UNITED STATES PATENT OFFICE.

FELIX C. THIELE, OF NEW ORLEANS, LOUISIANA, ASSIGNOR OF THREE-FIFTHS TO JOHN FINKE AND JOHN M. PARKER, OF SAME PLACE.

PROCESS OF REFINING CRUDE MINERAL OILS AND THEIR DISTILLATES.

SPECIFICATION forming part of Letters Patent No. 683,354, dated September 24, 1901.

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To all whom it may concern:

Be it known that I, FELIX C. THIELE, a citizen of the United States, residing at New Orleans, in the parish of Orleans, State of Louisiana, have invented certain new and useful Improvements in Processes of Refining Crude Mineral Oils and Their Distillates, of which the following is a specification.

This invention relates to a process for refining crude mineral oils and their distillates.

The process herein described is especially designed to further the purification of refractory crude mineral oils, such as are found in the Trenton limestone formation, present in Canada and several States in the United States, and particularly the oils discovered of late in the Southern States, as Texas, Louisiana, California, Mississippi, and others, the foregoing being hereinafter referred to in general as oils of the Lima type. It has for an object to manufacture marketable products from these crude oils, and consequently increase the value of the natural products.

Terpenes $(C_{10}H_{16})$ and polyterpenes $(C_{10}H_{16})_x$ have been found in almost every crude mineral oil, and they exist in the oils in different forms. One of them is asphaltum, (a mixture of sulfureted polyterpenes,) present in all crude mineral oils found on the Western Hemisphere. It can be readily detected by treating the crude oil with tetrachlorid of tin (see Thiele, *American Chemical Journal*, Vol. XXII, No. 6, December, 1899) and was found with certainty by me in Texas crude oils, Lima (Ohio) oil, and Canada oil, (Petrolia district.) A further confirmation of the occurrence of terpenes and polyterpenes in crude oils may be found in a paper by Charles F. Mabery, *Journal Franklin Institute*, Vol. CXL, page 1, 1896. As terpenes are nothing else but hydrated aromatic hydrocarbons, (Beilstein, *Organic Chemistry*, Vol. III, 1890, page 279,) their presence has been long suspected in crude oils; but their successful separation from the crude oil direct was first effected by me.

The process is capable of use upon oils of different characters and their distillates.

One method of using the process with crude oil not having a specific gravity higher than 0.835 is to mix with the oil from .5 to 1.5 per cent., by weight, of nitric acid of specific gravity 1.42. The oil or its distillates is agitated with the acid for about half an hour and then set at rest. When completely settled, the water which has separated out at the bottom of the vessel is withdrawn. The acid almost combines completely with certain compounds in the oil, and the following reactions can be observed during the above treatment. The first noticeable action of the acid on the oil is the discharge of sulfurous acid. The formation of sulfurous acid from the oil is partly due to the oxidation of the sulfureted hydrogen in the oil and partly due to the elimination of one atom of sulfur in the shape of SO_2 from the organic sulfur compounds in the oil. These sulfur compounds contain a nucleus (CS) and must be regarded as derivatives of the trithio carbonic acid, probably its esters, as in distilling sulfur-bearing oils very often the odor of allyl-alcohol is observed. A further confirmation of the above results is found in the fact that oils treated according to the herein-described process yield on distillation bisulfid of carbon (CS_2) in the light distillates, which can only have been formed by the primary destruction of the higher sulfids into the lower sulfids by the nitric acid. The following equation expresses this reaction:

$$\underbrace{CS_3\langle{}^{C_3H_5}_{C_3H_5}}_{\text{Trithiodially ester.}} + \underbrace{2HNO_3}_{\text{Nitric acid.}} = \underbrace{CS_2}_{\text{Bisulfid of carbon.}} + \underbrace{SO_2}_{\text{Sulfurous acid.}} + \underbrace{2C_3H_5OH}_{\text{Allyl-alcohol.}} + \underbrace{(NO)_2}_{\text{Nitrogen dioxid.}}$$

The second reaction of the nitric acid on the oil is the formation of nitriles and nitrolic acids in the oil.

The third and fourth reactions observed in the action of nitric acid on the oil is the elimination of asphaltum and terpene compounds, also of certain aromatic hydrocarbons, which settle as a very viscous tar on the bottom of the vessel. In order to fit the thus-treated oils for distillation, it is necessary to remove the nitrolic acids, the resins formed by the polymerization of the terpenes, to change the nitriles into amids and to remove the sulfurous acid first formed by the nitric acid. These results are obtained by agitating the treated oil with water to remove every trace of free acid and then adding to the neutral oil 0.3 to 0.5 per cent. of strong soda-lye (from 35° to 38° Baumé) and a small amount of a metallic powder, such as zinc-dust, mixed with an equal amount of finely-divided iron. Powdered aluminium may be used instead of the aforementioned mixture. Iron alone, mixed with a strong lye, does not generate free hydrogen at ordinary temperatures. To one gallon of the oil from 17.5 to twenty grams of soda-lye (38° Baumé) are added, together with five grams of zinc-dust and five grams of powdered iron.

