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DESULFURIZING LIMA OR ANALOGOUS PETROLEUM AND RELATED OILS.

No. 910,584.

Specification of Letters Patent.

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To all whom it may concern:

Be it known that I, CLARENCE I. ROBINSON, a citizen of the United States, residing at West New Brighton, in the county of Richmond and State of New York, have invented new and useful Improvements in Desulfurizing Lima or Analogous Petroleum and Related Oils, of which the following is a specification.

This invention relates to the removal of sulfur from petroleum similar to that produced (that is, obtained from wells) in the neighborhood of Lima, Ohio, and in the State of Indiana, and from other petroleum analogous thereto in the particulars hereinafter set forth, and also from certain related oils as hereinafter set forth; and it has more particular reference to the desulfuration of Lima petroleum in the form of burning oil (kerosene) distillate, that is to say, in the form of any distillate which is mainly or wholly composed of hydrocarbons proper for burning oil (kerosene). By means of said invention, with use of the ordinary stills and agitators to be found generally in oil refineries and of a cooler such as is not uncommon therein, one can make from Lima petroleum a burning oil (kerosene) of a low content of sulfur, not exceeding the percentage of sulfur contained in burning oil (kerosene) of similar grade from said petroleum heretofore made and marketed; and it is believed that such burning oil (kerosene) can be so made at a sufficiently low cost to be financially profitable. The said invention, however, relates to the desulfuration of Lima or analogous petroleum and related oils in whatever form to any extent which can be attained by means of the invention, or any part thereof, and which results in an industrially useful amelioration of the treated oil in respect to the sulfur therein.

The petroleum produced in the neighborhood of Lima, Ohio, and in the State of Indiana, and other petroleum similar thereto, is herein called Lima oil or Lima petroleum for convenience of reference and as indicating one place of production, but not as restricting the production to such locality. The petroleum, for example, which is produced in the province of Ontario, Canada, is Lima oil for the purposes of this specification; because it is considered to be of a nature

not only analogous, but also substantially similar, to that produced in the neighborhood of Lima, Ohio, and in the State of Indiana. For the purposes of this specification such similarity of nature is sufficiently shown for any petroleum by the fact that in the form of that distillate which distills over between 300° F. and 550° F. from the oil in its crude state and which consequently can be taken as fairly representing its uncracked burning oil (kerosene) fraction as a whole it responds to all four of the undermentioned tests, after it has been prepared therefor by treating it in the form of its said distillate with sulfuric acid and alkali (using sulfuric acid of about 66° B. at the rate of twenty pounds of such acid to each forty - gallon barrel of such distillate).

To obtain a proper distillate for testing, the crude petroleum can be distilled in a flask such as commonly used in the laboratory for fractional distillation, provided with a thermometer having its bulb in the neck of the flask just below where the side tube is joined thereto. The products which come over before the thermometer reaches 300° F. are rejected, and those which come over subsequently are collected in one receiver until the thermometer attains a temperature of 550° F., when the required distillate will have been collected. Thereupon the distillation is stopped or the receiver changed. To prepare this distillate for testing, it can be treated with sulfuric acid and alkali in a glass separator (say, the pear-shaped separator in common use in the laboratory).

The following are the four tests referred to above, to each of which Lima oil in the form of its said distillate, after being prepared for testing as aforesaid, responds, namely:

First. When tested by a refractometer, it exhibits a refractive index sufficiently less than 1.4600 to indicate a non-smoking oil. An oil with a refractive index of 1.4600 is to be considered smoky. An oil with a refractive index of 1.4545 is to be considered non-smoking.

Second. It turns yellow upon addition thereto of a clear solution of plumbate of sodium formed by dissolving litharge to saturation in caustic soda lye.

Third. It has a sulfur content of more than one-tenth of one per cent.

Fourth. Upon treating one quart of the prepared distillate by agitation for a few minutes with three-tenths of a pound of sulfuric acid of about 66° B. in a glass separator (say, the before mentioned pear-shaped separator) and another quart of the same distillate by agitation for the same time with the same weight (one-quarter pound) of non-fuming sulfuric acid of about 98% sulfuric monohydrate in a similar separator, the agitation to be followed in each case by settling, drawing off the sludge, and washing with water, caustic soda lye, and again with water, the portion which has so been treated with the acid of about 66° B. will be found to have a larger sulfur content than will the portion which has been treated with the 98% acid; and the difference will be sufficient to indicate a useful desulfuration of the said distillate by the 98% acid over and above the desulfuration of the same (if any) effected by an equal amount of acid of about 66° B. In other words, Lima oil in the form of its said distillate prepared as aforesaid contains sulfur compounds unremoved by sulfuric acid of about 66° B. which are removable to a useful extent by sulfuric acid of about 98%. Any petroleum which in the form of distillate yielded between 300° F. and 550° F. by the crude oil under the aforesaid conditions responds, after the described preparation thereof in said form, to all four of these tests is Lima oil or Lima petroleum for the purposes of this specification.

The preparatory treatment is important, because it removes the hydrogen sulfid and other easily removable sulfur compounds which might otherwise be present in the oil at the time of testing and whose presence therein at such time might materially affect the tests. Thus hydrogen sulfid would give a brown or black coloration with the plumbate of sodium solution; and this coloration would more or less obscure and might wholly obscure a yellow color developed also by said solution. There are also sulfur compounds which are removed by said preparatory treatment and which would give a yellow coloration with said solution, if they were present in the oil at the time of applying the tests. The hydrogen sulfid and other easily removable sulfur compounds would increase the sulfur content of oil containing the same and might give the sulfur percentage of the third test in a case where otherwise it would be less than said test requires. Were they to be present in the oil when it is subjected to the fourth test, they would be removed by the sulfuric acid of about 66° B. of this test, as well as by the 98% acid; and consequently they would tend to obscure the difference in resistance to removal exhibited by the more characteristic sulfur compounds of Lima oil

towards sulfuric acid of about 66° B. and towards 98% sulfuric acid, respectively. According to my experience, petroleum produced in the neighborhood of Lima, Ohio, and in Indiana, when in the form of its said distillate, prepared as aforesaid, has had a refractive index of about 1.4400; (2) has contained not less than 2/10 per cent. of sulfur; (3) has turned a pronounced canary yellow on addition of the sodium plumbate solution thereto, and (4) has had its sulfur content reduced from 225/1000 per cent. to about or below 1/10 per cent. by the specified proportion of 98% sulfuric acid, whereas another portion of the same prepared distillate had a sulfur content of more than 2/10 per cent. after it had been treated with the said proportion of sulfuric acid of about 66° B.

In setting forth the fourth test above reference is made to a certain proportion of acid to oil, not because a differential resistance is exhibited only with such proportion, but in order to state the test more definitely and by the use of a large proportion of the respective acids to show the stability of the sulfur compounds of Lima oil against removal by sulfuric acid of about 66° B. The tests may be made at any suitable temperature, say, at about 60° F. or at the actual temperature of the room in which the tests may be performed, whether above or below 60° F.

In the fourth test reference is made to non-fuming sulfuric acid of about 98% sulfuric monohydrate, not because it is the only sulfuric acid which is able to remove sulfur compounds of Lima petroleum which are not removed by an equal weight of sulfuric acid of about 66° B.; but by way of example and also because it is considered the most advantageous form of sulfuric acid stronger than that of about 66° B. to be used in carrying the present invention into effect. My experience leads me to conclude that from about 98% sulfuric monohydrate upward the desulfurizing action of sulfuric acid on Lima oil increases gradually with the acid strength, being somewhat greater for sulfuric monohydrate (100%) than for 98% acid and still greater for fuming sulfuric acid, and that from about 98% downward the desulfurizing action of sulfuric acid on Lima oil diminishes, at first gradually and then in increasing degree (being materially smaller for 96% acid than for 98% acid and still more so for 95% acid), until with the decreasing percentage of sulfuric monohydrate the desulfurizing action becomes substantially that possessed by acid of about 66° B. This last ordinarily contains, and for the purposes of this specification may be taken to contain, from 92½% to 93% sulfuric monohydrate. Sulfuric acid of about 98% is a commercial article and is producible either by driving off the water from

weaker acid, or by adding thereto sulfuric anhydrid or fuming sulfuric acid. In my opinion, it exhibits (at present prices) a higher ratio of desulfurizing action to cost than acid which is not so strong (and hence not so high in desulfurizing action, although slightly cheaper) or than still stronger acid (which is higher in cost, although also somewhat higher in desulfurizing action).

10 In making burning oil (kerosene) it is customary to treat the burning oil (kerosene) distillate with sulfuric acid of about 66° B. at about 60° F. initial; that is to say, burning oil (kerosene) distillate is ordinarily
15 cooled or heated, as the case may require, to bring it to about 60° F. (cooled in summer and heated in winter); and the acid is then added to the oil at about 60° F. in the agitator. The acid is added at the temperature
20 which it happens to have. The acid and oil are agitated with a blast of air having usually the existing atmospheric temperature. During the agitation the temperature usually rises, say, about 10° F., in consequence of the heat developed by the chemical reaction of the acid on the oil.

