

UNITED STATES PATENT OFFICE.

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PROCESS OF DESULFURIZING PETROLEUM.

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To all whom it may concern:

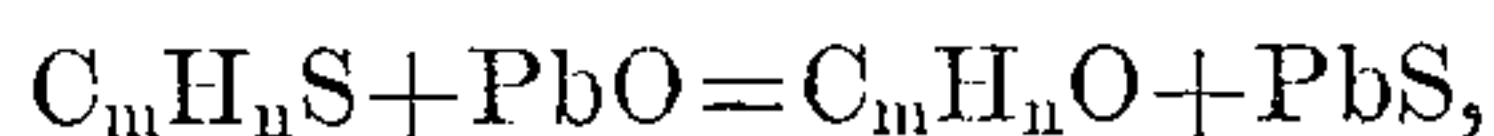
Be it known that I, THEODORE F. COLIN, a citizen of the United States, residing at Jersey City, in the county of Hudson and State of New Jersey, have invented certain new and useful Improvements in Processes of Desulfurizing Petroleum, of which the following is a specification.

The process of desulfurizing Ohio and similar petroleums forming the subject of my present application is more particularly designed to take the place of those heretofore used, in which the crude petroleum or its distillate is treated in a still during its vaporization with metallic oxids which attack the sulfur compounds in the oil, forming insoluble metallic sulfids that remain in the still, while the hydrocarbons pass over into the condenser. The chief characteristic of my invention which distinguishes it from such processes is in the employment in the treatment of such oils of agents which attack, primarily, the hydrocarbon instead of the sulfur and render the action more energetic and the desulfurization more complete.

In carrying out my invention I utilize the natural tendency of the hydrocarbons in the Ohio petroleum to oxidize by bringing them into contact during the process of distillation, but prior to vaporization, with a peroxid from which the oxygen is liberated at the normal temperature of distillation, and, preferably, a metallic peroxid in which such a condition exists, as in such case the metal will pass into the nascent state, in which its affinity for sulfur is exerted to the best advantage, and I thus facilitate the formation of those oxygen compounds of the hydrocarbons which take place with the greatest liberation of heat—that is, which tend to keep up the reaction; but while by this means I secure a useful action of the oxygen upon the hydrocarbons, a detrimental action as well will result, to counteract which I introduce another reagent, by a suitable selection and quantity of which I am enabled to actually increase the yield of merchantable product from a given quantity of crude petroleum as compared to a distillation without any reagent.

Heretofore in the treatment of crude petroleum its vapor or distillate with metallic oxids or salts the purpose has been to act pri-

marily on the sulfur combined in some unknown way with the hydrocarbons and to reduce it to an insoluble condition by providing a metal with which it would combine by reason of its natural affinity therefor either while in combination with the hydrocarbon or when separated therefrom by the physical action of a high temperature. Such metal was introduced in any form in which it could be mixed with the oil or exposed to the vapor of the same, as free metal, oxid, or salt, and dependence was placed entirely upon its affinity for the sulfur. Such affinity, however, particularly in the case of the heavier metals, is comparatively low, as measured by the heat of formation of the sulfids, and the reaction in consequence, even where external appliances were used to promote it, was but imperfect. In illustration of this, if we examine the following equation, which represents, schematically, the action of litharge upon such a petroleum as is under consideration,



it will be seen that the oxygen and the sulfur interchange places, producing lead sulfid and some kind of an oxygen compound of the hydrocarbon. The thermal equation for this reaction cannot be written out, as the heats of formation of those organic oxygen and sulfur compounds are not known; but we know that the heat of formation of lead oxid is 50.3 great calories, while that of lead sulfid is only 18.4. The conversion, therefore, of lead sulfid into the oxid is easier than the reverse, and such reaction as occurs in the still at all results merely from the excess in the heat of formation of the organic oxygen compound over the previously-existing hydrocarbon sulfid and from the fact that the lead sulfid is less soluble in the oil than the lead oxid. It is evident from this that the reaction heretofore depended upon is a forced one and that its results cannot be as good as if a spontaneous reaction were employed.

It has been observed long ago that Ohio petroleum has a tendency to oxidize with formation of acids, or, as some chemists maintain, of lacto-alcohols. I myself have obtained from such petroleum some unquestionable acids. This reaction is an exothermic

one—that is to say, it tends to proceed indefinitely as long as the hydrocarbons and oxygen remain in contact, and it is, moreover, greatly facilitated by the presence of an alkali with which the acid may immediately combine; but by introducing into the body of the oil or distillate the oxygen in an unstable condition, in which it has a tendency of itself to attack the hydrocarbons, I have made a substantial and highly-important advance in the art of treating sulfur petroleum.

