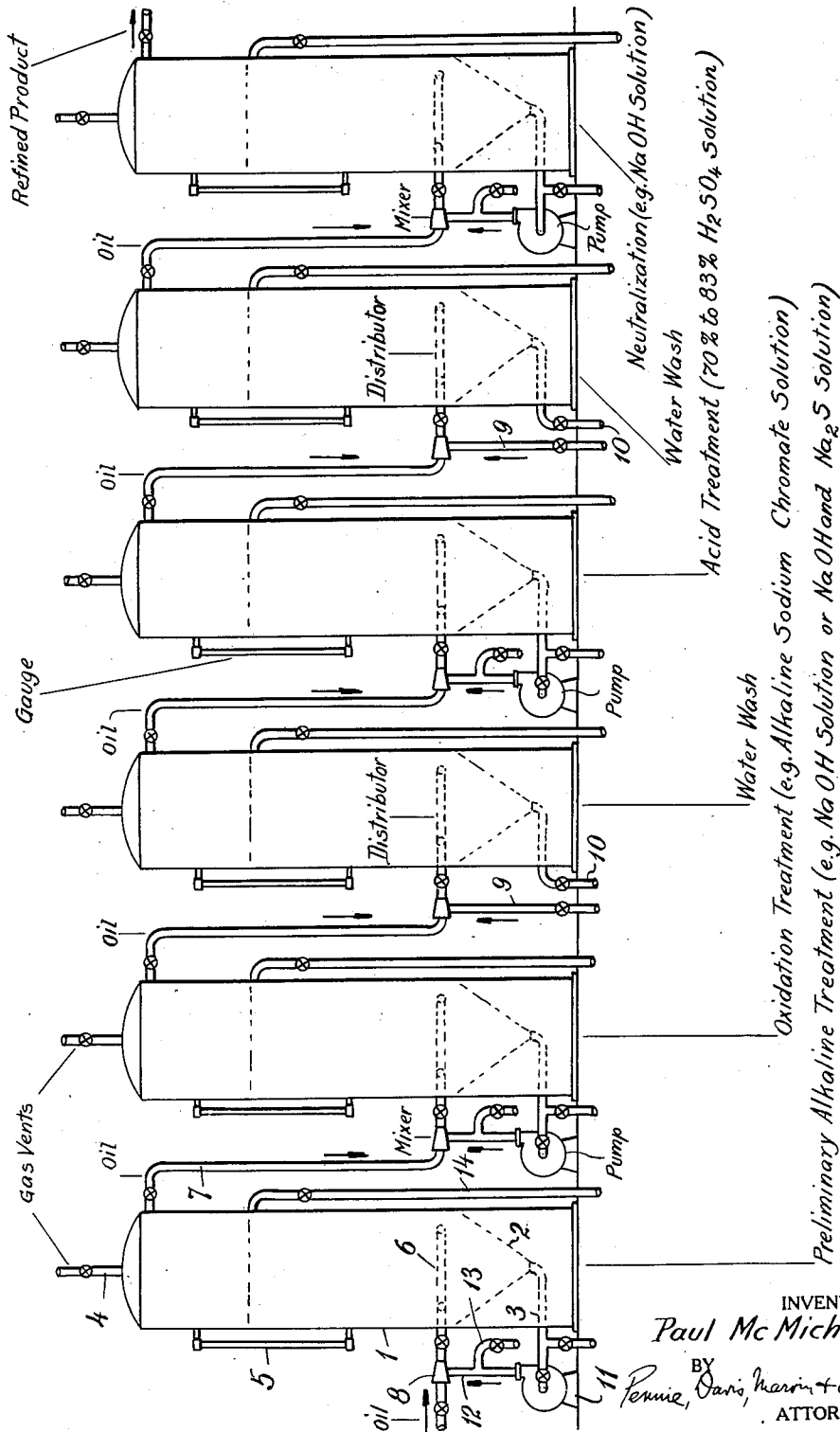


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REFINING PETROLEUM OILS

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REFINING PETROLEUM OILS

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This invention relates to an improved method for refining petroleum hydrocarbons. The method of the invention is of special value and application for refining light petroleum oils and distillates, for example fractions boiling up to about 220° C., and for refining oils and distillates containing unsaturated constituents in substantial amount, such as cracked oils and pressure distillates.