It is possible to desulfurize Lima petroleum in the form of burning oil (kerosene) distillate to the extent necessary to give a
30 marketable burning oil (kerosene) by treating such distillate at about 60° F. initial with sulfuric acid of about 98% sulfuric acid or with other sulfuric acid appropriately stronger than that of about 66° B.; but to do
35 so a large proportion of such stronger acid is needed in order to afford a sufficient reduction in sulfur content. For example, assume (as would be possible and as I have, in fact, experienced) that crude oil from the
40 neighborhood of Lima, Ohio, or from the State of Indiana, should be distilled and that an uncracked burning oil (kerosene) distillate should be collected as the stock to be treated and that it should constitute all the
45 distillate received from the beginning of distillation of said crude oil until the distillate from the tail pipe of the condenser has a gravity of about 41° B. and that it should amount in volume to fifty per cent. of the
50 crude oil (in other words, that the volume of collected distillate should be equal to the volume of the undistilled portion of the crude oil), and that it should contain an amount of naphtha equal to about eleven per cent. of
55 the crude oil, and that said stock (as obtained directly from the condenser) should show a sulfur content of three hundred and forty six one-thousandths of one per cent. (a not uncommon percentage for such a cut of
60 distillate). To treat this stock (hereinafter referred to as the above mentioned uncracked stock) at about 60° F. initial with 98% sulfuric acid in such manner as eventually to obtain burning oil (kerosene) containing not

more than one-twentieth of one per cent. of 65 sulfur (which fraction may be taken as sufficiently representative of the sulfur content of marketed burning oil, kerosene, heretofore made from a similar cut of Lima crude oil) would require, according to my experience, about sixty pounds of said 98% acid to each barrel of stock (forty gallons to the barrel). The stock, after the treatment with 98% acid, may contain about one-tenth of one per cent. of sulfur; but this percentage
75 can, in my experience, be reduced to or below one-twentieth of one per cent. by rerunning (that is, by distilling the treated distillate) and giving the rerun oil a light treatment with sulfuric acid and alkali, using, say, three or four pounds of sulfuric acid of about 66° B. to each barrel of rerun distillate, or the same proportion of acid sludge from the treatment with 98% acid, and finally steam stilling to drive off the naphtha and so to give burning oil (kerosene) of
85 suitable fire test. The steam stilling, it may be observed, increases somewhat the sulfur content, because the expelled naphtha holds a less percentage of sulfur than the residual
90 burning oil (kerosene) does.

If the above mentioned uncracked stock should be treated preliminarily with sulfuric acid and alkali, using twenty pounds of sulfuric acid of about 66° B. to the barrel of
95 stock; and if the so treated stock should then be treated at about 60° F. initial with 98% acid, using between forty and fifty pounds to the barrel, and be followed by rerunning and subsequent light treatment with sulfuric
100 acid and alkali and steam stilling, the finished burning oil (kerosene) so obtained should likewise have a sulfur content not exceeding one-twentieth of one per cent. After the preliminary treatment (that is, with acid
105 of about 66° B.) the sulfur content may be about two hundred and twenty five one-thousandths per cent., and after the main desulfuration (that is, with 98% acid) about one-tenth per cent. Some 98% acid would
110 be saved by the preliminary treatment, but not, it is believed, sufficient to counterbalance the cost of the acid of about 66° B.

With or without the preliminary treatment, the quantity of sulfuric acid needed to
115 give a marketable burning oil (kerosene) would be so large as to be a serious objection to an industrial manufacture, if not prohibitive thereof, especially in view of the other necessary expenses of refining. To use
120 other sulfuric acid substantially stronger than acid of about 66° B., in place of 98% acid, would not meet the difficulty; for the ratio of cost to desulfurizing action is probably least in the case of 98% acid; and, if it
125 were not so, so large a proportion of acid in any case would be needed that its cost would prove a serious (if not a financially fatal) ob-

jection. Moreover, the large proportion of acid stronger than that of about 66° B. would in any case destroy a considerable amount of hydrocarbons which otherwise would be useful constituents of the burning oil (kerosene) and would probably also prove injurious to the color of the oil, even after rerunning.

The first part of the present invention is based upon the discovery, first made I believe by me (a) that by operating on Lima oil in the form of burning oil (kerosene) distillate at about or below 38° F. initial a sufficient desulfuration to give a marketable burning oil (kerosene) can be effected with only about a third of the 98% sulfuric acid (or of other sulfuric acid appropriately stronger than that of about 66° B.) needed to effect the same desulfuration of the same quantity of the same stock at about 60° initial; (b) that by operating at temperatures between about 38° F. initial and about 60° F. initial an equal desulfuration demands more and more acid until a temperature is reached at which substantially the same proportion of 98% sulfuric acid or other sulfuric acid stronger than that of about 66° B. is needed as would be required at about 60° F. initial; (c) that the increase in acid demanded for a given rise in temperature above about 38° F. initial becomes larger and larger as 56° F. initial is approached, so that the difference between about 38° F. initial and about 44° F. initial is not so great as between about 44° F. initial and about 50° F. initial, and this in turn not so great as between about 50° F. initial and about 56° F. initial, and (d) that the amount of desulfuration at about or below 38° F. initial and at any temperature between the same and about 60° F. initial can be increased or decreased by using a larger or a smaller proportion of 98% sulfuric acid or of other sulfuric acid stronger than that of about 66° B., although I believe that for a given stock and a given stronger acid there is an irreducible minimum, or, in other words, a certain sulfur content which cannot substantially be reduced by using an increased proportion of the acid.

By treating the above mentioned uncracked stock with 98% sulfuric acid at about 38° F. initial, followed by rerunning, by a subsequent light treatment with sulfuric acid and alkali, and by steam stilling, I have obtained finished burning oil (kerosene) with not exceeding 1/20 per cent. of sulfur, by using the 98% acid at the rate of twenty pounds of the same to the barrel of stock treated. The following table shows, by way of example, the sulfur contents of finished burning oil (kerosene) which I have obtained by the above procedure, using different strengths of sulfuric acids stronger than that of about 66° B. on different samples of the

above mentioned uncracked stock at the rate of twenty pounds to the barrel, namely:

95% acid gave	75/1000 per cent. sulfur.
96% acid gave	55/1000 per cent. sulfur.
98% acid gave	50/1000 per cent. sulfur.
100% acid gave	40/1000 per cent. sulfur.
Fuming acid (10 per	
ct. anhydrid) gave	45/1000 per cent. sulfur.
Sulfuric anhydrid	
gave	40/1000 per cent. sulfur.

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By using more than twenty pounds of the 98% acid or other acid stronger than that of about 66° B. to the gallon of stock the sulfur content of the finished burning oil (kerosene) can be further reduced, until the irreducible minimum is attained. This latter will be higher or lower for the above mentioned uncracked stock, according to the particular strength of the acid used thereon. If burning oil (kerosene) containing 75/1000 per cent. of sulfur should not be marketable, one could either increase the proportion of 95% acid or use an acid still stronger. The latter course is considered more advantageous, as the increased effect of a given weight of 98% acid over 95% acid more than counterbalances its increased cost per pound. For the same reason, if an oil with a sulfur content of 75/1000 per cent. should be satisfactory, it would be more advantageous to use 98% acid. The use of acid less strong than that of about 98%, or even than that of about 95%, is not excluded from the invention; but its use is considered not so advantageous as the use of acid of about 98%; and cases may arise for which the less strong acid, or even 98% acid, would be available for part only of the desired desulfuration on account of the minimum percentage of sulfur obtainable therewith being higher than that desired. The use of sulfuric acid stronger than that of about 98% is also included in the invention. Where "98% or other extra strong acid" is hereinafter referred to, the expression will be understood to include not only non-fuming sulfuric acid containing about 98% sulfuric monohydrate but also other sulfuric acid appropriately stronger than that of about 66° B., whether stronger than or not so strong as non-fuming sulfuric acid of about 98% sulfuric monohydrate.

With the same initial temperature of treatment, the sulfur content of the finished burning oil (kerosene) depends not only on the particular strength and proportion used of the 98% or other extra strong acid, but also on the boiling points and percentages of the different hydrocarbons composing the stock, upon the sulfur content of such stock, and upon the character of the stock as composed in greater or less proportion of cracked products or as consisting substantially of distillate obtained without cracking; and if the stock should be more or less desulfurized (as

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it may within the limits of the invention be more or less desulfurized) before or after treatment with 98% or other extra strong acid, the sulfur content would also depend upon the extent and character of such prior or subsequent desulfuration. In a general way, according to my experience, in order to obtain burning oil (kerosene) of a given attainable sulfur content, the proportion of the 98% or other extra strong acid must be increased with increase in the average boiling point of the hydrocarbons composing the stock to be treated therewith, also with increase in the sulfur content of such stock before the treatment, and with increase in the proportion of cracked products in such stock; and it may be diminished with decrease in each of these respects. When a prior or a subsequent desulfuration by other means is to be resorted to, the treatment with 98% or other extra strong acid is carried on with a proportion of such acid adapted to the desulfuration to be performed by it.

To adjust usefully the proportion of 98% or other extra strong acid to the different conditions liable to be encountered in practice, it is not necessary to possess a mathematical formula. The invention does not consist in any particular mode of effecting such adjustment; but, by way of example, it may be observed that one available mode would consist in taking a small quantity (say enough to fill an agitator to the usual height) of the burning oil (kerosene) distillate of whatever kind, treating it at about 38° F. initial with 98% or other extra strong acid at the rate of twenty pounds (or of a smaller amount, if preferred) of such acid to the barrel of distillate, and ascertaining the sulfur content of the resulting burning oil (kerosene) after rerunning, and light subsequent treatment with sulfuric acid and alkali, and also after steam stilling when this is necessary to give the desired fire test. If the then ascertained content should be unsatisfactorily high, the rerun and subsequently lightly treated product can be treated at about 38° F. initial with successive lots of 98% or other extra strong acid in the proportion of five pounds of said acid to the barrel of said product, until either a satisfactorily low sulfur content is obtained, or it is seen that an irreducible minimum has been reached, or that cost of further acid would give a financially prohibitive total. After the treatment with each lot of acid at the five pounds to the barrel rate, the acid sludge would best be drawn off before the next lot of acid is applied; and, unless the oil refiner should be sufficiently experienced accurately to forecast the effect of rerunning, the oil would best also be rerun and subsequently given a light treatment with sulfuric acid and alkali before such application. With the same cut or cuts from the same Lima crude oil, the same propor-

tion of 98% or other extra strong acid may be expected to give burning oil (kerosene) of the same sulfur content.

