

UNITED STATES PATENT OFFICE.

ERIC A. STARKE, OF SAN RAFAEL, CALIFORNIA.

PROCESS OF PURIFYING AND REFINING CALIFORNIA PETROLEUM-OILS.

SPECIFICATION forming part of Letters Patent No. 597,920, dated January 25, 1898.

Application filed August 31, 1896. Serial No. 604,484. (No specimens.)

To all whom it may concern:

Be it known that I, ERIC A. STARKE, a citizen of the United States, residing at San Rafael, county of Marin, State of California, have invented an Improvement in the Processes of Purification and Refining of California Petroleum-Oils for Illuminating Purposes; and I hereby declare the following to be a full, clear, and exact description of the

10 same.

My invention relates to a new process of purifying and refining California petroleum-oils for illuminating purposes, in which I first remove from said oils the less refractory bodies contained therein by treating said oils with concentrated caustic lye or sulfuric acid, and in which I secondly remove from the resulting mass the more refractory bodies by treating said resulting mass with sulfuric anhydrid or such solution of sulfuric anhydrid, as is hereinafter more particularly described.

My invention is particularly applicable to and particularly concerns that class of petroleum-oils which on account of certain distinctive peculiarities has come to be known commercially and otherwise by the descriptive term of "California oils."

The term "California oils" is not used in the geographical sense or to signify geographical limitation to the State of California alone. On the contrary, it is used to designate a certain allied species or class of petroleum-oils occurring in the State of California and also to some extent in the States and Territories bordering upon or adjacent to the Pacific coast of the United States, which oils, by reason of their containing and being saturated with an excessive quantity of refractory bodies and matters of a carbonaceous nature, have hitherto resisted all efforts and attempts to make, manufacture, or in any way produce therefrom an illuminating-oil that would burn in any form of lamp or burner hitherto invented or known to the trade without giving off undue smoke and without emitting noxious vapors in undue quantities. These refractory bodies and matters of a carbonaceous nature so present in these California oils have constantly tended to clog and have clogged from time to time the wicks of any and of all kinds of lamps and burners, and

have impeded the flow of the illuminating-oil through said wicks and the wick-tubes, and have prevented perfect combustion of the said California oils. The great object always sought to be obtained in order to cause these California oils to burn without undue smoke and without emitting noxious vapors in undue quantities has been to eliminate from them the said refractory bodies and matters of a carbonaceous nature.

All methods and processes heretofore known and used in the treatment, purification, and refining of the said California petroleum-oils, so as to produce from them illuminating-oils, have been carried out by means of a treatment with sulfuric acid of about 66° Baumé at temperatures varying from 60° Fahrenheit to 250° Fahrenheit. The said methods and processes heretofore known and used in the treatment, purifying, and refining of California petroleum-oils have never been successful in producing from them an illuminating-oil that would burn without undue smoke and without emitting noxious vapors in excessive quantities or that could be sold by itself as an illuminating-oil in the regular and ordinary course of trade or commerce. So refractory have been these bodies and matters of a carbonaceous nature in these California oils that it has been necessary in the production and refining of illuminating-oils from them to resort to three or four separate and successive distillations of the same batches of oil accompanying and as part of the treatment with said sulfuric acid, thereby entailing large outlays and expenses in labor, fuel, loss of time, wear and tear of plant, and diminution by losses arising from successive distillations in percentages of illuminating-oils obtained.

In my invention and process I have overcome these difficulties by, first, removing the less refractory bodies contained in the California petroleum-oils or their distillates by treating the same with concentrated caustic lye or sulfuric acid, and, secondly, and as part of the same invention and process by treatment of the resulting mass with sulfuric anhydrid or such solutions of sulfuric anhydrid as are hereinafter described.

In the application of my invention and process I proceed substantially as follows: I first

subject the crude oil to a single distillation, thereby eliminating from it the heavier and non-volatile tarry matters. I then mix with the resultant distillate from five to twenty per cent., by weight, of the ordinary sulfuric acid of about 66° Baumé, or from ten to twenty-five per cent., by weight, of concentrated soda-lye or other caustic lye of about 45° Baumé, and heat the mass while so mixed to a temperature of about 160° Fahrenheit when sulfuric acid is employed; but in order to facilitate the reaction a temperature exceeding 200° Fahrenheit is preferable when soda-lye or other caustic lye is employed, and I agitate the mass all the while with an air-blast or other mechanical means for about an hour's time, the length of the time of agitation depending on the density of the distillate. The higher the specific gravity of the said distillate the greater would be the percentage of the said acid or of the said caustic lyes that I would use and also the longer the time I would allow for the agitation. After the completion of this first agitation with ordinary sulfuric acid or with caustic lye, as aforesaid, (and by which treatment all of the less refractory matters are removed, leaving only those of a more stable combination in the said resulting mass,) the said resulting mass is allowed to rest and the tarry residuum (or sludge) is drawn off. There has now been eliminated from the oil all refractory bodies and matters of a carbonaceous nature that are in any way or at all susceptible of elimination by any form or method of treatment with ordinary sulfuric acid or by any form or method of treatment with any alkaline substances; but there are still left in the oil certain other and still more refractory bodies and matters of a carbonaceous nature that cannot be taken away or eliminated in any way or at all by any form or strength of ordinary sulfuric acid, or by any method or kind of treatment therewith, or by any method or kind of treatment with any alkaline substances. Up to this point and at this stage of the process said oil could not be successfully burned in any form of lamp or burner hitherto invented or known to the trade. It becomes now, therefore, necessary to use some further and more powerful agent that will act upon and eliminate this class of still more refractory bodies and matters. For this purpose I now use and subject the oil to treatment with sulfuric anhydrid or solutions thereof, as are hereinafter described.