Light petroleum distillates, particularly those intended for use in automobile internal combustion engines, should be of good color, free from objectionable odour and substantially free from sulfur and from gum and resin forming constituents. Cracked oils and distillates usually contain a reduced amount of sulfur and an increased amount of unsaturated constituents. The formation of gummy and resinous masses on standing, and the instability of certain oils to prolonged exposure to light, are due, in large part, to the presence in the oil of unsaturated constituents such as the terpenes and diolefines. All unsaturated compounds, however, are not objectionable in these respects, and some unsaturated compounds, such as the olefines, constitute an excellent and advantageous constituent for motor fuels, and their removal constitutes an unnecessary loss. Sulfur compounds and gum forming compounds are particularly objectionable in oils intended for use in internal combustion engines because they tend to form gummy deposits in various parts of the engine and to form corrosive and foul smelling combustion products.

Hitherto, the general practice in the refining of petroleum oils and distillates has involved initial treatment with strong sulfuric acid, the reaction products of the initial treatment being of a character to require the use of strong sulfuric acid to remove them. Treatment with strong sulfuric acid substantially denudes the oil of any olefines and similar unsaturated compounds it may have contained prior to the acid treatment, and also tends to introduce sulfur into the oil in the form of alkyl sulfates. It has also been proposed to employ refining methods involving initial treatment of the oil with quite dilute sulfuric acid, but such methods, if carried out in a manner to avoid destruction or removal of the olefines and similar compounds do not produce a stable

product of good color and odour and free from gum and resin forming constituents.

I have found that by employing sulfuric acid corresponding to a concentration between about 70% and 83% H_2SO_4 in the treatment of petroleum oils and distillates, the diolefines and terpenes and similar gum and resin forming compounds are substantially completely removed while the acid acts very slowly if at all upon the olefines and related unsaturated compounds. In prior applications filed September 26, 1923, Serial No. 665,008, October 23, 1923, Serial No. 670,226, and January 11, 1924, Serial No. 685,703, I have described processes of refining petroleum hydrocarbons employing sulfuric acid of this advantageous range of strength. In an application filed February 14, 1924, Serial No. 692,896, I have also described a refining process in which the oil is first subjected to a preliminary oxidizing treatment and then subjected to treatment with dilute sulfuric acid, advantageously of a strength corresponding to a concentration between about 70% and 83% H_2SO_4 . In the process of the present invention, the oil is subjected to a preliminary oxidizing treatment and thereafter to treatment with dilute sulfuric acid, advantageously within this range of strength, and the process of the present invention may, in certain aspects, be considered an improvement upon the processes described in these prior applications.

According to the process of the present invention, the oil to be refined is subjected to treatment with dilute sulfuric acid, advantageously of a concentration between about 70% and 83% H_2SO_4 , and before the acid treatment the oil is subjected to treatment with an alkaline solution of a metallic oxidizing agent. By employing dilute sulfuric acid, the olefines may be largely retained in the refined product while the introduction of sulfur into the oil in the form of alkyl sulfates is also avoided. Certain of the unsaturated constituents which tend to form gums and resins, and other constituents which are otherwise objectionable, are more or less refractory to treatment with dilute sulfuric acid, but I have found that by subjecting the oil to preliminary oxidation in accordance with the present invention these objectionable constituents may be converted to a form in which they are readily removed by treatment with dilute sulfuric acid.