Zinc-dust, powdered aluminium, and finely-divided iron are mentioned here separately. In practice, however, zinc and iron are always employed together, as either alone would not generate any hydrogen at ordinary temperature (72° Fahrenheit) in this instance. Aluminium in powdered form may be employed by itself, as it causes a copious amount of hydrogen to be set free when coming in contact with the solution of an alkali of the above strength. The mixture is well agitated for about two hours and then left standing. After settling the pure oil, which has now acquired a pure-oil odor, is withdrawn from the tarry and almost solid residue on the bottom of the vessel.

The action of the mixture of strong soda-lye and zinc (mixed with an equal part of finely-divided powdered iron) is expressed in the following equation:

$$NaOH + 4H_2O + Zn + 2Fe = NaOH + ZnO + Fe_2O_3 + 8H.$$

By this it is seen that the mixture generates a large amount of hydrogen. The latter being generated from a strongly-alkaline solution at ordinary temperature possesses different properties from hydrogen generated from an acid solution or from an alkaline solution at higher temperatures. According to Tommasi this is due to the amount of calories developed during the reaction. The hydrogen generated according to the above equation is capable of converting the compounds produced by the action of nitric acid on crude oils, as described in the aforegoing treatise, into compounds which are easily removed by diluted acids from the oils subjected to such treatment. Primary among them is the quantitative conversion of nitrolic acids into fatty acids, ammonia, and hydroxyl amin, while the conversion of nitro compounds of the aromatic series into hydrazo compounds must be regarded as an achievement of importance.

When the above-treated oil is agitated with the mixture, the first noticeable action observed is the strong evolution of free ammonia. This is caused by the reduction of the above-mentioned "nitriles" and "nitrolic" acids, so called, into amids and hydroxyl amids. The following equations serve to illustrate this:

$$\underbrace{C_2H_5.CN}_{\text{Propio nitrile.}} + 4H = \underbrace{C_2H_5.CH_2.NH_2}_{\text{Propyl amin.}}$$

$$\underbrace{CH_3.CH(NO_2)(NO)}_{\text{Ethyl nitrolic acid.}} + \underbrace{6H = C_2H_4O_2}_{\text{Acetic acid.}} + \underbrace{NH_3}_{\text{Ammonia.}} + \underbrace{NH_2OH}_{\text{Hydroxyl amin.}}$$

The reaction of the free hydrogen on the nitrogen compounds takes place only in the presence of an alkali, either soda or potash, (lime being useless.) The added alkali does not serve any neutralizing purposes, as no free adids are present in the oil. The term "nitrolic acid" is still in use, but refers to the nitroso nitro hydrocarbon produced by this action.

The second reaction of the reducing mixture is the reduction of the nitro compounds of the aromatic hydrocarbons which have been formed. This takes place according to the following equation:

$$\underbrace{2C_6H_5.NO_2}_{\text{Nitrobenzene.}} + 10H = \underbrace{C_6H_5.NH.NH.C_6H_5}_{\text{Hydrazo-benzene.}} + \underbrace{4H_2O}_{\text{Water.}}$$

A further reaction which is observed is the decrease of the unsaturated hydrocarbons C_nH_{2n} and the increase of the saturated hydrocarbons $C_nH_{2n}+_2$, which takes place as follows:

$$\underbrace{CH:CH}_{\text{Acetylene.}} + 4H = \underbrace{CH_3:CH_3}_{\text{Ethane.}}$$

The yield of the paraffin hydrocarbons is thus increased and the amount is olefin hydrocarbons is decreased, thus insuring a larger amount of burning-oil to be obtained by this process. The oxidation products of the terpenes are formed into a very viscous tar, which, together with other organic compounds, the used alkali and the metals, settle to the bottom of the vessel. The treated oil is now drawn off and at first washed with water to remove the bulk of the formed free ammonia, (which forms a very valuable commercial by-product.) The oil is next washed with diluted sulfuric acid (five parts water, one part strong sulfuric acid) to remove the formed organic amido compounds. The amount of acid is previously determined by chemical analysis and calculated for the amount of basic compounds formed. For this purpose a measured sample of the oil in question is shaken with an equal amount of pure methyl alcohol and the mixture left standing until complete separation of the alcohol has taken place. The alcohol is now withdrawn from the oil and, if necessary, diluted with more alcohol in order to obtain a very light-colored transparent solution. A measured amount of normal sulfuric acid is added and the mixture well stirred during this operation. The amount of normal acid must be in excess of the basic compounds dissolved in the alcohol. This excess is determined by testing a drop of the mixture with sensitive blue litmus-paper, so-called "azo-litmine" paper. As soon as the blue paper has turned decidedly onion red the addition of the acid is stopped. To the milky mixture is now added ten drops of a solution of one part phenolphtalein in one hundred and twenty parts of pure methyl alcohol. The excess of acid in the mixture is determined by adding carefully a solution of normal soda-lye. As soon as the solution turns a deep violet (the color must not disappear before the expiration of two minutes) the addition of the normal lye is stopped. By calculating the amount of normal sulfuric acid which was neutralized by the normal soda-lye and deducting this amount from the total amount of normal acid previously added to the alcoholic solution the amount of normal sulfuric acid is obtained which was absorbed by the basic compounds dissolved in the alcohol. According to the equation

