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PROCESS FOR NEUTRALIZING AND SWEETENING GASOLINE

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In a copending application Serial No. 376,516, filed July 8, 1929, I have described and claimed a process for sweetening gasoline in which the mercaptans are continuously removed from gasolines and pressure distillates by passing such oils through a contacting vessel containing a mixture of lime, litharge, diatomaceous earth and a minute quantity of caustic soda, such mixture being a substantially dry powder.

In an application filed contemporaneously herewith, Serial No. 396,900, filed October 2, 1929, I have described and claimed a process for neutralizing acid treated gasolines and similar oils by treating them with a fluid magma composed of sodium hydroxid ground to a state of extreme subdivision in kerosene or a similar light oil vehicle, water being substantially excluded.

I have discovered that these two processes may be somewhat modified and then combined to produce a unitary process in which acid treated gasoline or distillate containing mercaptan sulfur may be simultaneously neutralized and sweetened at a reduced cost.

In putting my invention into practice I take the following steps. The gasoline (for example) is first treated with any desired quantity of sulfuric acid in any preferred manner. I prefer to treat continuously as my neutralization process is essentially continuous and continuous acid treatment gives the most even and dependable yield of treated stock.

The acid sludge should then be removed as completely as possible, preferably down to the point where the total acidity does not exceed 20 grams per barrel of oil, when calculated as sulfuric acid. This should not be considered a limitation on the usefulness of my process as it is essential to any successful treatment with alkalis and particularly where neutralization is conducted with aqueous alkalis instead of with my dry reagent.

To the stream of desludged oil should then be added a sufficient quantity of my sodium hydroxid reagent to completely neutralize the acidity and leave a very slight excess. This sodium hydroxid reagent is made by very finely grinding dry commercial sodium hydroxid, to a pasty or fluent condition in a high grade kerosene or equivalent petroleum product which may be mixed in small proportion with the gasoline without detriment to its qualities.

Either at this stage or else immediately after the desludging operation I add to the gasoline a sufficient quantity of a gasoline solution of sulfur to precipitate the lead from the lead mercaptide formed in the next stage of the operation. The quantity of sulfur added at this stage may equal the quantity of sulfur contained in the oil in mercaptan form, if this can be conveniently determined, or the correctness of the proportion may be checked from time to time by testing the effluent sweetened oil, as will hereafter be described.

The neutralized gasoline, containing the correct proportion of sulfur for sweetening and also retaining the neutralization reaction salts, is then passed to and through the lead contactor. This is a vessel of any convenient size and shape, preferably a vertical cylinder having a cone bottom and above this bottom a grid supports a wire mesh screen on which the lead powder may rest. The gasoline is pumped into this vessel at any point below the screen, rises through the lead pack, which it should keep in gentle agitation, rises further through the empty upper portion of the vessel, where any suspended lead powder subsides, and overflows through a vent situated near the top. From this vent the neutral sweet gasoline is pumped through any convenient type of filter press, equipped preferably with cotton cloths, from which it is pumped to storage.

The lead contactor should be filled to about half its height (measured above the screen) with a lead reagent consisting of litharge, diatomaceous earth and a little caustic soda. I prefer to make this reagent by dissolving in a little water one part by weight of commercial caustic soda, stirring into this solution thirty parts by weight of commercial powdered litharge, which produces a damp powder, and further incorporating five parts by weight of a high grade diatomaceous earth, which produces a substantially dry powder. The product consists of powdered litharge containing a little sodium plumbite and distended with a relatively large volume of light porous earth. The proportions given are suggestive only, it being possible to entirely omit the diatomaceous earth or to reduce or increase its proportion, and to quite materially alter the proportion of caustic soda, though it is not desirable to omit this entirely.

The rationale of this process is as follows: The acidity of the gasoline is neutralized by the dry sodium hydroxid without danger of emulsification or loss. The excess of alkali which is requisite to produce complete neutralization is carried forward and utilized in the sweetening process.

The small quantity of sodium plumbite in the lead contactors converts the mercaptans into

lead mercaptides which in turn are converted into lead sulfid and harmless dialkyl disulfids by the sulfur introduced into the entering oil.

As sodium hydroxid enters the lead contactors it regenerates lead sulfid, producing sodium plumbite and sodium sulfid. The lead present is thereby utilized at least several times before the charge becomes too inert due to the accumulation of sodium sulfid and neutralization reaction products.

Any portion of the sodium salts and any lead or earth which floats over from the contactors is caught in the filter which gives a pure brilliant gasoline, the filter cake being in condition to return to the contactors at intervals.

