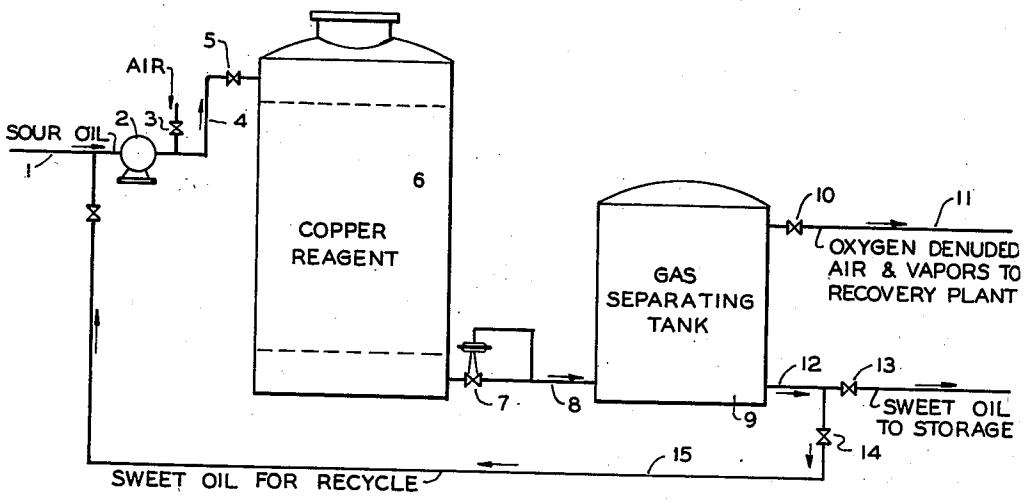
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TREATMENT OF HYDROCARBON OILS

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TREATMENT OF HYDROCARBON OILS

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This invention relates to the treatment of sour hydrocarbon oils to sweeten the same.

More specifically this invention relates to the sweetening of natural and refinery gasolines, naphthas, and kerosenes, hereinafter termed "light hydrocarbon oils," to remove therefrom sulfur compounds such as mercaptans which are responsive for bad odor or "sourness," and for corrosiveness of the oils and particularly to an improvement in the sweetening of mercaptan bearing light hydrocarbon oils by means of reagents containing copper salts.

The so-called copper sweetening processes are well known both in the art and in industry. One of these processes described by Buell in application Serial No. 121,908, filed January 22, 1937, and issued as U. S. Patent 2,094,085, employs solid sweetening reagents comprising adsorbent materials impregnated with solutions containing cupric copper and chloride salts. An important improvement has now been discovered in the operation of sweetening with the said copper reagents, said improvement being the invention described herein.

In the Buell process the "sour" oil is passed in liquid state, together with added air or oxygen, over the solid reagent at flow rates, preferably in the range of 1 to 5 volumes of oil per hour per volume of reagent. The temperatures of treating in such a process are ordinary atmospheric temperatures, say 60° to 110° F., and the total pressure on the air-oil system is usually 1 to 6 atmospheres.

When mercaptan-bearing light oils are passed in such a process over a copper containing reagent, the following reaction occurs:

(1) $4CuCl_2+4R-SH=2R-S-SR+4CuCl+4HCl$

Cupric chloride; mercaptan; alkyl disulfide; cuprous chloride; hydrochloric acid

Thus, it is seen that the mercaptans in the oil are converted to less objectionable disulfides, while the cupric compound is reduced to the cuprous state and hydrochloric acid is formed.

In order to maintain the activity of the solid copper-containing reagent, it is necessary to add to the oil prior to its passage over the reagent, a sufficient quantity of oxygen or air to regenerate the spent reagent according to this reaction:

(2) $4CuCl+4HCl+O_2=4CuCl_2+2H_2O$

Cuprous chloride; hydrochloric acid; oxygen; cupric chloride; water

Thus, when the air is present in solution in the oil at the time of sweetening, Reactions 1 and 2 occur simultaneously, and the reagent is maintained in an active state.

