the system is not overloaded, that is to say, so long as the amount of sweetening material in the system is not increased to such an extent as to make it difficult to effect contact and separation.

As a specific example of the use of my invention, I have obtained favorable results in sweetening sour gasoline by using a mixture of 208 pounds of $CuSO_4.5H_2O$, 625 pounds of sodium chloride and 167 pounds of finely divided asbestos, the sweetening material thus prepared being preconditioned and maintained in accordance with the disclosure of the aforesaid application Serial No. 284,117.

Various details of operation are disclosed in the various copending applications referred to, but need not be reviewed in detail here inasmuch as my present invention resides primarily in the use of asbestos in a system of the general character indicated, rather than in any specific operating details. Consequently, while I have described my invention hereinabove with respect to various operating details, my invention is not limited to such illustrative details as have been given hereinabove by way of example, but may be variously embodied within the scope of the claims hereinafter made.

What I claim is:

1. The method of sweetening sour petroleum oils containing mercaptans which comprises suspending in a flowing stream of said oil, in the presence of an oxygen-containing gas, a substantially dry solid mixture of asbestos and a substance capable of reacting with said mercaptans to form sweet sulfur compounds and of regeneration by said oxygen-containing gas.

2. The method of sweetening sour petroleum oils, which comprises suspending in a flowing stream of said oil, in the presence of an oxygen-containing gas, a substantially dry solid mixture of asbestos and a substance capable of yielding cupric and chloride ions upon ionization.

3. The method of sweetening sour petroleum oils which comprises suspending in a flowing stream of said oil, in the presence of any oxygen-containing gas, a substantially dry solid mixture of asbestos and a substance capable of yielding cupric and chloride ions upon ionization, passing the mixture to a settling zone, withdrawing sweetened oil from said settling zone, and recirculating the separated solid mixture into contact with the flowing stream of sour oil.

LESLIE U. FRANKLIN.