UNITED STATES PATENT OFFICE.

L. ATWOOD AND W. ATWOOD, OF WALTHAM, MASSACHUSETTS.

IMPROVEMENT IN THE PRODUCTION OF OIL FROM CANNEL-COAL.

Specification forming part of Letters Patent No. **15,505**, dated August 12, 1856.

To all whom it may concern:

Be it known that we, LUTHER ATWOOD and WILLIAM ATWOOD, both of Waltham, in the county of Middlesex and ommonwealth of Massachusetts, chemists, have invented or discovered an improved method of obtaining oil from the coals which yield paraffine; and we do hereby declare that the following is a true and exact description of the same.

The nature of our invention and improvement consists in modifying, by chemical processes conjoined with distilling operations, the proximate elements found in the distillates of coals and other bodies which yield paraffine, so as to produce an oleaginous body adapted in a high degree to lubricating purposes. Such coals are known as "cannel," "Breckenridge," "bog-head," brown" coal, and "Albert" coals, "peat," and some bitumens.

To render more clear our description we submit that we are the original discoverers, so far as we know, of certain reactions taking place among the constituents of such coals and bitumens, which produce ordinarily paraffine-oil and light oils, and it therefore becomes necessary for us to distinguish coals by new characteristics. We find that coals, when slowly heated to a certain high temperature, varying with the nature of the coal, decompose by changes taking place rapidly—not a species of distillation, but a rapid decomposition. This new arrangement of the constituents is always the first effect of heat applied to coals. Excepting a little water, they afford no fluids until such fluids form from the material of the coal. The condensable fluid products contain a variety of bodies; but all known coals and bitumens thus treated divide into two classes—viz., first, those yielding fluids containing no paraffine; second, those producing fluids containing paraffine. The first class includes some cannels, or coals having the physical characters of cannels, and some bitumens, all of which yield in their decomposition semi-fluids like common coal-tar. For the treatment of such distillates in a way to afford a lubricating-oil, called "coup-oil," of certain well-known specific characters we have Letters Patent. The second class of coals includes most cannels and some bitumens, brown coals, peat, and schists, and the fluids resulting from their decomposition contain paraffine, which is a distinctive feature, and enables us to class such native coals and bitumens under one head in relation to our new manufacture.

Heretofore much discrepancy of statement has existed; and in the books wood-tar, peat-tar, and brown-coal tar have been considered as specially containing paraffine, while coal-tar and pine-tar were supposed to contain, at most, traces of it. It was, however, found that schists, petroleums, and cannels—like bog-head and Breckenridge—produced it at the lowest temperatures of decomposition, and bog-head coal has become the basis of a manufacture of an oil known as "paraffine-oil." Those natural bodies which produce paraffine may be considered as the remains of wax-producing vegetation. In all that has been done heretofore to obtain lubricating-oils the greatest care has been observed to so conduct the decomposition of the cannel or brown coal that the temperature may below, thereby preventing the decomposition of the paraffine, which, as a solid, resembles spermaceti, and when dissolved in eupion formed with it constitutes "paraffine-oil," for the production of which Brown and Young have patent rights. Our discoveries and applications depart from this previous state of knowledge and relate to the rapid decomposition of these cannels and bitumens and their distillates, which produce paraffine at low temperatures by higher heats suddenly applied, and it is an essential feature of our application that we reject or decompose the paraffine and eupion, so as to avoid the presence of solid paraffine and fluid eupion and form a new oleaginous body, having a high boiling-point, an uncommon oily character, increased density, and resistance to refrigeration. We can use cannel and brown-coal tars from gas-manufacturers, consuming only the coals producing paraffine which has then been decomposed, or the waste products of the manufacture of light oils containing paraffine from schists, cannels, bitumens, &c.

The basis of our invention is the discovery that when we distill the hydrocarbons by heat of considerable intensity rapidly applied repeatedly at each successive distillation carbon appears as a final product, while the elements of the fluid distillates arrange themselves anew

to form a compound which becomes more and more oily in character. By withdrawing interfering bodies we control the results so as to give certainty to the manufacture.

In carrying out our invention we have found an advantage to arise from removing, by powerful chemical agents, acid, alkaline, and basic bodies from the crude products in the course of the operations, so as to prevent these crude products from reacting to produce other objectionable bodies. Thus when we operate on a tar-like body, natural or artificial, we remove, by a large volume of strong sulphuric acid, all the naphthaline and alkaloids, because experience has shown that these bodies form paranaphthaline at high heats. If after distillation, following in course, more naphthaline appears we remove it in the same way. Some crude materials produce acid hydrocarbons in breaking up their constituents, and we reverse the course and apply alkalies to remove them, in every case having in view the ultimate production of a neutral oil of specific characters which are distinctive, from whatever source it is obtained. The same processes applied to crude matters of different origins, although belonging to the same series, as commonly considered, will not produce our oil, nor will any number of distillations produce it.

The oils which have heretofore been obtained by distillation from cannel-coals are thin oils, holding in suspension and solution paraffine, to which they owe their density, and the favorite sources are the bog-head and Breckinridge coal and like bodies, from which they are obtained by moderated heat in distillation. It is an essential point in their production that the temperature should not approach 698° Fahrenheit, where paraffine is wholly decomposed, and where the eupion, which boils below 212° Fahrenheit, would be lost. They generally boil at from 450° to 550° Fahrenheit, and are saturated solutions of paraffine at 60° Fahrenheit, becoming a soft solid at 45° Fahrenheit. Young's oil, which includes the best of that class, gives off volatile products at 400° Fahrenheit which contain paraffine. Its specific gravity varies from 0.836 to 0.858, and it cannot be rendered more dense without decomposing it. Being a solution of paraffine in the lighter hydrocarbons, it presents two distinct bodies, and owes its lubricating power to the paraffine, and as it thickens at a moderately-low temperature with separation of solid paraffine, it has not the useful characters we deem essential in our oil.