From Reaction 2 it is apparent that the amount of oxygen (or air) to be added to maintain the reagent in an active state is directly proportional to the concentration of mercaptans in the "sour" oil. Since oxygen gas is expensive to provide in such a process, the common expedient is to provide oxygen in the form of air; and the supplying of air in solution in the "sour" oil is an essential step in the sweetening process.

From theoretical considerations of the equation of Reaction 2 the volume of air required per volume of oil is about 0.08 volume of air per volume of oil per 0.01 per cent of mercaptan sulfur originally in the oil. However, when only theoretical volumes of air are introduced along with the "sour" oil the regeneration reaction is not satisfactorily complete. In the first place, the speed of reaction according to Equation 2 is directly proportional to the oxygen concentration by the law of mass action. For high flow rates of "sour" oil in the sweetening process then it is imperative to speed up Reaction 2 by providing an oxygen concentration greater than theoretical requirement. Further, mechanical difficulties attending the diffusion of air throughout the oil prior to solution therein makes the resulting solution of non-uniform concentration in industrial installations. Due to this latter fact, it is necessary that the lowest concentration of air in any part of the incoming "sour" oil stream be substantially greater than the theoretical air requirement, hence an excess of air must be added. In actual practice it has been found that the minimum quantity of air supplied to the treaters must be at least twice the theoretical requirement. On this basis, an empirical formula is evolved as follows: The amount of air necessary to maintain the activity of the solid copper reagent is about 1 cubic foot of air per barrel of "sour" oil per 0.01 per cent mercaptan sulfur in the "sour" oil.

The addition of air to the liquid hydrocarbon oil involves the solubility of the air in the oil which depends in turn on (*a*) the temperature of the oil, and (*b*) the total pressure on the air-oil system. If the quantity of air to be added is very large as in an oil containing high percentages of mercaptan sulfur, the solution of said large amount of air in the oil becomes a problem since factors (*a*) and (*b*) listed above are not subject to wide variation in industrial installations of the sweetening process. Thus, the temperature of the oil may not be varied over a range wider than

about 60 to 110° F. for liquid phase treating. Also, the pressure at which air may be supplied cannot exceed the operating pressure limits of plant equipment, usually 15 to 100 pounds per square inch, since high pressure equipment would be relatively too expensive.

The solubility of air in hydrocarbon oils varies with temperature and pressure, and with the specific gravity of the oil. For example, the solubility of air in an oil decreases rapidly with rising temperature, other factors remaining constant. Or at constant temperature, the solubility of air in an oil increases with total pressure on the gas-liquid system. The effect of varying gravity of the oil on solubility of air in the oil is also tremendous, with air solubility decreasing rapidly and finally reaching very low figures as the average molecular weight of the hydrocarbon molecules increases. Thus, at a constant partial pressure of air in contact with a hydrocarbon oil, the solubility of air is greater, the higher the A. P. I. gravity of the oil (or the lower the specific gravity of the oil). In sweetening two oils of equal mercaptan content, one a natural gasoline, and the other a kerosene cut, much more difficulty is experienced in dissolving the requisite air in the kerosene. Thus, a mercaptan content of 0.04 per cent may be easily handled in a natural gasoline of 12 pound Reid vapor pressure and 80° A. P. I. gravity, but the same mercaptan content may present a serious sweetening problem in a kerosene. For instance, a gasoline of 60 to 80° A. P. I. gravity will dissolve about 3 to 5 cubic feet of air per barrel of oil at pressures of 50 to 60 pounds gage and temperatures between 60 and 100° F. On the other hand a kerosene fraction of 40° A. P. I. gravity may dissolve 0.5 to 2 cubic feet of air per barrel at the same temperatures and pressures.