In one way of carrying out the process of the present invention the unrefined petroleum oil or distillate is agitated at atmospheric temperature with an aqueous solution of sodium chromate and caustic soda. The agitation may be carried out, for example, for a period of from one to six hours and with lighter fractions may be carried out in a closed vessel to minimize evaporation losses. After agitation, the oil and treating solution are separated by allowing the aqueous layer to settle from the lighter layer of oil. After separation, the lower aqueous layer will contain some precipitated chromium oxide, probably in a hydrated form. After separation from the aqueous layer, the oil is washed with water to remove any alkali present and is then subjected to treatment with sulfuric acid corresponding to a concentration of about 70% to 83% H_2SO_4 . The total amount of sulfuric acid employed depends upon the character of the oil being refined. The total amount of sulfuric acid may be divided and the oil subjected to a series of successive treatments with the divided batches of the acid. After separation from the acid and the reaction products of the acid treatment, the oil is washed successively with water and with a dilute solution of caustic soda to remove or neutralize any acid constituents remaining therein. The oil is then distilled with steam in the presence of a fixed alkali, such as hydrate of lime or caustic soda, and the oil may be fractionated during this redistillation treatment.

Following the preliminary oxidizing treatment, the treating solution originally containing the metallic oxidizing agent may be regenerated for further use. Where an excess of the oxidizing solution is employed, it may be used several times before the oxidizing agent is exhausted and before regeneration is necessary. Precipitated and suspended material may or may not be removed from the oxidizing solution between successive treatments. In one way of regenerating the oxidizing agent, the aqueous layer containing sodium chromate and caustic soda together with chromium oxide in suspension is electrolyzed with insoluble electrodes, for example, with lead electrodes. This electrolysis for regeneration of the oxidizing solution may be carried out according to any of the well known methods. For example, the cathode may be suspended within a porous cell so that the hydrogen set free by the electrolysis is separated leaving the oxygen available in a nascent state for oxidation of the chromium oxide. The electrolysis may be continued until all of the chromium oxide has been reoxidized to the chromate state and until all of the suspended chromium oxide has again gone into solution. After the electrolysis, the regenerated solution may be allowed to stand and

any oil contained therein removed from the surface as by decantation. Sufficient milk of lime is then added to the solution to reconvert combined sodium to caustic soda. Losses of caustic soda or of sodium chromate may be made up by appropriate additions. The solution is then filtered to remove any suspended lime, calcium sulfate, calcium salts of organic acids, or other insoluble materials, and the filtrate is then ready for treating further quantities of the petroleum oil or distillate.

In some cases undesirable components of the oil or distillate which are susceptible to treatment with dilute sulfuric acid may be removed, at least in part, by treatment with dilute sulfuric acid before the oil is subjected to treatment with the alkaline solution of a metallic oxidizing agent. In another way of carrying out the process of the invention, accordingly, the oil or distillate may be agitated with sulfuric acid corresponding to a concentration of about 70% to 83% H_2SO_4 before it is subjected to the oxidizing treatment. Following this acid treatment, the separated oil may be washed successively with water and a dilute solution of caustic soda, or other suitable alkaline agent, and then subjected to treatment with an alkaline solution of a metallic oxidizing agent followed by treatment with dilute sulfuric acid in the manner which has been described.

With oils or distillates which contain a substantial amount of sulfur, either in the form of hydrogen sulfide or as elemental sulfur, for example, it is advantageous to remove this sulfur initially before subjecting the oil or distillate to the oxidizing treatment of the invention. Sulfur present as hydrogen sulfide may be removed by agitating the oil or distillate with a dilute aqueous solution of an alkaline agent such as caustic soda. Sulfur present dissolved in the oil or distillate may be largely removed by agitation of the oil or distillate with an aqueous alkaline solution of an alkali sulfide, for example a solution containing sodium sulfide and caustic soda. Following such treatments, the oil may be subjected to refining in the manner which has been described.