Oxygen exists in an unstable condition such as meets the requirements of my invention, so that it is liberated at the normal temperature necessary for the distillation of the petroleum in the peroxids, either basic, such as Na_2O_2 , BaO_2 , and PbO_2 , (also Pb_3O_4), and some corresponding salts, such as Na_2PbO_3 , or acid peroxids, such as Mn_2O_7 , MoO_3 , and their salts. Some peroxids of the metalloids, such as H_2O_2 and ozone, might also be employed to advantage, provided they can be produced cheaply on a large scale; but I prefer the metallic peroxids, as their metal on becoming free at the same time combines with the sulfur to form a sufficiently-stable body. I would state that there are other substances, including certain peroxids, such as MnO_2 and Fe_2O_3 , which contain oxygen in an unstable condition, but which are not available for my purpose, for the reason that at the temperature employed their decomposition is not sufficiently complete, they being merely reduced to lower oxids. Only such peroxids are useful in carrying out my invention as will give up in the presence of the hydrocarbons substantially all of their oxygen at the normal or practical temperature of distillation. In such case the reaction in the still, using lead dioxid as the reagent, would be thus represented: $\text{C}_m\text{H}_n\text{S} + \text{PbO}_2 = \text{PbS} + \text{C}_{m-1}\text{H}_{n-1}\text{CO}_2\text{H}$. Here the sum of the heats of formation of the members on the right-hand side of the equation is considerably higher than that on the left, and the reaction in consequence starts readily—in fact, it begins at once in the cold—and tends to a full completion.

The oxidation of the hydrocarbons, however, as above stated, may not be confined wholly within useful limits, for, although with the opportunity afforded for combination of the sulfur with a metal those hydrocarbons mainly which are in combination with the sulfur will oxidize, still this action is not an exclusive one, and some of the other hydrocarbons may also be attacked. The oxidation of the sulfo-hydrocarbons may, moreover, proceed too far, giving rise to acids of lower molecular weight and bodies very rich in carbon or even free carbon. The usual practical result in the treatment of petroleum distillate of such an excessive oxidation is a darkening of the distillate, which cannot be remedied by the subsequent refining. Such action would, therefore, greatly reduce the yield of water-white kerosene from the petroleum unless an additional distillation be carried out, during

which the dark hydrocarbon is dissociated by the heat into a body richer in carbon or free carbon, which would remain in the still, and a lighter hydrocarbon, which would pass over.

To increase the practical and commercial effectiveness of my process, therefore, I provide for overcoming the injurious effects of oxidation by the presence in the still during vaporization of an alkali, which I have found to largely prevent the darkening of the distillate. I believe that this result is due to the combination of the alkali with the hydrocarbon acid to form a salt which is more stable in the heat than the free acid, and therefore does not decompose nor pass over with the vapors. The presence of the alkali in the still, moreover, not only affords a material for the saturation of the acid, but it also facilitates the process in that the heat of neutralization of the acid is added to the sum of the heats on the right-hand side of the equation last stated, besides which, if the alkali be a solid, forming a non-volatile, or, under the conditions of use, a permanent salt with the acid, its heat of solidification is also added. All of these conditions promote the most desirable reaction, and no mechanical or physical conditions of facilitated contact by applied pressure or agitation can take their place.

In carrying out my process I prefer to use lead dioxid mixed with about one-half of its weight of caustic soda, and by such means I not only facilitate the first oxidation, but also obtain a distillate, which becomes clear water-white after the usual refining. The result of the whole treatment is a direct increase in the yield of water-white kerosene, for while an ordinary distillation of this petroleum furnishes only thirty-five to forty per cent. of water-white kerosene my process yields fifty per cent. and over.

It is theoretically possible to obtain the combined action of the metallic peroxid and the alkali by using a substance which, from a peroxid, becomes an alkaline oxid or hydroxid—as, for instance, Na_2O_2 , (sodium peroxid,) or, similarly, BaO_2 , (barium dioxid;) but in practice this would be attended with disadvantages, as sodium peroxid is comparatively expensive, while barium dioxid requires a rather high temperature before it begins to give off its excess of oxygen. My preference for the use of PbO_2 is because it begins to give off oxygen at a low temperature, and at the same time it does not do this too rapidly, so that the reaction continues through the distillation. Its production and regeneration seem also to be easier.

In practice I mix the lead dioxid with caustic soda or caustic and carbonate in substantially the proportions named, grind or powder the whole as finely as possible, and introduce it into the still. It may all be put in at once in a quantity necessary to effect the desired result or introduced gradually during the distillation. It may be used in a dry condition;

but I prefer to mix it with a little of the petroleum or the tarry residue from a previous distillation in order to prevent the absorption of moisture during its manipulation. The distillation and refining of the distillate by means of sulfuric acid and alkali are conducted in the usual manner.

I make no attempt at any solution of the reagent in the oil, nor do I regard this as desirable or to any material extent useful. The solubility of metallic oxids in Ohio petroleum I have found to be a very limited one, and the only practical value such a solution possesses is as an aid to mixing the reagent with the oil. Chemically considered, however, the dissolved metallic oxid has less affinity for sulfur than the metal in its nascent state which I provide, as some energy is absorbed in dissociating the metallic oxid or its hydrocarbon compound, so as to free the metal ready for the intended action. In fact, I have demonstrated by the distillation of petroleum with metallic hydrocarbon compounds—such as acetates, resinates, &c.—that their action does not extend to the more stable sulfur compounds, only those being attacked which are dissociated by the heat or are on the point of dissociation.