The amount of sulfuric anhydrid (SO_3) I employ depends wholly on the density of the distillate to be purified and also on the purity of the original petroleum.

When distillates of about 45° Baumé are to be treated, five per cent. of sulfuric anhydrid (SO_3) is generally sufficient to purify the oil; but the oil from some wells requires much more, often as much as fifteen per cent. When a distillate of greater gravity is to be refined, more of the SO_3 is required, as it seems that

the heavier oils contain more of the refractory bodies than the lighter.

When the sulfuric anhydrid is added to a distillate, the reaction is very violent, but of short duration, depending to some extent on the gravity of the oil employed and the form of the sulfuric anhydrid. When a light-gravity oil is treated, the solid SO_3 can be employed. When a heavier form of distillate is used, the solid form of sulfuric anhydrid cannot be employed, as the crystals of the SO_3 are at once completely surrounded with a coating of black tarry matter, which prevents any further action. Therefore an admixture of some other matter is necessary in order to prevent this coating. Sulfuric acid (H_2SO_4) as an admixture making fuming acid must then be employed, as it is the cheapest method of diluting the SO_3 . Phosphoric acid is better than sulfuric acid as a diluent, and boric acid makes a solid form, which gives good results. In fact, almost any substance that will not make a stable compound with the SO_3 will answer the purpose of a diluent. The idea is to get it into the oil and prevent the coating of the crystals with tarry matter. When once in the oil, sulfuric anhydrid seems to attack the refractory bodies, making a tarry mass. It also seems to split off from the molecules of the oil some of the carbon and hydrogen sufficient to make a light hydrocarbon and then combine therewith, the resulting combination not being soluble in the oil. I have come to this conclusion from the fact that the fire test of oil thus treated is raised from 20° to 40° Fahrenheit. This may possibly be explained also by the fact that light hydrocarbon oils are held in solution by the petroleum and that sulfuric anhydrid is capable of combining therewith. Be this as it may, ordinary sulfuric acid (H_2SO_4) is wholly incapable of effecting its removal. I then agitate the mass, at the same time never allowing the temperature to fall below 80° Fahrenheit. This agitation is continued until all chemical activity has ceased, which is made evident by the amount of heat required to be applied to the mass in order to maintain the temperature thereof above 80° Fahrenheit. After all chemical action has ceased the mass is allowed to rest and the black and thick tarry residue is drawn off, and the oil is then subjected to successive washings with water and soda-lye or other alkaline substances in the ordinary way. The oil is now ready for use and is fully equal in quality and in illuminating power to the best grades and brands of Eastern water-white illuminating-oils and equally with them will burn in any form of lamp without giving off smoke or emitting noxious vapors.

By my invention and process as above described there is accomplished for the first time that which has never been accomplished or brought about by any other process or method of treatment hitherto invented, used, or employed upon or in connection with the

said California oils—that is to say, the production from the said California oils of an illuminating-oil that will burn in any form of lamp or burner that has ever been invented or known to the trade with equal illuminating power and in all respects as well as the best brands of eastern water-white illuminating-oils.

Among the other advantages and improvements resulting from the application of my invention and process to the treatment of the said California oils may be mentioned the following: First, the raising of the fire test of said oils; secondly, the ability to refine and produce high-grade illuminating-oils from and thereby to utilize California crude petroleum of a higher specific gravity than has ever been susceptible of successful treatment or refining by any other method or process hitherto employed; thirdly, the obtaining from said California crude petroleum of a percentage of high-grade illuminating-oil greater even than the percentage of poor and inferior illuminating-oil hitherto obtained therefrom, and, fourthly, the accomplishing by one distillation of what has never been accomplished with or in regard to California oils even when employing the three or four distillations hitherto always made use of in treating and refining said oils, and from this result large economy and saving in labor, fuel, time, and general wear and tear of plant and machinery and in

the percentage of loss consequent upon and hitherto regularly ensuing from the repeated and successive distillations that have been necessarily employed.

Having thus described my invention, what I claim as new, and desire to secure by Letters Patent, is—

1. The process herein described of treating, purifying and refining "California" petroleum-oils, so as to produce from them illuminating-oils which process consists, essentially, in first removing the less refractory substances by treating said oils with a solvent or menstruum and then treating the resulting product with sulfuric anhydrid to remove the more refractory substances.

2. The improved process herein described of treating, purifying and refining "California" petroleum-oils, so as to produce from them illuminating-oils, which consists, essentially, in first removing the less refractory bodies by treating said oils, with a solvent or menstruum in the presence of heat and then removing from the resulting mass the more refractory bodies by treating said mass with sulfuric anhydrid.

In witness whereof I have hereunto set my hand.

ERIC A. STARKE.

Witnesses:

WM. F. BOOTH,
HOLLAND SMITH.