While the use of sodium chromate in the alkaline oxidizing solution has been found particularly advantageous, other metallic oxidizing agents may be employed. For example, sodium or potassium manganate, sodium peroxide, or potassium peroxide, are useful in carrying out the process of the present invention. Where chromates or manganates are employed, the reduction of the chromate or manganate results in the precipitation of the corresponding oxide or hydrate. While one advantageous method of regenerating a sodium chromate oxidizing solution has been described, it will be apparent that other methods of recovering the used alkaline oxi-

dizing solution may be employed. For example, if an alkaline solution of a manganate is employed, after separation from the petroleum oil or distillate the solution containing the reduced manganese compounds, in part at least in suspension, may be reoxidized and made available for the treatment of further quantities of the oil or distillate by blowing with steam and air. Likewise, it is not necessary that combined alkali should be immediately released, as by causticizing the solution with lime, immediately after reoxidation. Before the solution is further employed for refining the oil or distillate, however, it should contain sufficient free alkali to combine with any acids resulting in the oxidizing treatment of the oil or distillate. Where a considerable excess of alkali is originally employed in the oxidizing solution, the causticizing treatment thus need not be carried out after each regeneration of the oxidizing solution but may be applied only as the amount of free alkali is depleted to an objectionable degree. When the causticizing operation is omitted, filtration of the solution may also be omitted.

In another way of regenerating spent oxidizing solutions originally containing sodium chromate and caustic soda, the solution, after separation of the oil or distillate, is filtered to remove insoluble suspended material. This insoluble material is then suspended in a solution of caustic soda and the suspension subjected to electrolysis in the manner which has been described. The electrolyzed solution may then be employed to make up fresh oxidizing solution or it may be added to the filtrate obtained in the operation in which the precipitated insoluble material was removed. So long as the amount of sodium chromate remaining in the filtrate is sufficient, however, the filtrate may be employed for the treatment of additional quantities of oil before additional sodium chromate is added thereto.

The preparation of the aqueous alkaline oxidizing solution will be illustrated by the following example which describes the preparation of one particularly advantageous treating solution. A solution of sodium bichromate is prepared by dissolving about 12.2 parts by weight of crystallized sodium bichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) in sufficient water to make a solution containing about 10% by weight of the sodium bichromate. A solution of caustic soda is prepared by dissolving about 48 parts by weight of caustic soda (NaOH) in sufficient water to make a solution containing about 35% by weight of the caustic soda. About 28 parts by volume of the caustic soda solution are then added to about 72 parts by volume of the sodium bichromate solution converting the sodium bichromate to sodium chromate. The resulting solution will contain an amount of caus-

tic soda somewhat greater than the amount of sodium chromate and will have a gravity of about 20° Bé. I have found it advantageous to employ a solution of gravity not less than about 20° Bé. to promote the separation of the oil and the oxidizing solution.

While the solution just described has been found particularly advantageous, it will be apparent that the actual composition of the oxidizing solution and the method of preparation may be widely varied. For example, it has been found advantageous to employ solutions containing an amount of free alkali in excess of the amount of sodium chromate, but solutions containing a smaller amount of free alkali may be used. Other metallic oxidizing agents, such as those previously described may also be employed. Where sodium dichromate, a relatively inexpensive salt, is employed in making up the oxidizing solution sufficient alkali should be used to convert all of the sodium dichromate to sodium chromate and to leave an excess of free alkali, so that the solution employed for treating the oil will be alkaline. Sufficient excess of alkali should also be provided so that the oxidizing solution is still alkaline at the end of the treatment of the oil.

The amount of alkaline oxidizing solution employed for the treatment of any particular oil or distillate will vary with the character of the oil or distillate as well as the free alkali content and oxidizing power of the solution. A sufficient amount of the alkaline oxidizing solution should be employed so that all of the undesirable components of the oil are oxidized to a condition in which they are easily removed by subsequent treatment with the dilute acid employed. An excess of the oxidizing agent also promotes the rapidity and completeness of the oxidizing treatment. The amount of the alkaline oxidizing solution employed should also be sufficient to provide free alkali enough to combine with all acid constituents liberated during the oxidizing treatment, or otherwise present in the oil subjected to the oxidizing treatment. The presence of a relatively large excess of alkali is advantageous in that it increases the gravity of the oxidizing solution and so facilitates the separation of the solution from the oil or distillate after treatment. The presence of an excess of alkali also precludes the possibility of formation of chromic anhydride where chromates are employed and which if formed might have an objectionable destructive action upon the oil or distillate.