According to my experience, there is no advantage, or at least none commensurate with the increased cost of cooling, in reducing the initial temperature of the stock below about 38° F.; although much the same desulfurizing effect per pound of 98% or other extra strong acid can be obtained at lower temperatures. The following table shows the pounds of 98% sulfuric acid to the barrel of stock which I have found to be needed to make a finished burning oil (kerosene) of 1/20 per cent. sulfur from the above mentioned uncracked stock by treating it with said acid at different temperatures at about and above 38° F. initial and then rerunning the so treated stock and giving the rerun distillate a light treatment with sulfuric acid and alkali, followed by steam stilling to remove the naphtha, namely:

At about 38° F. initial	20 pounds.	
At about 44° F. initial	25 pounds.	90
At about 50° F. initial	37 pounds.	
At about 56° F. initial	54 pounds.	

The explanation of the ability of a smaller proportion of 98% or other extra strong acid, when applied to Lima oil at about or below 38° F. or at other temperature substantially below about 60° F. initial, to accomplish the same desulfurizing effect as a larger proportion of the same acid, when applied to the same stock at about 60° F. initial or at any lower temperature which is yet above 38° F. and also above that at which the smaller proportion of acid is used, consists in the fact (as I believe) that the affinity of 98% or other extra strong acid for the sulfur compounds of Lima oil is diminished by such decrease in temperature less than its affinity for the unsulfured hydrocarbons of Lima oil is diminished thereby. The chemical energy of the 98% or other extra strong acid expends itself, I believe, at all the temperatures both upon the said sulfured and the unsulfured compounds; but the ratio in which it acts upon them, respectively, is different at the different temperatures; and the larger proportionate expenditure is upon the sulfur compounds at the lower temperatures herein above set forth. But, whatever the explanation, an equal desulfurizing effect is produced by a smaller proportion of acid at said lower temperature; and there is less destruction of useful unsulfured hydrocarbons by the smaller proportion of the desulfurizing acid and also less injury (if any) by it to the color of the oil after rerunning.

The burning oil (kerosene) distillate from Lima crude oil to be desulfurized in accordance with this first part of the present invention may include all or any part of the

cracked oil of a boiling point or gravity suitable for burning oil (kerosene) along with all or any part of the uncracked distillate of suitable boiling point or gravity; or it may consist of either or any part of either of them without the other; or it may include hydrocarbons too light and volatile (and consequently not safe) or not light and volatile enough (and consequently too viscous) to be suitable for burning oil (kerosene) along with hydrocarbons suitable therefor.

In desulfurizing the above mentioned uncracked stock in the manner above set forth, the naphtha driven off in the steam stilling should have a sulfur content not exceeding 1/100 of one per cent. A naphtha cut can also be desulfurized apart from the burning oil (kerosene) hydrocarbons; although it is considered ordinarily more advantageous to desulfurize them together and afterwards to separate the desulfurized naphtha from the desulfurized burning oil (kerosene).

The second part of the present invention is based upon the discovery first made I believe by me (a) that in desulfurizing Lima oil in the form of cracked oil with 98% or other extra strong acid, a burning oil (kerosene) of lower sulfur content (within the limits attainable with the particular strength of acid employed) can be made by desulfurizing the heavy end of the burning oil (kerosene) fraction of a given cracked oil apart from the light end thereof than can be made by desulfurizing the said light and heavy ends together by means of an equal proportion of 98% or other extra strong acid, and (b) that by treating the heavy end of the burning oil (kerosene) fraction of Lima cracked oil apart from the light end thereof with 98% or other extra strong acid, said heavy end can be obtained with a sulfur content substantially lower than the minimum heretofore obtainable (as I believe) from the Lima cracked oil of the same original sulfur content, by means of any prior process of desulfurizing Lima petroleum at like (or even at any) cost.

The discoveries which form the basis of this second part of the present invention are best made available by employing the 98% or other extra strong acid at temperatures below about 60° F. initial as above set forth, on account of the saving of acid and oil and the avoidance of injury to the color of the oil, and such treatment is specially claimed; but the application of these discoveries is not necessarily confined wholly to the use of the 98% or other extra strong acid at such lower temperatures; for there is a saving of acid by treating the heavy end separate from the light end, even at about 60° F. initial (and I believe at even higher temperatures, if it should be desired for any reason to employ a higher temperature) as compared with a treatment at the same tem-

perature of the said heavy end in admixture with said light end; and I believe that by such separate treatment, even at about or above 60° F. initial, it is possible to obtain said heavy end of a lower sulfur content than has been attainable hertofore.

The ability profitably to secure the hydrocarbons which compose the heavy end of the burning oil (kerosene) fraction of Lima cracked oil with a lower sulfur content than the minimum heretofore attainable at like cost (if at all) gives to such hydrocarbons a substantially increased value as constituents of burning oil (kerosene) where the lowest sulfur content previously attainable is so high as to interfere with the fitness of said hydrocarbons to serve as such constituents. Thus, for example, in my experience, the cracked oil from the same Lima crude petroleum from which I have obtained the above mentioned uncracked stock has yielded a light and a heavy end of the following respective descriptions, when said cracked oil was itself distilled in the ordinary way, namely: a light end of the burning oil (kerosene) fraction equal in volume to about eight per cent. of the crude oil and containing an amount of naphtha equal to about one per cent. of the crude oil and having a gravity of 49° B. and a sulfur content of two hundred and thirty-six one-thousandths per cent., and a heavy end of the same fraction equal in volume to about twelve and a half per cent. of the crude oil and having a gravity of 37 4/10° B. and a sulfur content of three hundred one-thousandths per cent., the receiver being changed during the distillation when the gravity of the oil from the tail pipe of the condenser reached 43° B., and the collection of said heavy end stopped when the gravity of oil therefrom reached 35° B. A mixture of some of the light and heavy ends with each other in proportion to their respective volumes as collected, so as to give a third stock representing the distillate which would be obtained by collecting both light and heavy ends in the same receiver, had a gravity of 41 2/10° B. and a sulfur content of two hundred and seventy one-thousandths per cent. It, of course, represented about twenty and a half per cent. of the crude oil and contained naphtha equal to about one per cent. of the crude oil. By separate treatment of each of these three cracked stocks with 98% sulfuric acid at the rate of twenty pounds to the barrel and at a temperature of about 38° F. initial, followed in the cases of the light and heavy ends by separate rerunning, and subsequent separate light treatment with sulfuric acid and alkali, and in the case of the mixed stock by rerunning with change of receiver when the distillate from the tail pipe of the condenser reached 43° B. and subsequent light treatment of the so collected light and heavy ends separately with sulfuric acid

and alkali, and also followed in the case of the two light ends by steam stilling to the same extent, I have obtained products with sulfur contents as under, namely:

5	Concurrently desulfurized	
	light end.....	55/1000 per cent.
	Concurrently desulfurized	
	heavy end.....	130/1000 per cent.
10	Separately desulfurized	
	light end.....	50/1000 per cent.
	Separately desulfurized	
	heavy end.....	100/1000 per cent.

The increased desulfurizing effect due to the desulfuration of the heavy end separately from the light end is apparent.

By treating the three cracked stock separately at about 38° F. initial with a larger proportion of 98% sulfuric acid, namely in the proportion of thirty pounds to the barrel, followed in each case by the corresponding procedure as set forth above, I have obtained heavy end of still lower percentage of sulfur as follows:

25	Concurrently desulfurized	
	light end.....	52/1000 per cent.
	Concurrently desulfurized	
	heavy end.....	123/1000 per cent.
30	Separately desulfurized	
	light end.....	48/1000 per cent.
	Separately desulfurized	
	heavy end.....	90/1000 per cent.

I do not believe that the heavy end of the same Lima cracked oil is obtainable by any prior process of lower sulfur content than that given in the last table above for concurrently desulfurized heavy end, if indeed it can be so obtained of as low a content of sulfur. The still lower sulfur content of the separately treated heavy end can be seen on inspection of this table; and it is to be noted that no additional acid has been needed to obtain this lower sulfur content.

The third part of the present invention is based upon the discovery first made I believe by me that in the heavy end of the burning oil (kerosene) fraction of Lima cracked oil there are present sulfur compounds which are unremoved not only by sulfuric acid of about 66° B., but also by some at least of the materials (other than 98% or other extra strong acid) heretofore employed or proposed as desulfurizers of Lima petroleum and having on the latter a more energetic desulfurizing action that is possessed by sulfuric acid of about 66° B., but which compounds are, nevertheless, removable by means of 98% or other extra strong acid. And I believe that when Lima cracked oil is desulfurized, under whatever conditions, by materials which have been heretofore used or proposed as desulfurizers of Lima oil (including various metals, metallic oxides, metallic salts, and non-metallic

desulfurizing agents) other than 98% or other extra strong acid, it retains in its heavy end sulfur compounds removable by 98% or other extra strong acid; although it may be that exceptions exist. In accordance with this third part of the invention the heavy end of the burning oil fraction of Lima cracked oil is first desulfurized to such extent as may both be feasible and also be considered desirable by means of another desulfurizing agent (say, copper oxid); and then a further amelioration of the same in respect to its sulfur content is effected by means of 98% or other extra strong acid. In either or in each desulfuration the said heavy end can be subjected to the desulfurizing agent either in connection with or apart from the light end of said fraction; and the 98% or other extra strong acid can be applied to the oil at about 60° F. or at other preferred temperature; but it is considered more advantageous and a special improvement to subject the heavy end to the 98% or other strong acid apart from the light end, and also to subject the same thereto at temperatures below about 60° F., as mentioned above.

Lima cracked oil in general, even in the lighter end of the burning oil (kerosene) fraction, is improved in its sulfur content by subjection to 98% or other extra strong acid after it has been desulfurized by some other material, say copper oxid, which is more energetic as a desulfurizer of Lima oil than is sulfuric acid of about 66° B.; and it may in some cases be advisable to subject Lima oil in other forms than that of cracked oil to such subsequent treatment with 98% or other extra strong acid. Such subsequent subjection of Lima cracked or uncracked oil in general to 98% or other extra strong acid is included in this third part of the invention.