The oil which we regard as our invention contains rarely traces of a solid body, which at 32° Fahrenheit appears in needly crystals. Its specific gravity at 60° Fahrenheit is 0.864 to 0.870, and its oleaginous characters are remarkable, exceeding in this respect any known oil. When heated it gives off no vapor at 500° Fahrenheit, and has a nearly fixed boiling-point at 700° Fahrenheit. In its chemical relations it differs from any known fluid, and appears to be isomeric with paraffine. It does not exist ready formed in any natural bitumen or naphtha, but is a result of chemical decomposition of hydrocarbons which afford paraffine under the combined action of chemical agents applied in succession with a high heat in distillation.

In the following description of our processes it will be observed by those who are skilled in the art that we do not seek to simply separate and purify bodies which have been known before and as articles of commerce, but by different steps, applicable to the particular crude matter of the cannels and bitumens which produce paraffine, we arrange anew the component parts of crude distillates.

We do not commence with the coal, but take the fluid matter condensed by distilling coals of the paraffine series, however obtained, and subject it, in an iron vessel, to a careful washing in water to remove soluble matter. The washed tar-like fluid introduced into an agitator must have all its acid hydrocarbons removed by means of successive portions of caustic soda or caustic potash at 36° Baumé, added, agitated, and withdrawn until the solution of alkali appears to become no longer changed, even at 212° Fahrenheit. In this step we not only remove the acids present in a free state, but we decompose acid salts or combinations of positive and negative hydrocarbons, so as to eliminate the bases, while we remove the acid or positive constituent, which is essential to the success of the other step of the processes. The tarry matter removed from the last portion of alkali must be distilled from an iron retort by naked heat or heat aided by steam, the distillate being rejected until the mass in the retort shows the temperature of 600° Fahrenheit, when the distillate sought for begins to appear. By increasing the heat a large bulk of the distillate is obtained, and when the temperature of 750° to 800° Fahrenheit is reached the distillate becomes brown-colored, when the process is stopped. In the systematic manufacture it is usual to save the oil boiling at 450° Fahrenheit or below 600° Fahrenheit and mix it with that distilling above 850° Fahrenheit. If the mixture has not at this stage a density of about 0.850, or when we wish to increase the density of the distillate, we add a heavier crude product obtained from a coal or bitumen which affords it of greater density. Each coal or bitumen gives a crude product differing in density from that of another. We find it advantageous to mix their distillates, and thus insure a medium density and corresponding equality of finished oil. By the reactions in the retort colored and basic bodies are formed, requiring for their removal usually two hundred pounds of oil of vitriol for one hundred gallons of the distillate, agitation for two hours, and repose in air at 80° or 90° until subsidence of the acid compounds has taken place. The clear oil must now be washed with five gallons of caustic soda at 36° Baumé for one hour. This solution withdrawn, six pounds of manganate of potash or soda dissolved in five gallons of wa-

ter must be added and the whole agitated one or two hours, the temperature being as high as 100° Fahrenheit to allow of subsidence of all impurities. The clear oil must then be transferred to an iron retort and distilled by the gradual application of heat, with the aid of heated steam above the oil, reserving for future steps the distillate rising between 600° and 800° Fahrenheit only. This operation has produced a new quantity of colored and basic matter, which must be removed by treating one hundred gallons of the distillate in an agitating apparatus with one hundred pounds of oil of vitriol and violently mixing for two hours. After the action of the acid the oil must be washed with five gallons of soda solution at 36° Baumé by agitation for one hour and allowing to subside. The resulting product being again distilled with the precautions above stated will have become permanent and uniform. A small amount of acid present must be removed by agitating the distillate with three gallons of caustic-soda solution, leaving the oil for the separation of the soda solution at a temperature of 80° or 90° Fahrenheit. After the removal of the oil from the impurities it must be thoroughly washed by jets of steam in the usual manner and subsequently exposed in shallow pans to the sun's rays until all moisture has become dissipated.

It is not always necessary to subject the oil to the last distillation here named, as some of the crude distillates are more easily broken up than others; but it is essential that the oil be freed from all bodies having low boiling-points and that the solid hydrocarbons which appear in the first steps be removed by pressing or decomposed almost wholly into an oleaginous body having a density above 0.864.

We are aware that oils for lubrication have before been obtained from coals, bitumens, and schists which afford paraffine in distillation, and they have been purified by acids and alkalies. These oils are solutions of paraffine in light oils or eupion obtained in the first distillations, deriving their density and essential qualities from the paraffine. They do not resemble the heavier uniform oils which result from the decompositions and recompositions taking place in the same distillates at high temperatures, aided by chemical agents applied in large quantities at different steps in the manufacture, and we disclaim such oils.

We also disclaim mixed crude products heretofore obtained by distillation from schists, &c., and confine ourselves to a transparent nearly colorless oil, having its boiling-point above 600° Fahrenheit, remaining fluid at 32° Fahrenheit, and of a density above 0.864 at 60° Fahrenheit, which is formed from coals, bitumens, and other bodies affording paraffine in their treatment by the above processes.

What we claim, and wish to secure by Letters Patent, is—

An improved oil obtained, by the processes substantially as set forth above, from natural bodies which alone or when mixed afford paraffine in destructive distillation, and which oil possesses the properties above described.

LUTHER ATWOOD.
WM. ATWOOD.

Witnesses:
JAMES W. ROLLINS,
W. H. L. SMITH.