The reagent may be maintained in more complete suspension in the oil by some mechanical agitation or by a current of steam or other vapor or gas, or any other suitable means that experience may suggest, employed to facilitate the reaction or to keep down the excess of reagent otherwise necessary. The practical operation of my invention, however, involves no special form of still or other apparatus, and these may be of widely-different construction. When the distillation is completed, the residual metallic salts (sulfids, carbonates, &c.) are separated from the tar by settling and draining and then incinerated and oxidized. The sodium salts may be extracted with water, rendered caustic with lime, and used together with lead oxid obtained by the previous ignition to produce again lead dioxid and caustic soda. In this way the reagents are used many times and only the unavoidable loss of material need be made up.

I modify the process of producing the lead dioxid somewhat, so as to better adapt it to the conditions of the work. After having prepared it for the first time from caustic soda and litharge by boiling these together with free access of air and afterward in the presence of carbonic acid in the subsequent regenerations I use partly the so-called "alkaline sludge," which is a mixture of NaOH, Na₂CO₃, and other sodium salts of the organic acids found in petroleum and partly the alkali dissolved out from the residue of a previous operation and recausticized, as mentioned above, and the lead I introduce in the form of the ignited and partly-purified residue, which would be mainly PbO. These are boiled together and, owing to the presence of much combined CO₂, give at once a precipitate

rich in PbO₂. The mixture of NaOH, Na₂CO₃, Na₂PbO₃, and PbO₂ is poured into a shallow vessel to solidify and then at once broken up and ground to powder while still warm. To prevent the absorption of moisture, I prefer to add to it during this operation some petroleum or tarry residue from a previous distillation. This mixture is then introduced into the still in the proportion of six to eight per cent. of the weight of the petroleum. I try to have as much PbO₂ in the mixture as is convenient, and also to have much caustic soda rather than the carbonate. The other constituents are not harmful in any way, but less effective.

I am familiar with the use of oxidizing bodies in the treatment of Ohio and similar petroleum heretofore proposed; but, so far as I have any information on the subject, there has been no suggestion of using for such purpose, in combination with the crude oil or distillate, anything but substances containing comparatively free oxygen, the intention being merely to replace the sulfur in the hydrocarbon compound by oxygen. I have, however, hereinbefore demonstrated theoretically and I have also proved by practical tests that such action is forced and incomplete. By distilling crude petroleum with litharge (PbO) I have obtained a distillate with 0.043 per cent. of sulfur, while by using lead dioxid (PbO₂) under the same conditions I have obtained a kerosene with only 0.025 per cent. of sulfur. Instead of the fortuitous replacement of sulfur by oxygen in the hydrocarbon combination I designedly provide for the direct action of the oxygen on the hydrocarbon, the exchange of sulfur to the metal being a secondary reaction. It has also been proposed to oxidize the sulfur combined with the hydrocarbons by means of oxidizing bodies; but this process is of but limited value, for the reason that only the free or gaseous sulfur is attacked, while the more stable combinations are not affected.

I am further aware that it has been proposed to raise the vapor of Ohio and similar petroleum to a temperature well above the boiling-point of sulfur in the presence of certain of the higher oxids and a caustic alkali, the purpose being to vaporize the sulfur in the oil and to crack or split up the sulfur compounds in order to effect a union of the sulfur with the oxidizing agents; but in such process the object has been the same as in the immediately-preceding process referred to, and although in such case similar chemical actions to those especially provided for in my process may have taken place they were merely an incident to the presence of the reagents employed and were not affected under the most advantageous conditions.

By carrying out my complete process as hereinbefore described I have obtained from crude Ohio petroleum in one distillation a yield of fifty per cent. of water-white kerosene with only about 0.03 to 0.04 per cent of sulfur.

It is further obvious that this process may be equally well applied to the distillate obtained from crude petroleum. The advantages of such a proceeding are the greater
5 ease of regaining the reagent and a greater yield of merchantable product against the disadvantage of an additional distillation.

What I claim is—

10 1. The process of purifying Ohio and similar petroleum oils, which consists in distilling the crude oil or distillate with a peroxid, from which the oxygen is liberated in the presence of the hydrocarbons at the normal temperature of distillation, as set forth.

15 2. The process of purifying Ohio and similar petroleum oils, which consists in distilling the crude oil or distillate with a compound containing oxygen in an unstable condition and which is decomposed in the presence of the

hydrocarbons at the normal temperature of 20 distillation, liberating a metal in a nascent state that combines with the sulfur in the oil.

3. The process of purifying Ohio and similar petroleum oils, which consists in distilling the crude oil or distillate with a substance con- 25 taining oxygen in an unstable condition so as to be liberated in the presence of the hydrocarbons at the normal temperature of distillation, and an alkaline hydroxid, as set forth.

4. The process of purifying Ohio and similar 30 petroleum oils, which consists in distilling the crude oil or distillate with a mixture of such a substance as lead dioxid and caustic soda, as herein set forth.

THEODORE F. COLIN.

Witnesses:

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EDWIN B. HOPKINSON.