$$2C_6H_7N+H_2SO_4=(C_6H_7N)_2.H_2SO_4$$

the amount of basic compounds present in the alcohol (and consequently extracted by it from the measured amount of oil) is calculated. Knowing the total quantity of the oil which was analyzed, it is now easy to determine the amount of acid (five parts of water one part strong sulfuric acid) to be added to the oil to exactly neutralize the amido compounds in it. The strength of the diluted sulfuric acid must always be determined before using it for the neutralizing purpose. The amid compounds are expressed in the above equation as "anilin," this term answering best the obtained results. The dark-brown aqueous liquid which was formed by washing the oil with the diluted sulfuric acid and is worked successfully into valuable commercial products, is withdrawn from the oil which has now acquired a light color as against a cherry-red color when treated first. The removal of the basic compounds before distillation is necessary, as it is found that their presence yields yellow distillates, which are only with great difficulty turned into white products. The oil is afterward distilled in a retort and divided into the different merchantable products—such as naphtha, illuminating-oil, lubricating-oil, cylinder-oil, and others. The obtained distillates are washed in the usual way with sulfuric acid and lye. It is found, however, that a great deal less of the reagents is necessary to obtain perfect products than has been used formerly in the refining of refractory mineral oils. According to *Chemiker-Zeitung*, 1896, No. 56, page 515, the distillates of Lima (Ohio) oil have been washed with concentrated sulfuric acid and soda-lye until they became marketable. The amount of acid used amounted approximately to seven per cent. of the volume of the oil. Oils treated first by the herein-described process do not require any more than one per cent. of the volume of the distillate, and this constitutes undoubtedly a noticeble saving in the final treatment of the oil. The acid being reduced from seven to one per cent. indicates that only a small portion of olefins remain to be removed from the oil. These olefins are formed by the unavoidable action of the heat on the paraffins, and in order to obtain a sweet-smelling oil they must be eliminated from the distilled products.

Crude oils having a specific gravity higher than 0.835, such as found in Texas, Wyoming, Louisiana, California, and other States, are preferably first subjected to a single distillation in order to separate the liquid oils from the solid or semisolid bitumen. The crude distillate is then subjected to the same treatment as described above for the lighter oils, and the products of similar properties and value may be obtained from them.

In order that the several steps of this process may be accurately determined, the following statement thereof is given: The process of refining oils of the Lima type consists in adding nitric acid thereto with agitation till the absence of sulfurous acid (formed by the decomposition of the sulfur compounds in the oil) is shown by testing the escaping gases with sensitive moistened logwood paper until the latter ceases to be bleached by the gases and the absence of the terpenes and polyterpenes by testing the oil with tetrachlorid of tin until no further precipitate is formed on the addition of this reagent, washing them with water till the latter does not change blue litmus-paper any more, thus showing the neutrality of the oil; removing the washed oil and agitating it with lye and a metal capable of producing hydrogen with the lye until a sample of the oil mixed with a small amount of sulfuric acid of 57° Baumé strength does not discharge any more nitrous vapors, then washing it with water until the free ammonia is removed from the oil, and then washing it with dilute sulfuric acid until a sample of the oil shaken with dilute sulfuric acid does not color the latter any more, showing the absence of basic compounds in the oil.

It will be obvious that changes may be made in the details and proportions of the process hereinbefore described in order to adapt the same for use with oils of different characters and varying specific gravities, while the acids and reagents used may be varied or changed in order to effect equivalent reactions to those hereinbefore set forth for refining of any particular character of oil or to remove therefrom an impurity not ordinarily present in oils of a similar character, such changes being within the knowledge of a chemist skilled in the art.

Having described my invention, what I claim is—

1. The process of refining crude mineral oils of the Lima type consisting in the addition of nitric acid thereto until sulfurous gases cease to be evolved; the conversion of the nitro and nitroso compounds into basic compounds by the addition of a nascent hydrogen-producing substance until in a tested portion nitrous gases cease to be evolved in the presence of sulfuric acid, and the removal of the newly-formed products by a subsequent acid treatment; substantially as specified.