In the treatment of gasolines with mercaptan sulfur contents of about 0.05 per cent or less, the amount of air required usually does not exceed the maximum solubility value under the operating conditions normally obtainable. However, in the treatment of gasolines with mercaptan sulfur contents of from 0.05 to 0.30 per cent or more the amount of air required for adequate regeneration is in excess of the solubility of air in the said oils at pressures within the nominal operating range. Similarly, kerosenes or heavy naphthas with even moderate mercaptan sulfur contents cannot be handled in the usual manner. If under these conditions, air be added in excess of its solubility, it does not dissolve and its utility in reactivating the sweetening reagent is almost nil. In such an instance the reagent shows a gradual spending and migration of copper salts, which greatly shortens its life in the sweetening process and allows the transfer of deleterious decomposition products from the reagent to the sweetened oil. Also, the admission to the reagent bed of entrained air in the oil has the effect of displacing mechanically the reagent particles, giving rise to harmful channeling effects which decrease the efficiency of the reagent.

An object of my invention is to provide a process whereby the sweetening of the very sour gasolines or heavy naphthas and kerosenes by means of solid reagents comprising solutions of copper salts and chlorides adsorbed on a solid adsorbent material such as fuller's earth may be accomplished efficiently and economically.

A further object of my invention is to improve existing copper sweetening processes utilizing solid copper containing reagents by accomplishing regeneration of the useful reagents within more economical limits of time and operating pressures.

I have now discovered an important improvement in the sweetening of light hydrocarbon oils according to the previously described process utilizing a solid copper containing reagent when the mercaptan content of the "sour" oil is so great, or air solubility of the oil is so low that air in an amount equal to or greater than the solubility of air in the oil at convenient pressures is required. This improvement comprises returning to the sweetening reagent ahead of the point of air introduction and along with the "sour" oil a controlled percentage of sweetened oil. This sweetened oil acts as a carrier of air to the sweetening reagent, thus helping to maintain the activity of the reagent. Also the average mercaptan content of the oil passing to the reagent is decreased thereby, in an amount depending on the percentage of sweet oil recycled. Thus, the mercaptan content of the oil passing to the sweetening reagent may be reduced to a value which does not require the admixture of air in excess of the solubility of air in the oil at convenient working pressures and temperatures. With lowered mercaptan content, better regeneration is assured so that deterioration of the reagent and migration of the adsorbed copper salts is prevented. Such migration occurs only when the rate of Reaction 1 exceeds that of Reaction 2.

By operation in this manner, it is possible for the life of the reagent to be prolonged indefinitely because deterioration due to insufficient regeneration is avoided. Also, the cost of equipment for treating installations and air supply is reduced by the reduction in the pressure at which the necessary air must be supplied to obtain regeneration. Finally, a more satisfactory sweetened product is assured, free of decomposition products from the reagent.

The previously sweetened oil which I propose to recycle should first be stabilized by "flashing" or releasing part of the pressure in a separate flashing tank such as is shown in the figure of the drawing. This step is necessary because the sweetened oil having been saturated with air prior to sweetening still contains the oxygen denuded air (most of which is nitrogen) which must be allowed to escape, or the desired quantity of air cannot be dissolved in the mixture of sour and recycled sweetened oil.

In the drawing the figure represents one sort of apparatus in which I may operate my process. The sour oil enters through line 1 and is mixed with a predetermined quantity of recycled sweetened oil from line 13 by means of the control valve 14. The mixture passes through pump 2, whereby the pressure is raised to the desired level and into line 4 where a controlled quantity of air under the desired pressure is added through valve 3. The air may preferably be added through a porous diffuser to get uniform distribution which will aid in obtaining rapid solution of the air in the oil. The mixture of oil and air enters the copper reagent tower 6 by way of valve 5, passes downward through the reagent and leaves the tower through the pressure reducing valve 7. This mixture now at lower pressure passes through line 8 into a separating tank 9 where the oxygen denuded air flashes off the liquid oil. The denuded air and vapors may pass from the top of the separating tank through the valve 10 and the line 11 to the vapor recovery plant. The oil leaves the separating tank 9 by

way of line 12 and the stream is split, one part passing through valve 13 to sweet storage, and the other part through valve 14 and line 15 for recycling into the sour stream.