The amount of the aqueous alkaline oxidizing solution required for treating any particular oil or distillate may be estimated by the following method. The specific gravity of the petroleum distillate or petroleum oil to be treated is determined and 100 cc. are

evaporated to approximately constant weight in a hemispherical copper dish about three inches in diameter, first in a steam bath, and then in a drying oven at about 105° C. The amount in weight of the residue in the oil or distillate to be treated is thus determined, and an amount of an aqueous alkaline solution of sodium chromate such that its content by weight of sodium chromate is approximately one half the weight of the residue in the oil or distillate to be treated is usually an appropriate quantity. For example, to treat one thousand gallons of a petroleum distillate having a specific gravity of 0.78, and an evaporation residue of 1% by weight, about 33 pounds of sodium chromate could be employed. If the solution of sodium chromate and caustic soda which has been particularly described were employed, this would correspond to about 41 gallons of the solution.

Where an alkaline oxidizing solution containing potassium permanganate and caustic soda is employed, it may be prepared by dissolving about five parts by weight of potassium permanganate in sufficient water to make a solution containing about 1% by weight of potassium permanganate. A solution of caustic soda is prepared by dissolving about 48 parts by weight of caustic soda in sufficient water to make a solution containing about 35% by weight of the caustic soda. Approximately 15 parts by volume of the caustic soda solution are then added to about 85 parts by volume of the potassium permanganate solution. To estimate the amount of a solution of this character to employ for treating any oil or distillate, the amount in weight of the residue in the oil or distillate may be determined and an amount of the solution of potassium permanganate used such that its content by weight of potassium permanganate is approximately 0.3 to 0.4 pounds per pound of residue in the oil or distillate. For example, to treat 1,000 gallons of a petroleum distillate having a specific gravity of 0.78 and an evaporation residue of 1% by weight, about 65 gallons of the solution just described could be employed.

Where an alkaline oxidizing solution containing sodium peroxide is employed, it may be prepared by dissolving about one part by weight of sodium peroxide in about two parts by weight of cool water, the sodium peroxide breaking down in solution to form caustic soda and hydrogen peroxide. To estimate the amount of a solution of this character to employ for treating any oil or distillate, the amount in weight of the residue in the oil or distillate may be determined and an amount of the solution of sodium peroxide used such that its content by weight of sodium peroxide is approximately 0.3 to 0.4 pounds per pound of residue in the oil

or distillate. For example, to treat 1,000 gallons of a petroleum distillate having a specific gravity of 0.78 and an evaporation residue of 1% by weight about 50 gallons of the alkaline oxidizing solution just described could be employed.

The process of the invention may advantageously be carried out in a continuous manner, and one form of apparatus adapted for carrying out the process of the invention in a continuous way is illustrated in the accompanying drawing. The drawing shows a series of six treating tanks through which the oil or distillate to be refined is successively passed. Each of these tanks consists of a vertically arranged cylinder 1 with a conical bottom 2 connected to an outlet connection 3. A gas vent 4 is provided communicating with the upper end of the cylinder and a gauge 5 is arranged to indicate the level of the treating solution or wash water in the cylinder. The oil is introduced into each cylinder through a perforated distributing pipe 6 and after rising through the treating solution therein is withdrawn through outlet connection 7. An orifice mixer 8 is provided for intimately mingling the oil and treating solution or wash water as it enters the cylinder through the distributor 6. In the washing tanks water is supplied to the mixer 8 through connection 9 and the wash water is discharged through connection 10. In the treating tanks a pump 11 is arranged to withdraw the treating solution from the lower end of the cylinder through connection 3 and to recirculate it to the cylinder through connection 12 and the mixer 8. A connection 13 is arranged for discharging spent treating solution and a connection 14 is provided for supplying fresh treating solution to the upper part of the body of treating solution in the cylinder.