By taking the mixed stock mentioned above in setting forth the second part of the invention and distilling said stock in the presence of copper oxid mixed with or dissolved in the same, with separate collection of the distillate which came over before and that which came over after the distillate from the tail pipe of the condenser reached 43° B., I have obtained two desulfurized products which I then divided each into two portions. I finished one lighter and one heavier portion for burning oil (kerosene) by application to them separately of the ordinary sulfuric acid and alkali treatment (using sulfuric acid of about 66° B. at the rate of six pounds to the barrel). Each of the other two portions I treated separately with 98% sulfuric acid at about 38° F. initial, using ten pounds of 98% acid to the barrel of oil; and, after rerunning, I gave each of the so treated portions a further light treatment with sulfuric acid and alkali. I also steam stillled the

two light products separately. I thus obtained four finished burning oil (kerosene) products of the following respective sulfur contents, namely:

- 5 Light end desulfurized with copper oxid only. 60/1000 per cent.
- Heavy end desulfurized with copper oxid only. 160/1000 per cent.
- 10 Light end desulfurized with copper oxid followed by 98% sulfuric acid. 840/1000 per cent.
- Heavy end desulfurized with copper oxid followed by 98% sulfuric acid. 80/1000 per cent.

The amelioration of the oil (especially the heavy end) by the subsequent treatment with 98% acid is plain; and I believe that similar amelioration of the oil is obtainable with other extra strong acid as well as with 98% acid. In obtaining this amelioration, it will be observed that the whole cost of the 25 98% or other extra strong acid is not to be charged against it; since said cost is partly offset by the larger amount of acid of about 66° B. required in the ordinary treatment given to the first two products of this last 30 table, as compared with the smaller amount of such acid used in the light treatment given after rerunning to the last two products of said table.

Specific reference herein above has been 35 made to Lima oil only and to it only in the form of burning oil (kerosene) distillate or in the form of the yet lighter naphtha. There are, however, oils not within the above given definition of Lima oil which are so far 40 analogous thereto as to admit of useful desulfuration in the form of burning (kerosene) distillate or of the yet lighter naphtha by means of 98% or other extra strong acid; although by reason of their less content of 45 refractory sulfur compounds or by reason of the smoky character of their burning oil (kerosene) fraction, their desulfuration with 98% acid as above set forth would not present all the advantages which attend such 50 desulfuration of Lima oil as above defined. For example, according to my experience, petroleum produced in Kansas, when in the form of the distillate yielded between 300° F. and 550° F. by the crude oil and prepared as 55 aforesaid, responds to the first, third and fourth of the above mentioned tests; but it usually remains uncolored when clear plum-bate of sodium solution is added thereto. In other words, in said prepared form, it 60 usually fails to respond to the second test mentioned and to this test only of the four. Such failure tends to show a less content of refractory sulfur compounds in the general run of oil from the Kansas oil fields than in 65 Lima oil as above defined. Special oils

from Kansas wells have, however, in my experience responded in said prepared form to all four of the above mentioned tests; and such special oils are consequently within the above definition of Lima oil. 70

Again, according to my experience, petroleum produced near Beaumont, in Texas, when in the form of the distillate yielded between 300° F. and 550° F. by the crude oil and prepared as aforesaid, responds to the 75 second, third and fourth of the above mentioned tests; but it is smoky. When tested by the refractometer its refractive index is more than 1.4600. In other words, in said prepared form, it fails to respond to the first 80 test mentioned, and to this test only of the four. In making burning oil (kerosene) from such petroleum, it would, in my opinion, be preferable ordinarily to subject the burning oil (kerosene) distillate to 98% or 85 other extra strong acid at a higher temperature than about 60° F. and in larger proportion than even sixty pounds to the barrel in order to diminish the content of smoky hydrocarbons as set forth in my application 90 of August 21, 1903, No. 170,327. Desulfuration will be effected as a concomitant result by the same operation. In case smokiness is otherwise cured, and possibly in other cases also it may be desirable, however, to 95 subject Beaumont petroleum in the form of burning oil (kerosene) distillate (smoky or non-smoking, as the case may be) to desulfuration by means of 98% or other extra strong acid as herein set forth. Beaumont petroleum yields little naphtha; but that which is obtainable therefrom, and also the lighter non-smoking portion of its burning oil (kerosene) fraction (cracked or uncracked, or a mixture of both), may well be 1 desulfurized in accordance with the present invention. Moreover, other petroleum no doubt exists which is not within the above definition of Lima oil, in that in case it should be tested in the said prepared form it would not respond to all four of the above mentioned tests, but which is analogous to Lima oil in that in such case it would respond to the third and fourth of said tests, or to the fourth of them at least, with or without also 1 responding to one or other of the first two tests (or to both of these, if the prepared distillate should fail to respond to said third test). Such other petroleum, with that from the Kansas oil fields (not within the definition of Lima oil) and that from the oil fields near Beaumont, in Texas, constitutes the analogous petroleum of the present specification. Further, I believe that Lima petroleum as above defined, and petroleum analogous thereto as aforesaid, can by means of 98% or other extra strong acid be desulfurized usefully in other distillate forms (as well as in those of burning oil and naphtha distillates) and even in undistilled forms. I do

not believe that Lima or analogous petroleum can be desulfurized thereby anywhere near so advantageously in undistilled as in distillate forms; and consequently it is considered a special advantage and improvement to desulfurize the same in accordance with the present invention as distillates whenever distillation would not interfere with the usefulness for their intended purposes of the products to be obtained.

As indicated above, I believe that more pounds of sulfur can be removed by a given weight of 98% of other extra strong acid from lower boiling than from higher boiling products; and hence special claims are made to the desulfuration of Lima or analogous petroleum in the form of distillate lighter than .865 specific gravity (about 32° B.), which expression (at least when applied to Lima oil) includes the distillate next heavier than burning oil (kerosene) as well as the latter and naphtha. Hence also special claims are made to the desulfuration of burning oil (kerosene) and naphtha distillates separately or together, for the desulfuration of which distillates the invention is primarily designed. I also believe that petroleum exists which is not within the above definitions of Lima and analogous petroleum, but which is sufficiently related thereto to admit of useful desulfuration in some form at least by means of 98% or other extra strong acid; although such desulfuration would probably not present all the advantages of a desulfuration of Lima (or even of analogous) petroleum. The specified relationship for the purposes of this specification will be established for any petroleum by the fact that in some form at least, although not in the form of distillate yielded between 300° F. and 550° F. by the crude oil, it responds (after the aforesaid preparation) to the third and fourth, or to fourth at least, of said tests, with or without responding also to one or other or to both of the first two tests. Such petroleum forms part of the related oils of the present specification.

Lastly, I believe that hydrocarbon oils derived from sources other than petroleum, say from maltha, asphalt, bituminous shale, bituminous coal, and so on, are (some of them at least) sufficiently related to Lima or analogous petroleum to admit of useful desulfuration in some form at least by means of 98% or other extra strong acid; although I would not venture to say that any desulfuration thereof would present all the advantages of a desulfuration of Lima or analogous petroleum by such acid. The specified relationship for the purposes of this specification will be sufficiently shown for any non-petroleum hydrocarbon oil by the fact that in some form at least, after the aforesaid preparation, it responds to the third and fourth, or to the fourth at least, of said tests,

with or without responding also to one or other or to both of the first two tests. Such non-petroleum hydrocarbon oils form part of the related oils of the present specification. Some of them have a burning oil fraction which corresponds at least approximately in refractive index, boiling point and viscosity, with the burning oil (kerosene) fraction of petroleum heretofore refined and marketed in the form of burning oil (kerosene).

The invention includes all and singular the new, useful and original parts, improvements or combinations herein set forth.

The following is a description of what is considered the best mode of carrying the invention into effect, taking, by way of example, the Lima crude oil from which the above mentioned uncracked stock has been obtained and considering in order three cases, in the first of which cases all the desulfuration of three different burning oil (kerosene) distillates is effected by 98% or other extra strong acid without assistance from any other material more energetic as a desulfurizer than sulfuric acid of about 66° B., in the second of which cases the same three burning oil (kerosene) distillates are, respectively, desulfurized, one distillate by 98% or other extra strong acid as in the first case and the other two distillates by material other than 98% or other extra strong acid, which material is more energetic as a desulfurizer of Lima oil than is sulfuric acid of about 66° B., and in the third of which cases one (or more, if preferred) of the three burning oil (kerosene) distillates is desulfurized by treatment with 98% or other extra strong acid after it has been desulfurized by another material also more energetic as a desulfurizer of Lima oil than is sulfuric acid of about 66° B.

First case.—The said Lima crude oil is placed in the ordinary cheese box or cylinder still and is distilled in the ordinary way, with collection of the distillate in one receiver from the beginning of distillation until a specimen of distillate intercepted for the purpose at the tail pipe of the condenser has a gravity of about 41° B. The receiver is then changed; and the distillation is continued with cracking, which commences in my experience when the temperature of the oil in the still reaches about 620° F. It is carried on so long as it is considered safe to do so.