When operating according to my process in order to obtain a throughput of sour oil equivalent to that obtained in the absence of recycling, treating rates may be increased or larger reagent towers may be employed. With the more efficient regeneration resulting from recycling a portion of the sweet oil, the flow rate may easily be increased if desired to compensate for the portion of oil being recycled, without exceeding maximum permissible flow rates or causing channeling in the reagent bed. In fact, the increase in permissible flow rates according to my process may result in an increase in the capacity of a given installation, or permit a smaller installation to handle a definite volume of "sour" oil.

The following examples will serve to illustrate specific applications of my invention, but should not be construed as limitations therefor.

Example 1.—In sweetening a New Mexico natural gasoline of 80° A. P. I. gravity, having a mercaptan sulfur content of 0.24 per cent, the empirical formula governing the air requirement called for 24 cubic feet of air per barrel of gasoline, or about four times as much air as could be dissolved in the gasoline at temperatures between 60 and 110° F. and 75 pounds per sq. in. pressure. The copper sweetening reagent life in this instance was extremely short due to continuous deterioration, and the reagent became spent so rapidly that the process could not be utilized economically. By recycling 75 per cent of sweetened gasoline to the reagent along with 25 per cent of "sour" gasoline the regeneration process was accomplished so completely that the reagent showed no appreciable deterioration after long periods of continuous use.

Example 2.—In sweetening a West Texas kerosene containing 0.04 per cent mercaptan sulfur with a reagent of fuller's earth impregnated with a solution of cupric chloride, difficulty was experienced in providing sufficient air in solution in the kerosene to maintain the activity of the reagent. This condition was due to the slight solubility of air in the 40° A. P. I. gravity kerosene. By recycling 50 per cent of sweet kerosene along with the "sour" kerosene, it was possible to maintain the activity of the reagent and to prevent migration of the adsorbed copper salts and deterioration of the reagent.

I claim:

1. A process for sweetening mercaptan-containing light petroleum oil which comprises dissolving air in said oil, contacting said oil containing dissolved air with a solid sweetening reagent comprising an absorbent material impregnated with a solution of a copper salt and a chloride, passing the sweetened oil to a zone of lower pressure to remove an appreciable portion of the oxygen-denuded air from the oil, and recycling a controlled portion of the sweetened gasoline to the mercaptan-containing oil prior to the point of air introduction.

2. In a process for sweetening sour petroleum oil which comprises dissolving air in said oil and contacting the oil stream containing dissolved air with a solid reagent comprising an adsorbent carrier impregnated with a solution of a copper salt and a soluble chloride, the step of recycling to the sour oil stream prior to the point of air introduction a controlled portion of the sweet oil stream partially freed of oxygen-denuded air whereby the ratio of dissolved air to the mercaptan content of the sour oil is increased.

3. In a process for sweetening gasolines with mercaptan sulfur content greater than 0.10 weight per cent which comprises dissolving air in a stream of said gasoline and contacting the gasoline containing dissolved air with a solid reagent comprising an adsorbent carrier impregnated with a solution of a copper salt and a soluble chloride, the step of recycling to the sour oil stream prior to the point of air introduction a controlled portion of the sweetened oil stream partially freed of oxygen-denuded air whereby the ratio of dissolved air to the mercaptan content of the sour oil is increased.

4. In a process for sweetening mercaptan-containing petroleum oil by dissolving air therein and then contacting with a solid reagent comprising an adsorbent carrier impregnated with a solution of a copper salt and a chloride wherein the reagent is maintained at a substantially constant activity by the regenerating action of the dissolved air, the improvement of increasing the ratio of the volume of dissolved air to the mercaptan content of said oil by returning a controlled quantity of sweet oil partially freed of oxygen-denuded air to the untreated oil ahead of the point of air introduction.

5. In a process for sweetening mercaptan-containing petroleum oil by dissolving air therein and then contacting with a solid reagent comprising an adsorbent carrier impregnated with a solution of a copper salt and a chloride wherein the sweetening reagent is maintained at substantially its original activity by the action of the oxygen content of the dissolved air, the step of regulating the mercaptan content of said oil to a value compatible with the solubility of air in said oil by returning a controlled quantity of sweetened oil partially freed of oxygen-denuded air to the stream of untreated oil ahead of the point of air introduction.

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