In the apparatus illustrated, the first tank may be filled with a solution of caustic soda or of caustic soda and sodium sulfide to about the level indicated, the second with an alkaline solution of sodium chromate, the third with water, the fourth with sulfuric acid corresponding to a concentration of about 70% to 83% H_2SO_4 , the fifth with water, and the sixth with a dilute solution of caustic soda. The oil in passing through the apparatus is thus successively subjected to a preliminary alkaline treatment, to a preliminary oxidizing treatment, and to treatment with dilute sulfuric acid. A considerable excess of the treating agents are present in each case so that the refining operation is promoted. The refining operation is also promoted by the intimate admixture of the treating solutions and the oil. As the treating agents in the various solutions are consumed, the spent solution is withdrawn and fresh solution is supplied.

The refining operation may thus be carried out in a rapid and effective and substantially continuous manner. It will be apparent, however, that the refining process of the present invention may be carried out, in whole or in part, as a series of batch operations.

The invention will be further described in connection with the following examples, but it will be understood that these examples illustrate the invention and that the invention is not limited thereto.

A petroleum distillate which had a specific gravity at 15° C. of 52° Bé., a residue upon evaporation at 105° C. to approximately constant weight of 0.50 percent by weight, a sulphur content of 0.15% by weight, and of which 79% by volume distilled up to 225° C., was agitated over a period of about four hours at atmospheric temperature in a closed agitator with about 2% by volume of an aqueous solution of sodium chromate and caustic soda of a composition corresponding to that which has been particularly described. After agitation the oil was allowed to settle for about 30 minutes and the aqueous layer of sodium chromate and caustic soda, containing some suspended chromium oxide, was separated from the oil. The oil was then washed with several successive portions of water and after separation from the final wash water was agitated in a closed vessel at atmospheric temperature with an aggregate of about 5% by volume of sulfuric acid corresponding to a concentration of about 77% H₂SO₄. The acid was applied in three successive portions of approximately 1%, 2% and 2% respectively, and the total period of agitation was about 3 hours. After separation of the oil from the acid, the oil was washed with several successive portions of water to remove excess acid and any remaining acid constituents and was finally washed once with about 5% by volume of a 2% by weight solution of caustic soda. The loss in treatment up to this point in the refining operation, including all mechanical and chemical losses, was approximately 3.4% by volume of the petroleum distillate treated. The gum forming components in the treated oil, determined by the evaporation of 100 cc. in a three inch hemispherical copper dish to constant weight at about 105° C., was approximately 0.04% by weight and the sulfur content was approximately 0.03% by weight. The treated petroleum distillate was then distilled with steam in the presence of a 2% by weight solution of caustic soda until about 82% by volume of the oil was distilled off. The distillate was water white in color, and a portion exposed to direct sunlight over a period of two months showed no discoloration. The oil was

sweet and agreeable in odour and successfully withstood the "doctor" test applied over a period of 24 hours, had a sulfur content, determined by combustion, of about 0.009% by weight, and a gum forming content, determined as previously described, of 0.01% by weight.

After separation of the petroleum distillate, the aqueous layer of sodium chromate and caustic soda containing suspended chromium oxide was subjected to electrolysis with insoluble electrodes until the chromium content had been again converted to sodium chromate. After standing, some oil which collected on the surface of the regenerated solution was removed and the solution was ready for the treatment of another portion of petroleum distillate.