All the distillate which comes over after the distillate from the tail pipe of the condenser has attained a gravity of about 41° B. and which constitutes the cracked oil (although containing uncracked products also) is collected in one receiver. When the crude oil distillation is over this cracked oil is transferred to an ordinary cheese box or cylinder still, and is distilled in the ordinary way, with collection of the distillate by itself in one receiver until the oil from the tail pipe of the

condenser has a gravity of about 43° B. and with subsequent collection of the distillate by itself in another receiver until the oil from the tail pipe of the condenser has a gravity of about 35° B. The residuum in the still can be disposed of as may be thought best. Three stocks to be desulfurized are thus obtained, namely, an uncracked Lima burning oil (kerosene) distillate, the light end of the burning oil (kerosene) fraction of Lima cracked oil, and the heavy end of the same fraction. The first of these, being identical with the above mentioned uncracked distillate, would represent the first fifty per cent. of the crude oil and would contain an amount of naphtha equal to about eleven per cent. of the crude oil and would have a sulfur content of 346/1000 per cent. The said light end would represent about eight per cent. of the crude oil and would contain an amount of naphtha equal to about one per cent. of the crude oil and would have a sulfur content of 236/1000 per cent. The said heavy end would represent about twelve and a half per cent. of the crude oil and would have a sulfur content of 300/1000 per cent. Each of the said three stocks is treated by itself with 98% sulfuric acid at an initial temperature of about 38° F., which can best be secured by running the stock on its way to the agitator through a continuous cooler, say, through pipes immersed in brine, which latter is kept cold by an ice machine, or through chambers containing pipes filled with the refrigerating fluid of an ice machine, or through any other appropriate apparatus for continuous cooling. Each of the so cooled stock is run by itself into an ordinary lead lined agitator until the latter is filled to the ordinary height. The stock is then dried by means of sulfuric acid of about 66° B., using the same say at the rate of from 1/10 to 2/10 of a pound of the acid to the barrel of stock. After the addition of this small proportion of acid, the mixture of acid and stock is agitated by blowing with ordinary air for ten minutes, the mixture is allowed to settle for thirty minutes, and the acid sludge is then drawn off.

The stock, being now dry, is ready for desulfuration by 98% sulfuric acid. For this purpose, it is best to divide the charge of the 98% acid into two or more batches, and, after adding each batch, except the last, to the stock to agitate the mixture of acid and stock by blowing with ordinary air for thirty minutes, then to allow to settle thirty minutes, and lastly to draw off the sludge before adding the next batch of 98% acid. After the addition of the last batch, blow for thirty minutes and allow to settle for an hour and then draw off the sludge.

If the object is to obtain from the uncracked stock a burning oil (kerosene) product containing not more than 1/20 per cent. of sulfur, said stock would best be treated

with two batches of 98% acid, each consisting of ten pounds of such acid to each barrel of said uncracked stock.

If the object is to obtain from the light end of the cracked oil a burning oil (kerosene) product containing not more than 50/1000 per cent. of sulfur, said light end would best be treated with two batches of 98% acid, each consisting of ten pounds of such acid to each barrel of said light end.

If the object is to obtain from the heavy end of the cracked oil a burning oil (kerosene) product containing not more than 100/1000 per cent of sulfur, said heavy end would best be treated with two batches of 98% acid, each consisting of ten pounds of such acid to each barrel of said heavy end.

After each stock has been treated with 98% acid (twenty pounds to the barrel, as just mentioned), it is washed in the manner usual in the sulfuric acid and alkali treatment, first with water, then with caustic soda lye and finally with water. Each stock is then rerun by itself and each resulting distillate is given by itself a light treatment with sulfuric acid and alkali, using say three or four pounds of sulfuric acid of about 66° B., or the same weight of sludge from the preceding treatment with 98% acid. The uncracked stock is then steam stillled by itself, until it has attained the desired fire test, the naphtha being collected. The light end and the heavy end of the cracked oil are mixed and the whole is steam stillled with collection of the naphtha until the oil has the desired fire test; or the light end can be steam stillled by itself with collection of naphtha and then be mixed with the heavy end. The resulting products are two grades of burning oil (kerosene) having a sulfur content of not more than 50/1000 per cent. for the uncracked and not more than 83/1000 per cent. for the cracked product, and also two grades of naphtha having a sulfur content of not exceeding 10/1000 per cent. for the uncracked and 19/1000 per cent. for the cracked product. The heavy end of the burning oil fraction of the cracked oil, after separate rerunning and the subsequent separate light treatment, should have a sulfur content of not more than 100/1000 per cent. The light end, after steam stilling and before mixture of the same with the heavy end, should have a sulfur content of not more than 50/1000 per cent.

In rerunning either or both the naphtha containing stocks, a naphtha cut can be taken, the same to be given by itself a light treatment with sulfuric acid and alkali. Also a naphtha cut for desulfuration apart from the burning oil (kerosene) distillate can be taken in the crude oil distillation or in the cracked oil distillation. In such case, assuming that the same Lima crude oil as before is taken as an example, and that two

naphtha cuts are to be made, the two naphtha stocks may well represent, respectively, the uncracked about eleven and the cracked about one per cent. of the crude oil. In desulfurizing them with 98% sulfuric acid, the most advantageous proportion would be ten pounds of 98% acid to the barrel, applied in two batches each of five pounds to the barrel, of each naphtha distillate. If only one grade of naphtha should be desired, the two naphtha cuts can be mixed with each other before desulfuration.

Instead of changing the receivers and stopping the distillations at the points mentioned the receivers can be changed and the distillations, or any of them, stopped at any desired points; although under the assumed conditions the points indicated are in general considered the most advantageous, or at least as advantageous as any. Lima crude oil as above defined will vary both in its percentage of hydrocarbons of different boiling points, in its sulfur content, and I believe also in the kinds of its constituents; and crude petroleum analogous to Lima oil are likely to vary yet more in each of these respects.

In the first part of this specification sufficient directions have been given to enable the proportion of 98% sulfuric acid to be adjusted to the varying conditions, only it seems well to say here that, judging from my experience, whenever a crude petroleum yields an uncracked burning oil (kerosene) distillate a specimen of which has a sulfur content of less than 2/10 per cent. after treatment with sulfuric acid and alkali, using sulfuric acid of about 66° B. at the rate of twenty pounds to the barrel, and especially if it further fails to respond to the second of the before mentioned tests, the sulfur content of such uncracked distillate can be reduced to or below 1/20 per cent. by the use of less than twenty pounds of 98% sulfuric acid at about 38° F. initial. For using (if desired) some other sulfuric acid appropriately stronger than that of about 66° B. in place of 98% acid, the foregoing directions it is believed will suffice.

Instead of initially cooling the stocks (or any of them) to about 38° F., they could be cooled to a lower temperature; or they need not be cooled so low; only it is believed that there would be a disadvantage rather than advantage in departing from about 38° F. initial. It is not considered advantageous to cool either the 98% or other extra strong acid applied to the oil or the air for agitating the mixture; nor is it considered advantageous to restrain the rise of temperature which naturally follows the reaction of the said acid on the sulfur compounds and other constituents of the oil; but any or all of these things may be done, the only objection to them being on the score of unnecessary expense.

Second case.—The said Lima oil is distilled at first in the ordinary way and then with cracking, the uncracked distillate and the cracked oil being collected in separate receivers, as in the first case. The cracked oil is distilled with change of receiver, also as in said first case. The uncracked distillate and the light end of the cracked oil are then separately desulfurized in any known or suitable manner by some known or suitable material other than 98% or other extra strong acid, which material is a more energetic desulfurizer of Lima oil than is sulfuric acid of about 66° B., say, with copper oxid mixed with or dissolved in the oil to be desulfurized while the latter is undergoing distillation; and the heavy end of the cracked oil is desulfurized with 98% sulfuric acid applied in the manner and proportion above set forth in describing the first case. The uncracked distillate and the light end of the cracked oil are separately treated in the ordinary manner with sulfuric acid and alkali (with use, say, of six pounds of sulfuric acid of about 66° B. to the barrel of oil treated). As in the first case, the heavy end, after treatment with 98% sulfuric acid, is rerun; and the distillate obtained in the rerunning is finished by a light treatment with sulfuric acid and alkali. The heavy end and the light end of the cracked oil are then mixed together; and the mixture is steam stillled to obtain the desulfurized naphtha and also to give a proper fire test to the burning oil (kerosene). The desulfurized uncracked oil is steam stillled for the same purposes. The light end of the cracked oil could be steam stillled before admixture with the heavy end; and subsequent steam stilling could then be dispensed with. Naphtha cuts to be desulfurized separately can be taken in the ordinary distillation of the crude oil and the cracked oil, respectively. And such naphtha cuts can be made and the naphtha distillates mixed before desulfuration, if only one grade of naphtha should be desired. The receivers can be changed and the distillations (or any of them) stopped at any desired points. In place of 98% acid, other extra strong acid can be used; and the proportion of the acid used can be adjusted to the condition of the stock to be treated; and the temperature of treatment therewith can be varied, all as herein above set forth.

Third case.—The said Lima crude oil is distilled at first in the ordinary way and then with cracking, the uncracked and the cracked distillate being collected in separate receivers, as in the first case. The cracked oil is distilled without change of receiver; and the distillation is stopped when the distillate from the tail pipe of the condenser has a gravity of about 35° B., as in the first case. The uncracked distillate and the entire cracked oil distillate are then separately desulfurized in any known or suitable way, more espe-

cially, but not exclusively, by means of an appropriately energetic metal, metallic oxid or metallic salt (or of one or more of them), say by means of copper oxid mixed with or dissolved in the oil while this is undergoing distillation. In thus distilling the cracked stock for removal of sulfur the receiver is changed when the distillate from the tail pipe of the condenser has a gravity of about 43° B., as in the first case; and the distillation is stopped when such distillate has a gravity of about 35° B., so as to obtain as near as may be the same light and heavy ends of said burning oil fraction of said Lima cracked oil which were obtained in the first case. The desulfurized uncracked distillate and the desulfurized light end are then separately given each of them an ordinary treatment with sulfuric acid and alkali (using say six pounds of sulfuric acid of about 66° B., to the barrel of stock treated). The desulfurized heavy end, in order still further to desulfurize it, is given a treatment with 98% sulfuric acid at about 38° F. initial, and is rerun and is then finished by a light treatment with sulfuric acid and alkali, all as set forth for the corresponding heavy end in the first case, only instead of the proportion of 98% acid there given it is now necessary to use a proportion of only ten pounds of acid to the barrel of heavy end, in order to obtain the same with a content of sulfur even below that given in the description of the first case; and, unless a still lower sulfur content should be desired, this smaller proportion of 98% acid would best be used. It would best be applied in two equal batches. The light end and the heavy end are mixed with each other; and the mixture is steam stillled to obtain the desulfurized naphtha and also to raise the fire test of the finished burning oil (kerosene). The latter, (according to my experience) may be expected to contain about 73/1000 per cent. of sulfur, its light end having a sulfur content of about 60/1000 per cent. and its heavy end about 80/1000 per cent. The uncracked oil is steam stillled to recover the naphtha therefrom and to raise the fire test of the finished burning oil (kerosene). The light end of the cracked oil could first be steam stillled and then mixed with the heavy end, dispensing with steam stilling after the mixture.