2. The process of refining crude mineral oils of the Lima type consisting in the addition of nitric acid until sulfurous gases cease to be evolved, the conversion of said nitro and nitroso compounds into basic compounds by the addition of an alkali and a metallic substance until in a tested portion nitrous gases cease to be evolved in the presence of sulfuric acid; substantially as specified.

3. The process of refining mineral oils of the Lima type consisting in adding thereto nitric acid until the evolution of sulfurous gas ceases, removing or reducing the resultant compounds by the addition of an alkali and a metallic substance capable of producing hydrogen until in a tested portion the evolution of nitrous gas in the presence of sulfuric acid ceases; substantially as specified.

4. The process of refining mineral oils of the Lima type consisting in adding thereto nitric acid until the evolution of sulfurous gas ceases, removing or reducing the resultant compounds by the addition of an alkali and a metallic substance capable of producing hydrogen, until in a tested portion the evolution of nitrous gases in the presence of sulfuric acid ceases, and a subsequent washing of the oil with a dilute sulfuric acid, until the oil fails to color said acid, to remove the basic compounds; substantially as specified.

5. The process of refining crude mineral oils of the Lima type having a specific gravity not higher than 0.835, consisting in adding thereto not more than 0.5 per cent. by weight of nitric acid of specific gravity of 1.42 until the evolution of sulfurous gas ceases, and the addition of an alkali and a hydrogen-producing substance for the subsequent removal of the nitrolic acids and resultant compounds; substantially as specified.

6. The process of refining crude mineral oils of the Lima type having a specific gravity not higher than 0.835, consisting in adding thereto not more than 0.5 per cent. by weight of nitric acid of specific gravity of 1.42 until the evolution of sulfurous gas ceases, and the subsequent removal of the nitrolic acids and resultant compounds by the addition of not more than 0.5 per cent. of soda-lye at not less than 35° Baumé and the addition thereto of a powdered metallic substance until, in a tested portion, the evolution of nitrous gas in the presence of sulfuric acid ceases; substantially as specified.

7. The process of refining crude mineral oils of the Lima type having a specific gravity not higher than 0.835, consisting in adding thereto not more than 0.5 per cent. by weight of nitric acid of specific gravity of 1.42 until the evolution of sulfurous gas ceases and the subsequent removal of the nitrolic acids and resultant compounds by the addition of not more than 0.5 per cent. of soda-lye at not less than 35° Baumé the addition thereto of a powdered metallic substance until in a tested portion, the evolution of nitrous gas in the presence of sulfuric acid ceases, a washing of the treated oil with water to remove free ammonia, and a washing of the oil with dilute sulfuric acid, until the oil fails to color said acid, to remove the formed organic amido compounds; substantially as specified.

8. The process of refining crude mineral oil of the Lima type, consisting in treating said oil with nitric acid until the evolution of sulfurous gas ceases, the addition of an alkali and a metallic substance capable of producing hydrogen with an alkali until in a tested portion nitrous gases cease to be evolved in the presence of sulfuric acid, and the subsequent washing of the treated oil with water to remove free ammonia therefrom, substantially as specified.

9. The process of removing the nitro and nitroso products from a crude mineral oil after treatment with nitric acid until the evolution of sulfurous gas ceases consisting in the addition thereto of a strong soda-lye and a metallic powder until in a tested portion nitrous gases cease to be evolved in the presence of sulfuric acid, subsequently agitating the mixture and then permitting the solid residue to precipitate; substantially as specified.

10. The process of refining crude mineral oils of the Lima type consisting in the addition of nitric acid thereto until sulfurous-acid gas ceases to be evolved, and the addition of a substance for producing nascent hydrogen for the removal of the newly-formed products by a subsequent treatment; substantially as specified.

11. The process of refining crude mineral oils of the Lima type consisting in adding thereto nitric acid until the evolution of sulfurous-acid gas ceases, reducing the resultant compounds by the addition of an alkali and metallic substance capable of producing hydrogen with the alkali, agitating a test portion of the mixture until diluted sulfuric acid ceases to generate nitrous acid from the oil; substantially as specified.

12. The process of refining crude mineral oils of the Lima type consisting in adding thereto nitric acid with which the oil is agi-

tated until the evolution of sulfurous-acid gas ceases, an agitation of the treated oil with an alkali and a hydrogen-producing metal until in a test portion dilute sulfuric acid ceases to generate nitrous acid, a washing of the treated oil with water to remove free ammonia therefrom, the subsequent washing of the oil with dilute sulfuric acid until the oil fails to color said acid to remove the formed basic compounds, and the distillation of the oil; substantially as specified.

In witness whereof I affix my signature in presence of two witnesses.

FELIX C. THIELE.

Witnesses:
H. HILLEBRAND,
JNO. HILLEBRAND.