In another operation, a petroleum distillate corresponding in character and analysis to that, the treatment of which has just been described, was agitated over a period of about 6 hours at atmospheric temperature in a closed agitator with about 3% by volume of an aqueous solution of potassium permanganate and caustic soda of a composition corresponding to that which has been particularly described. After standing for a period of about 12 hours the aqueous layer of potassium permanganate and caustic soda, containing some suspended manganese oxides, was separated from the oil. The oil was then washed with water, treated with sulfuric acid corresponding to a concentration of about 77% H₂SO₄, washed again with water and finally with a dilute caustic soda solution, all as has been described in the preceding example. The loss in treatment up to this point in the refining operation, including all mechanical and chemical losses, was approximately 3.9% by volume of the petroleum distillate treated. The evaporation residue, determined as has been described, was approximately 0.042% by weight and the sulfur content was approximately 0.03% by weight. The treated oil was then distilled with steam in the presence of a solution of caustic soda until about 80% by volume of the oil was distilled off. The distillate was water white in color, a portion exposed to direct sunlight over a period of two months showed no discoloration, the distillate was agreeable in odour and successfully withstood the "doctor" test, had a sulfur content of about 0.01% by weight, and a gum forming content of about 0.011% by weight.

After separation of the petroleum distillate, the aqueous layer of potassium permanganate and caustic soda containing suspended oxides of manganese was heated to boiling and a slow current of air passed through the liquid for about two hours. The solution was then filtered and a separated precipitate, after being dried, was fused with caustic

soda. The fusion product was then dissolved in the filtrate and the solution thus obtained was ready for the treatment of a further quantity of petroleum distillate.

5 In another operation, a petroleum distillate which had a specific gravity at 15° C. of 52° Bé., an evaporation residue of about 0.32% by weight, a sulfur content of 0.19% by weight, and of which about 90% by volume
10 distilled up to 220° C., was agitated over a period of about 2 hours at atmospheric temperature in a closed agitator with about 1.5% by volume of a freshly prepared solution of sodium peroxide of a composition
15 corresponding to that which has been particularly described. After agitation the oil was allowed to settle for about 15 minutes and the aqueous layer was separated from the petroleum distillate. The oil was then
20 washed, as in the preceding examples, and then agitated in a closed agitator at atmospheric temperature with an aggregate of about 6% by volume of sulfuric acid corresponding to a concentration of about 83%
25 H₂SO₄. The acid was applied in three successive portions of about 2% each and the total period of agitation was about 3 hours. After separation from the final portion of acid, the oil was washed, as in the preceding
30 examples, and finally distilled with steam in the presence of about an equal volume of a 2% by weight solution of caustic soda until about 90% by volume of the oil was distilled off. The distillate was water white in color,
35 a portion exposed to direct sunlight over a period of weeks showed no discoloration, the distillate had an agreeable odour and successfully withstood the "doctor" test, and had a sulfur content of about 0.018% by
40 weight and a gum forming content of about 0.012% by weight.

In another operation, a petroleum distillate which had a specific gravity at 15° C. of 49.5° Bé., an evaporation residue of 0.59%
45 by weight, and a sulfur content of 0.054% by weight, was fractionally distilled with steam in the presence of a 2% solution of caustic soda until about 65% by volume of the oil was distilled off. The entire distil-
50 late came over below a temperature of about 225° C. The distilled fraction was then agitated at atmospheric temperature in a closed agitator with the described solution of sodium chromate and caustic soda for a
55 period of about 4 hours, about 2% by volume of the oxidizing solution being employed. After washing the oil was agitated with an aggregate of about 6% by volume of sulfuric acid corresponding to a concentration of
60 about 83% H₂SO₄ for a period of about 3 hours. After separation from the acid, the oil was again washed with water and finally washed with about 5% by volume of a caustic soda solution of about 40° Bé.,
65 gravity. The final product amounted to

about 62% of the original petroleum distillate. The treated oil was water white and did not discolor on exposure to direct sunlight, had an agreeable odour, successfully
70 withstood the "doctor" test, and had a sulfur content of about 0.021% by weight and a gum forming content of about 0.02% by weight.