If the percentage of sulfur in either the light end of the cracked oil or in the uncracked distillate should be regarded as too high, either or each of them could be treated with 98% sulphur at about 38° F. and rerun and then finished by a light treatment with sulphuric acid and alkali, the ordinary treatment of them with sulphuric acid and alkali being best omitted.

Separate naphtha cuts (to be separately desulfurized) can be taken in the ordinary distillation of the crude oil and in the dis-

tillation of the cracked oil, respectively. And such naphtha cuts could be made and the naphtha distillates mixed before desulfuration, if only one grade of naphtha should be desired. The receivers can be changed and the distillations (or any of them) stopped at any desired points. In place of 98% sulfuric acid, other extra strong acid can be used; and the proportion of the acid used can be adjusted to the condition of the stock to be treated and the temperature of treatment therewith can be varied, all as herein above set forth.

In order to have particular distillates (cracked or uncracked) in a desulfurized state, it is not necessary first to obtain and then to desulfurize them; they can be obtained first in a desulfurized state. For example, in carrying out the present invention in accordance with said third case, the uncracked burning oil (kerosene) distillate can be obtained in a desulfurized state by effecting the requisite desulfuration in the crude oil distillation, the vapors from the crude oil being passed over copper oxid after said vapors have been given off from the body of the crude oil and while they are on their way to the condenser, and the receiver being changed when the oil from the tail pipe of the condenser attains a gravity of about 41° B.; and the two ends of the burning oil (kerosene) fraction of the cracked oil can be obtained in a desulfurized condition by effecting the desulfuration either in the crude oil or in the cracked oil distillation, the vapors being passed over copper oxid after said vapors have been given off from the body of the crude oil or of the cracked oil while they are on their way to the condenser, and the receiver being changed in the cracked oil distillation when the oil from the tail pipe of the condenser attains a gravity of about 43° B. For effecting the desulfuration of both uncracked and cracked distillate in the crude oil distillation, the passage of vapors from the crude oil over the copper oxid would first be carried on until the collection of the uncracked distillate should be completed; and thereupon the receiver would be changed and the passage of the vapors from the crude oil over the copper oxid would be continued until all the cracked oil should be received. This desulfurized cracked oil would then be distilled with change of receiver when the oil from the tail pipe of the condenser attains a gravity of about 43° B. and with stoppage of the distillation when it reaches about 35° B., so as to separate the light end and the heavy end from each other, as well as from still heavier hydro-carbons.

For effecting the desulfuration of the uncracked distillate in the crude oil distillation and that of the light and heavy ends in the cracked oil distillation, the vapors from the crude oil would best be passed over the

copper oxid only until the uncracked distillate should be collected; and thereupon the receiver would be changed and the vapors from the crude oil be passed directly to the condenser until all the cracked oil should be received. This latter would then be distilled with passage of the vapors therefrom over copper oxid on their way to the condenser, and with change of receiver when the oil from the tail pipe of the condenser attains a gravity of about 43° B., the distillation being stopped when a gravity of about 35° B. is attained by such oil. The uncracked distillate and the light end of the cracked oil (in whichever way obtained) could then be given (each of them separately) a treatment with sulfuric acid and alkali. The heavy end (in whichever way obtained) could be further desulfurized at about 38° F. initial by means of 98% sulfuric acid, ten pounds to the barrel, with subsequent re-running, followed by a light treatment with sulfuric acid and alkali. The uncracked distillate could be steam stillled; and the light end of the cracked oil could be mixed with the heavy end thereof and the whole steam stillled; or the light end could be steam stillled and then be mixed with the heavy end.

If it should be desired to make only one grade of burning oil (kerosene), to be composed of both the cracked and uncracked distillates, it will, nevertheless, be more advantageous ordinarily to desulfurize uncracked oil separately from cracked oil (at least when their desulfuration is effected by means of 98% or other extra strong acid) as well as to desulfurize the heavy end of the burning oil fraction of the cracked oil by such acid after separation of the light and heavy ends from each other; but if the advantages of separate desulfuration should not be desired, cracked and uncracked oils can be desulfurized together and the heavy end of the cracked oil can be desulfurized without previous separation of the light and heavy ends thereof from each other.

With respect to the desulfuration by means of 98% or other extra strong acid of petroleum and other hydrocarbon oils related as aforesaid to Lima or analogous petroleum, the same would always be treated in a form in which, after the aforesaid preparation, they, respectively, respond to the third and fourth, or to the fourth at least, of the above mentioned tests. It will be found most advantageous, as I believe, to cool the oil to be desulfurized to about 38° F. by running the same on its way to the agitator through a continuous cooler; and to treat it at such initial temperature with 98% or other extra strong acid in the manner above described, the proportion of acid to oil being adjusted to the desulfuration to be effected thereby. The best proportion can be determined after the mode above described, or otherwise, if

preferred. The oil, after finally drawing off the sludge, would be rerun; and the resulting distillate would be given a light treatment with sulfuric acid and alkali and be steam stillled, if necessary or if desired. Related oil in the form of burning oil distillate will in most cases, perhaps always, be cracked oil; and it will be found, I believe, advantageous to desulfurize the heavy end of such cracked oil apart from its light end; and in some cases at least I believe that it will be advantageous thus to desulfurize said heavy end with 98% or other extra strong acid, after it shall have been desulfurized with another material, as copper oxid, more energetic as a desulfurizer of Lima petroleum than is sulfuric acid of about 66° B.

The modifications set forth above are not all which can be made; they are given by way of example; and the statement of them is not to be construed as an intention to exclude others; and generally it may be said that each of the improvements composing the invention is intended to be secured for all the uses to which it can be applied, with or without modification.

In the hereinafter written claims the following expressions have, respectively, the following meanings wherever they occur, namely:

"Lima or analogous petroleum or related oil" includes:

First. Petroleum within the above definition of Lima oil, that is to say, petroleum which, in the form of the distillate yielded between 300° F. and 550° F. by the crude oil and prepared as aforesaid, responds to all four of the above mentioned tests;

Second. Petroleum which is not within the above definition of Lima oil, in that in the form of said distillate prepared as aforesaid it does not respond to all four of said tests as Lima oil does, but which is, nevertheless, analogous to the latter in that in said form it responds to the third and fourth of said tests, or to the fourth of them at least, with or without also responding to one or other of the first two tests (or to both of these, if the prepared distillate should fail to respond to said third test);

Third. Petroleum which in the form of distillate yielded between 300° F. and 550° F. by the crude oil and prepared as aforesaid fails to respond to said fourth test, but which, nevertheless, is related to Lima or analogous petroleum, in that in some form at least, after the aforesaid preparation, it does respond to the third and fourth of the above mentioned tests, or to the fourth at least of them, with or without also responding to one or other or to both of the first two tests; and

Fourth. Hydrocarbon oils which are derived from sources other than petroleum and which cannot, therefore, be regarded as petroleum in any form, but which are, never-

theless, related to Lima or analogous petroleum, in that in one or more forms such non-petroleum hydrocarbon oils respond, after the aforesaid preparation, to the third and
 5 fourth of said tests, or to the fourth or least of them, with or without responding also to one or other or to both of said first two tests.

"Sulfuric acid stronger as specified than that of about 66° B." primarily means non-
 10 fuming sulfuric acid of not less than about 96% sulfuric monohydrate and also fuming sulfuric acid containing not more than about four per cent. sulfuric anhydrid; but by extension it means also, on the one hand, non-
 15 fuming sulfuric acid of less than about 96% sulfuric monohydrate, while yet enough stronger than sulfuric acid of about 66° B. to have a useful desulfurizing effect on Lima or analogous petroleum or related oil not pos-
 20 sessed by the latter acid, and, on the other hand, fuming sulfuric acid of more than about four per cent. sulfuric anhydrid, as well as sulfuric anhydrid (100%) itself. Non-fuming sulfuric acid of about 98% sul-
 25 furic monohydrate is considered to have the greatest ratio of desulfurizing activity to cost and consequently to be the most advantageous to use as a desulfurizer of Lima or analogous petroleum; but non-fuming acids
 30 of less than about 98% and not less than about 96% sulfuric monohydrate have so nearly the same desulfurizing effect as 98% acid at slightly less cost and fuming acids of all strengths up to not more than about four
 35 per cent. sulfuric anhydrid cost so little more than 98% acid with slightly greater desulfurizing effect that I class them all with 98% acid as included in the sulfuric acid stronger than that of about 66° B. which it
 40 is primarily intended to employ.

"Which is sulfur bearing as specified" means that the stock, the distillate, the cracked oil, or the heavy end of cracked oil of the burning oil fraction referred to by said ex-
 45 pression responds, after the aforesaid preparation, to the third and fourth, or to the fourth at least, of the before mentioned tests. It may also respond to one or other or to both of the first and second of said tests, according
 50 to the case; or it may fail to respond to either of them. The word "stock" merely means the oil to be desulfurized. It includes undistilled oils whose desulfuration may be desired, as well as all sorts of distillates.