When the lead reacts too slowly, for the reason above given, a material proportion of the original quantity may be recovered by draining off the gasoline, washing until all the soluble salts have been extracted with hot water (these being neutralization salts, sodium sulfid and sodium plumbite), blowing the mixture with air until substantially dry and mixing in a small quantity of sodium plumbite. It is not necessary to oxidize the lead sulfid of which the mass is principally composed as it will begin to convert as soon as the cycle is reestablished. No lead is lost except the small quantity washed out as sodium plumbite.

The sulfur solution may conveniently be prepared by percolating gasoline through a tower partly filled with solid sulfur, separating any suspended sulfur and placing the solution in tanks. In these it may be brought to any convenient standard by the addition of further quantities of gasoline.

In order to keep the sulfur solution in correct proportion to the oil it is preferable to test the filter effluent rather than to calculate the proper proportion of solution. If the filter effluent gives a positive reaction to the well known "doctor" test it is "sour" and the dosage of sulfur oil is insufficient. If it is negative to doctor and positive to the copper strip test or, more sensitively, to the butyl mercaptan test, it is "corrosive" and the dosage of sulfur is too great.

The process above described will be found highly economical of reagents and particularly of oil. In its application there need be no exposure of the oil to air or contact with water from the time the oil enters the acid treater until it emerges from the filter as finished sweetened gasoline. Losses due to evaporation, sludging, emulsification and entrainment are therefore almost entirely avoided, practically the only loss of raw material being that due to the action of the acid, and even this is materially reduced as there need be no loss of color after the acid treatment and the acid dosage may therefore be materially reduced.

The portion of the above process which refers to the sweetening of the oil may be separately applied by passing into the lead contactors an oil intermixed with finely comminuted solid sodium hydroxid, or even without such intermixture, in which latter case the lead mass will function only until the sodium hydroxid contained therein is completely converted into lead sulfid. The entire process above described is preferably carried out at normal atmospheric temperatures.

I claim as my invention:

1. The method of sweetening oils containing mercaptans which comprises: adding to said oil finely comminuted solid sodium hydroxid and sulfur in quantity sufficient for sweetening, and passing said liquid mixture through a substantially dry powdered mass comprising lead monoxid and sodium hydroxid, the addition of water being avoided.

2. The method of sweetening oils containing mercaptans which comprises: adding to said oil finely comminuted solid sodium hydroxid and sulfur in quantity sufficient for sweetening, and passing said liquid mixture through a substantially dry powdered mass comprising lead monoxid, sodium hydroxid and a finely comminuted porous earthy material, the addition of water being avoided.

3. The method of neutralizing and sweetening acidified oils containing mercaptans which comprises: adding to said oil finely comminuted sodium hydroxid in quantity exceeding that which corresponds to the acidity of the soil and also adding to said oil sulfur in quantity sufficient for sweetening, and contacting said liquid mixture with a substantially dry powdered mass comprising lead monoxid and sodium hydroxid, the addition of water being avoided.

4. The method of neutralizing and sweetening acidified oils containing mercaptans which comprises: adding to said oil finely comminuted sodium hydroxid in quantity exceeding that which corresponds to the acidity of the soil and also adding to said oil sulfur in quantity sufficient for sweetening, and contacting said liquid mixture with a substantially dry powdered mass comprising lead monoxid, sodium hydroxid and a finely comminuted porous earthy material, the addition of water being avoided.

5. The continuous method of acid treating and sweetening oils containing mercaptans, which comprises: continuously treating said oil with sulfuric acid; continuously separating and withdrawing the major portion of the acid sludge formed by said treatment; adding to said acidified oil finely comminuted sodium hydroxid in quantity sufficient to slightly overneutralize the remaining acidity and adding to said oil sulfur in quantity sufficient for sweetening; continuously contacting said liquid mixture with a substantially dry powdered mass comprising lead monoxid and sodium hydroxid and filtering from the oil any suspended solids, the aforesaid operations being performed substantially out of contact with air and addition of water being avoided throughout.

6. The continuous method of acid treating and sweetening oils containing mercaptans, which comprises: continuously treating said oil with sulfuric acid; continuously separating and withdrawing the major portion of the acid sludge formed by said treatment; adding to said acidified oil finely comminuted sodium hydroxid in quantity sufficient to slightly overneutralize the remaining acidity and adding to said oil sulfur in quantity sufficient for sweetening; continuously contacting said liquid mixture with a substantially dry powdered mass comprising lead monoxid, sodium hydroxid and a finely comminuted porous earthy material, and filtering from the oil any suspended solids; the aforesaid operations being performed substantially out of contact with air and addition of water being avoided throughout.

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