In another operation, a petroleum distillate which has a specific gravity at 15° C. of 75 54.5° Bé., an evaporation residue of about 0.6% by weight, and a sulfur content of 0.22% by weight was washed with about 5% by volume of a 2% by weight solution of caustic soda and was then agitated for about
80 one hour at atmospheric temperature in a closed agitator with about 2% by volume of sulfuric acid corresponding to a concentration of about 83% H₂SO₄ in 2 successive portions of about 1% each. The oil was then
85 successively washed with water and with about 5% by volume of a 2% by weight solution of caustic soda. The oil was then agitated over a period of about 3 hours at
90 atmospheric temperature in a closed agitator with about 3% by volume of the solution of sodium chromate and caustic soda which has been particularly described. After agitation, the oil was allowed to settle for about
95 30 minutes and the aqueous layer of sodium chromate and caustic soda, containing some suspended chromium oxide, was separated from the oil. The oil was then washed with several successive portions of water and after
100 separation from the final water was agitated in a closed agitator at atmospheric temperature with an aggregate of about 2.5% by volume of sulfuric acid corresponding to a concentration of about 83% H₂SO₄. The
105 acid was applied in three successive portions of approximately 0.5%, 1% and 1% respectively, and the total period of agitation was about 3 hours. After separation of the oil from the acid the oil was washed with several
110 successive portions of water and was finally washed once with about 5% by volume of a 2% by weight solution of caustic soda. After separation from the wash solution, the petroleum distillate was distilled with steam in the presence of caustic soda, the distil-
115 lation being continued until the distilled fraction gave a dry point at about 220° C. when 100 cc. were distilled according to the standard distillation test. The oil product so obtained was water white and did not dis-
120 color on exposure to direct sunlight, had an agreeable odour, successfully withstood the "doctor" test, and had a sulfur content of 0.018 by weight, and a gum forming content of 0.016% by weight.

The improved process of the present invention enables the production of a motor spirit or gasoline which will distill substantially completely within the desired tempera-
130 ture range, which is substantially free from

sulfur, and from gum and resin forming constituents, which is water white in color and which is substantially stable even on exposure to direct sunlight, which contains a major portion of the olefines and similar desirable constituents distilling within its boiling range which were contained in the unrefined oil, and which will have an agreeable odour. Oils and distillates refined according to the present invention may frequently have an iodine number higher than the iodine number of the unrefined oil or distillate.

I claim:

1. A method of refining cracked petroleum oils and distillates, which comprises subjecting the cracked oil to treatment with an alkaline aqueous solution of sodium chromate having a gravity of not less than about 20° Bé. and subsequently subjecting the cracked oil to treatment with dilute sulfuric acid.

2. A method of refining cracked petroleum oils and distillates, which comprises subjecting the cracked oil to treatment with an aqueous solution containing sodium chromate and a greater amount of caustic soda and subsequently subjecting the cracked oil to treatment with dilute sulfuric acid.

3. A method of refining cracked petroleum oils, which comprises subjecting the cracked oil to treatment with an alkaline aqueous solution of sodium chromate and subsequently subjecting the oil to treatment with sul-

furic acid containing about 70% to 83% H_2SO_4 .

4. A method of refining cracked petroleum oils, which comprises subjecting the cracked oil to treatment with an aqueous solution containing sodium chromate and a greater amount of caustic soda and subsequently subjecting the cracked oil to treatment with sulfuric acid containing about 70% to 83% H_2SO_4 .

5. A method of refining cracked petroleum oils, which comprises subjecting the cracked oil to treatment with an alkaline aqueous solution of sodium chromate and subsequently subjecting the cracked oil to treatment with dilute sulfuric acid.

6. A method of refining cracked petroleum oils and distillates, which comprises subjecting the cracked oil to treatment with an aqueous solution of caustic soda, thereafter subjecting the cracked oil to treatment with an alkaline aqueous solution of sodium chromate and subsequently subjecting the cracked oil to treatment with dilute sulfuric acid.

7. A method of refining cracked petroleum oils and distillates, which comprises subjecting the cracked oil to treatment with dilute sulfuric acid, thereafter subjecting the cracked oil to treatment with an alkaline aqueous solution of sodium chromate and subsequently subjecting the cracked oil to treatment with dilute sulfuric acid.

In testimony whereof I affix my signature.

PAUL McMICHAEL.