"Temperature lower as specified than about 60° F. initial" primarily means a temperature not higher than about 44° F. initial; but by extension it means also, first, a temperature higher than about 44° F. initial and not higher
 60 than about 50° F. initial, and, secondly, a temperature higher than about 50° F. and not higher than about 56° F. initial. This temperature is expressly said in certain claims to be "artificially produced." Those claims
 65 which mention a "temperature lower as speci-

fied than about 60° F." and do not contain the words "artificially produced" include such lower temperature as specified when produced otherwise as well as when produced arti-
 70 ficially. For example, in winter a tank of oil might naturally have a "temperature lower as specified than about 60° F." merely by standing exposed to the cold weather. The most advantageous temperature, considering
 75 expense for artificial cooling in connection with saving of acid, is about 38° F. initial; but at temperatures below about 38° F. initial the cost of cooling may be so little more and at temperatures above about 38° F. initial to
 80 and including about 44° F. initial the saving in acid is so little less than at about 38° F. initial that I class them all with this last temperature as included in the temperature below about 60° F. initial, which it is primarily
 85 intended to employ. It will be observed that in a number of claims this "temperature" expression does not occur.

"Distillate lighter as specified than .865 specific gravity" means primarily distillate
 90 which is mainly or wholly composed of hydrocarbons not too heavy nor too light to serve usefully as constituents of burning oil; but by extension it means also in the first place distillate which is mainly or wholly composed of
 95 hydrocarbons too light to serve usefully as constituents of burning oil, and, secondly, distillate which is mainly or wholly composed of hydrocarbons too heavy for such service, but not so heavy as to have a specific gravity of
 100 .865.

"Rate not exceeding about sixty pounds to the barrel as specified" means primarily a proportion of not more than about thirty pounds of acid to the forty-gallon barrel of the stock to be desulfurized, yet sufficient to produce a
 105 useful desulfuration; but by extension it means also, first, a proportion exceeding about thirty and not exceeding about forty pounds of acid to the barrel of stock, and, secondly, a proportion exceeding about forty and not ex-
 110 ceeding about fifty pounds of acid to the barrel of stock, and, thirdly, a proportion exceeding about fifty and not exceeding about sixty pounds of acid to the barrel of stock. With less than about thirty pounds of 98% acid
 115 (namely, with about twenty pounds) to the barrel of the above mentioned uncracked stock I have obtained burning oil (kerosene) with a percentage of sulfur therein about as low as in burning oil (kerosene) of similar grade
 120 heretofore made and sold; but higher proportions are likely also to be practically useful. I have accordingly included three successively higher proportions in the extended meaning of this "rate" expression; and I have also
 125 made claims which do not specify any particular rate.

"Light end" means primarily hydrocarbons suitable for burning oil with boiling points below about 500° F.; but it means also by exten-
 130

sion the lighter portion generally of a series of hydrocarbons capable of serving usefully as constituents of burning oil.

"Heavy end" means primarily hydrocarbons suitable for burning oil with boiling points between about 500° F. and about 600° F., both inclusive; but it means also by extension the heavier portion generally of a series of hydrocarbons capable of serving as constituents of burning oil. Stock which "consists of heavy end" is composed wholly or mainly, or at the least in large part, of such heavier hydrocarbons. Lima or analogous petroleum or related oil can be desulfurized in the form of said heavy end with or without previously separating the heavy and light ends from each other; and such separation, when effected, may be nearly or quite complete or in large part only, so as to obtain for desulfuration a distillate free from said light end, or nearly so, or one deprived in large part only of said light end.

"Material as specified other than said stronger acid, which material is more energetic as a desulfurizer of Lima petroleum than is sulfuric acid of about 66° B." means primarily one or more oxids of metals precipitable in acid solution by hydrogen sulfid, of which copper oxid and lead oxids are examples; but it means also by extension, first, one or more of the metals in general, oxids in general of metals not precipitable in acid solution by hydrogen sulfid, and metallic salts in general, known as desulfurizers of Lima petroleum or suitable for such use either when mixed with or dissolved in Lima oil undergoing distillation or when exposed to vapors of Lima oil after they have been given off, or in both such ways, and, secondly, any other known or suitable material except sulfuric acid stronger than that of about 66° B. for depriving Lima petroleum of sulfur compounds unremoved therefrom by said sulfuric acid of about 66° B.

In specifying in certain claims that the heavy end of cracked oil of the burning oil fraction is to be desulfurized after separation of the light and heavy ends from each other and is then to be rerun or distilled, it will be understood that the heavy end is most advantageously rerun or distilled apart from the light end, but that this is not necessarily so; since the separately desulfurized heavy end could be rerun or distilled after a mixture of the same and the light end with each other following upon the separate desulfuration of the heavy end; and both modes of rerunning or distilling the separately desulfurized heavy end are intended to be included within the scope of said claims. So likewise in specifying in certain claims that the said heavy end is to be subjected to successive desulfurizing operations in the later of which the said heavy end is desulfurized

after separation of the light and heavy ends from each other, the earlier desulfuration could be made with or without previous separation of the light and heavy ends from each other; and both modes are intended to be included within the scope of these claims. Further in specifying in certain claims that the light end and the heavy end are to be mixed, it is not intended to specify the point in the procedure at which the mixing is to be effected further than it is to be after a desulfurizing treatment of the heavy end following upon a separation of the light and heavy ends from each other.

"Non-smoking cracked oil of the burning oil fraction" means a cracked oil which fairly represents said burning oil fraction as a whole and which, after the aforesaid preparation, has a refractive index sufficiently below 1.4600 to indicate a non-smoking oil. Such a representative oil is obtainable by distilling the cracked oil in a laboratory flask provided with a thermometer as above mentioned and collecting the distillate which comes over between 300° F. and 550° F. If the heavy and light ends of such non-smoking cracked oil should be separated from each other, and if the heavy end should then be tested by itself, after the aforesaid preparation, it might or might not have a refractive index below 1.4600.

"Obtaining from Lima or analogous petroleum or related oil burning oil desulfurized by means of sulfuric acid stronger as specified than that of about 66° B." means obtaining in part at least from Lima or analogous petroleum or related oil burning oil so desulfurized at least in part. Heavy end of cracked oil of the burning oil fraction obtained from Lima or analogous petroleum or related oil and desulfurized by means of said stronger acid, with or without assistance from other materials, might, for example, be mixed with light end or with light and heavy ends (cracked or uncracked) of suitably low sulfur content obtained also from Lima or analogous petroleum or related oil; or it might be mixed with light end or light and heavy ends (cracked or uncracked) of suitably low sulfur content obtained from any other petroleum or hydrocarbon oil.

Claim 26 specifies a desulfuration by means of another material previous to the desulfuration with said stronger acid; and claim 27 does not so specify; but claim 27 does not exclude such previous desulfuration; and neither of the claims excludes a subsequent desulfuration; nor does either claim exclude a desulfuration of any kind in addition to that specified therein. None of the twenty seven claims, in fact, excludes a desulfuration of any kind in addition to that specified therein; nor does any claim exclude the admixture of other petroleum or

hydrocarbon oil with the Lima or analogous petroleum or related oil to be desulfurized as therein specified.

I claim as my invention or discovery:

5 1. In desulfurizing Lima or analogous petroleum or related oil by means of sulfuric acid stronger as specified than that of about 66° B., the improvement consisting in
10 subjecting the same, in the form of stock which is sulfur bearing as specified, to the action of said stronger acid at a temperature lower as specified than about 60° F. initial, substantially as described.

2. In desulfurizing Lima or analogous
15 petroleum or related oil by means of sulfuric acid stronger as specified than that of about 66° B., the improvement consisting in subjecting the same, in the form of distillate which is sulfur bearing as specified and also
20 lighter as specified than .865 specific gravity, to the action of said stronger acid at a temperature lower as specified than about 60° F. initial, substantially as described.

3. In desulfurizing Lima or analogous
25 petroleum or related oil by means of sulfuric acid stronger as specified than that of about 66° B., the improvement consisting in subjecting the same, in the form of distillate which is sulfur bearing as specified and also
30 lighter as specified than .865 specific gravity, to the action of said stronger acid at a rate not exceeding about sixty pounds to the barrel as specified and at a temperature lower as specified than about 60° F. initial, substantially as described.
35

4. In desulfurizing Lima or analogous petroleum or related oil by means of sulfuric acid stronger as specified than that of about 66° B., the improvement consisting in sub-
40 jecting the same, in the form of stock which is sulfur bearing as specified, to the action of said stronger acid at a rate not exceeding about sixty pounds to the barrel as specified and at a temperature lower as specified than
45 about 60° F. initial, substantially as described.

5. In desulfurizing Lima or analogous petroleum or related oil by means of sulfuric acid stronger as specified than that of about
50 66° B., the improvement consisting in subjecting the same, in the form of stock which is sulfur bearing as specified, to the action of said stronger acid at a rate designedly adjusted with respect to the removal of sulfur
55 and at a temperature lower as specified than about 60° F. initial, substantially as described.

6. In desulfurizing Lima or analogous petroleum or related oil by means of sulfuric
60 acid stronger as specified than that of about 66° B., the improvement consisting in subjecting the same, in the form of burning oil distillate which is sulfur bearing as specified, to the action of said stronger acid at a temperature lower as specified than about 60° F.
65

initial and at a rate not exceeding sixty pounds to the barrel as specified and not less than sufficient, when followed by rerunning and a subsequent treatment with sulfuric acid and alkali, to reduce the sulfur content
70 to a percentage admissible in marketable burning oil, substantially as described.

7. In desulfurizing Lima or analogous petroleum or related oil by means of sulfuric acid stronger as specified than that of about
75 66° B., the improvement consisting in subjecting the same, in the form of distillate which is sulfur bearing as specified and also lighter as specified than about .865 specific gravity, to the action of said stronger acid at
80 a temperature lower as specified than about 60° F. initial, and subsequently rerunning said distillate and giving to the rerun oil a treatment with sulfuric acid and alkali, substantially as described.
85

8. In desulfurizing Lima or analogous petroleum or related oil by means of sulfuric acid stronger as specified than that of about 66° B., the improvement consisting in cooling a stream of the Lima or analogous petroleum or related oil, in the form of stock which is sulfur bearing as specified, to a temperature lower as specified than about 60° F. by extracting the heat from the flowing oil by means of a cooling medium which is separated therefrom by heat conducting walls, subjecting the so cooled oil to the action of said stronger acid at such artificially produced temperature lower as specified than about 60° F., and subsequently distilling the
90 so treated oil and giving the resulting distillate a treatment with sulfuric acid and alkali, substantially as described.
95

9. In desulfurizing Lima or analogous petroleum or related oil by means of sulfuric acid stronger as specified than that of about 66° B., the improvement consisting in subjecting the same, in the form of stock which is sulfur bearing as specified, to the action of said stronger acid at an artificially produced
10 temperature lower as specified than about 60° F. initial, substantially as described.
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10. In desulfurizing Lima or analogous petroleum or related oil by means of sulfuric acid stronger as specified than that of about
11 66° B., the improvement consisting in subjecting the same, in the form of distillate which is sulfur bearing as specified and also lighter as specified than .865 specific gravity, to the action of said stronger acid at an artificially produced temperature lower as specified than about 60° F. initial, substantially as described.
1

11. In desulfurizing Lima or analogous petroleum or related oil by means of sulfuric
121 acid stronger as specified than that of about 66° B., the improvement consisting in subjecting the same, in the form of distillate which is sulfur bearing as specified and also lighter as specified than .865 specific gravity,
12

to the action of said stronger acid at a rate not exceeding about sixty pounds to the barrel as specified and at an artificially produced temperature lower as specified than about 60° F. initial, substantially as described.

12. In desulfurizing Lima or analogous petroleum or related oil by means of sulfuric acid stronger as specified than that of about 66° B., the improvement consisting in subjecting the same, in the form of stock which is sulfur bearing as specified, to the action of said stronger acid at a rate not exceeding about sixty pounds to the barrel as specified and at an artificially produced temperature lower as specified than about 60° F. initial, substantially as described.

13. In desulfurizing Lima or analogous petroleum or related oil by means of sulfuric acid stronger as specified than that of about 66° B., the improvement consisting in subjecting the same, in the form of stock which is sulfur bearing as specified and consists of the heavy end of cracked oil of the burning oil fraction after separation of the light and heavy ends from each other, to the action of said stronger acid at a temperature lower as specified than about 60° F. initial, substantially as described.

14. In desulfurizing Lima or analogous petroleum or related oil by means of sulfuric acid stronger as specified than that of about 66° B., the improvement consisting in subjecting the same, in the form of stock which is sulfur bearing as specified and consists of the heavy end of non-smoking cracked oil of the burning oil fraction after separation of the light and heavy ends from each other, to the action of said stronger acid, substantially as described.

15. In desulfurizing Lima or analogous petroleum or related oil by means of sulfuric acid stronger as specified than that of about 66° B., the improvement consisting in subjecting the same, in the form of stock which is sulfur bearing as specified and consists of the heavy end of cracked oil of the burning oil fraction after separation of the light and heavy ends from each other, to the action of said stronger acid at a rate designedly adjusted with respect to the removal of sulfur, substantially as described.

16. In desulfurizing Lima or analogous petroleum or related oil by means of sulfuric acid stronger as specified than that of about 66° B., the improvement consisting in subjecting the same, in the form of stock which is sulfur bearing as specified and consists of the heavy end of cracked oil of the burning oil fraction after separation of the light and heavy ends from each other, to the action of said stronger acid at a rate not exceeding about sixty pounds to the barrel as specified, substantially as described.

17. In desulfurizing Lima or analogous

petroleum or related oil by means of sulfuric acid stronger as specified than that of about 66° B., the improvement consisting in subjecting the same, in the form of stock which is sulfur bearing as specified and consists of the heavy end of non-smoking cracked oil of the burning oil fraction after separation of the light and heavy ends from each other, to the action of said stronger acid, and subsequently rerunning said heavy end and giving to the rerun oil a treatment with sulfuric acid and alkali, substantially as described.

18. In desulfurizing Lima or analogous petroleum or related oil by means of sulfuric acid stronger as specified than that of about 66° B., the improvement consisting in subjecting the same, in the form of the heavy end of cracked oil of the burning oil fraction, which heavy end is sulfur bearing as specified, to successive desulfurizing operations, in the later at least of which the said heavy end is desulfurized after separation of the light and heavy ends from each other, the earlier desulfuration being effected by means of material as specified other than said stronger acid, which material is more energetic as a desulfurizer of Lima petroleum than is sulfuric acid of about 66° B., and the later being effected by means of said stronger acid, substantially as described.

19. In desulfurizing Lima or analogous petroleum or related oil by means of sulfuric acid stronger as specified than that of about 66° B., the improvement consisting in subjecting the same, in the form of the heavy end of cracked oil of the burning oil fraction, which heavy end is sulfur bearing as specified, to desulfuration by means of material as specified other said stronger acid, which material is more energetic as a desulfurizer of Lima petroleum than is sulfuric acid of about 66° B., and subsequently to further desulfuration by means of said stronger acid, substantially as described.

20. In desulfurizing Lima or analogous petroleum or related oil by means of sulfuric acid stronger as specified than that of about 66° B., the improvement consisting in subjecting the same, in the form of cracked oil which is sulfur bearing as specified, to desulfuration by means of material as specified other than said stronger acid, which material is more energetic as a desulfurizer of Lima petroleum than is sulfuric acid of about 66° B., and subsequently to further desulfuration by means of said stronger acid, substantially as described.

21. In desulfurizing Lima or analogous petroleum or related oil by means of sulfuric acid stronger as specified than that of about 66° B., the improvement consisting in subjecting the same, in the form of stock which is sulfur bearing as specified, to desulfuration by means of material as specified other than said stronger acid, which material is

more energetic as a desulfurizer of Lima petroleum than is sulfuric acid of about 66° B., and subsequently to further desulfuration by means of said stronger acid, substantially as described.

22. In desulfurizing Lima or analogous petroleum or related oil by means of sulfuric acid stronger as specified than that of about 66° B., the improvement consisting in subjecting the same, in the form of stock which is sulfur bearing as specified, to desulfuration by means of material as specified other than said stronger acid, which material is more energetic as a desulfurizer of Lima petroleum than is sulfuric acid of about 66° B., and subsequently to further desulfuration by means of said stronger acid, distilling the so desulfurized oil, and giving to the resulting distillate a treatment with sulfuric acid and alkali, substantially as described.

23. In desulfurizing Lima or analogous petroleum or related oil by means of sulfuric acid stronger as specified than that of about 66° B., the improvement consisting in subjecting the same, in the form of stock which is sulfur bearing as specified, to desulfuration by means of material as specified other than said stronger acid, which material is more energetic as a desulfurizer of Lima petroleum than is sulfuric acid of about 66° B., and subsequently to further desulfuration by means of said stronger acid at a rate designedly adjusted with respect to the removal of sulfur, substantially as described.

24. In desulfurizing Lima or analogous petroleum or related oil by means of sulfuric acid stronger as specified than that of about 66° B., the improvement consisting in subjecting the same, in the form of stock which is sulfur bearing as specified, to desulfuration by means of material as specified other than said stronger acid, which material is more energetic as a desulfurizer of Lima petroleum than is sulfuric acid of about 66° B., and subsequently to further desulfuration by means of said stronger acid at a rate designedly adjusted with respect to the removal of sulfur and at a temperature lower as specified than about 60° F. initial, substantially as described.

25. In desulfurizing Lima or analogous petroleum or related oil by means of sulfuric acid stronger as specified than that of about

66° B., the improvement consisting in subjecting the same, in the form of stock which is sulfur bearing as specified, to desulfuration by means of material as specified other than said stronger acid, which material is more energetic as a desulfurizer of Lima petroleum than is sulfuric acid of about 66° B., and subsequently to further desulfuration by means of said stronger acid at a temperature lower as specified than about 60° F. initial, substantially as described.

26. In obtaining from Lima or analogous petroleum or from related oil burning oil desulfurized by means of sulfuric acid stronger as specified than that of about 66° B., the improvement consisting in subjecting such Lima or analogous petroleum or related oil, in the form of the heavy end of cracked oil of the burning oil fraction, which heavy end is sulfur bearing as specified, to successive desulfurizing operations performed the earlier by means of material as specified other than said stronger acid, which material is more energetic as a desulfurizer of Lima petroleum than is sulfuric acid of about 66° B., and the later by means of said stronger acid, and the later at least of said operations being performed after separation of the light and heavy ends from each other, and mixing the so desulfurized heavy end with light end of suitably low sulfur contents, substantially as described.

27. In obtaining from Lima or analogous petroleum or from related oil burning oil desulfurized by means of sulfuric acid stronger as specified than that of about 66° B., the improvement consisting in subjecting such Lima or analogous petroleum or related oil, in the form of the heavy end of cracked oil of the burning oil fraction, which heavy end is sulfur bearing as specified, to the action of said stronger acid after separation of the light and heavy ends from each other, and mixing the so desulfurized heavy end with light end of suitably low sulfur contents, substantially as described.

In testimony whereof I affix my signature, in presence of two subscribing witnesses.

CLARENCE I. ROBINSON.

Witnesses:

J. E. EGGLESTON,
CHARLES G. BLACK.

It is hereby certified that in Letters Patent No. 910,584, granted January 26, 1909, upon the application of Clarence I. Robinson, of West New Brighton, New York, for an improvement in "Desulfurizing Lima or Analogous Petroleum and Related Oils," errors appear in the printed specification requiring correction, as follows: In line 12, page 8, "840/1000 per cent" should read *40 1000 per cent*; line 13, page 9, the word "of," second occurrence, should read *or*, and in line 5, page 14, the word "or," second occurrence, should read *at*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 23rd day of February, A. D., 1909.

[SEAL.]

C. C. BILLINGS,
Acting Commissioner of Patents.