No. 771,859. PATENTED OCT. 11, 1904.

F. S. CLARK & E. A. HARRIS.

PROCESS OF MANUFACTURING PINE OILS FROM WOOD.

APPLICATION FILED JULY 10, 1903.

NO MODEL. 2 SHEETS—SHEET 1.

Fig. 1.

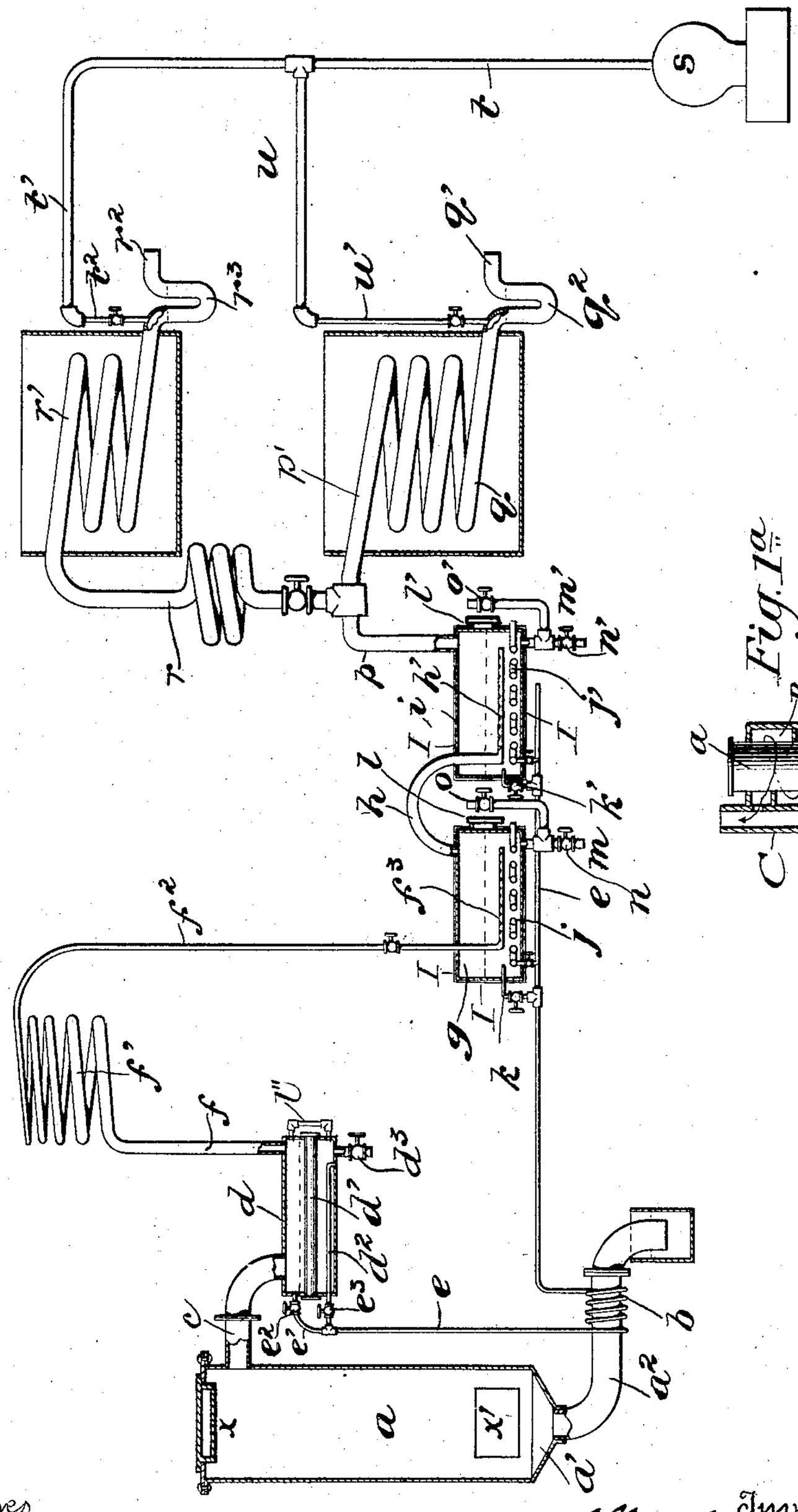
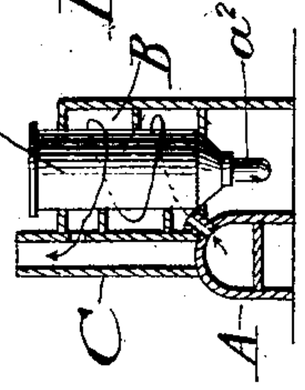


Fig. 1a.



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NO MODEL. 2 SHEETS—SHEET 2.

Fig. 2.

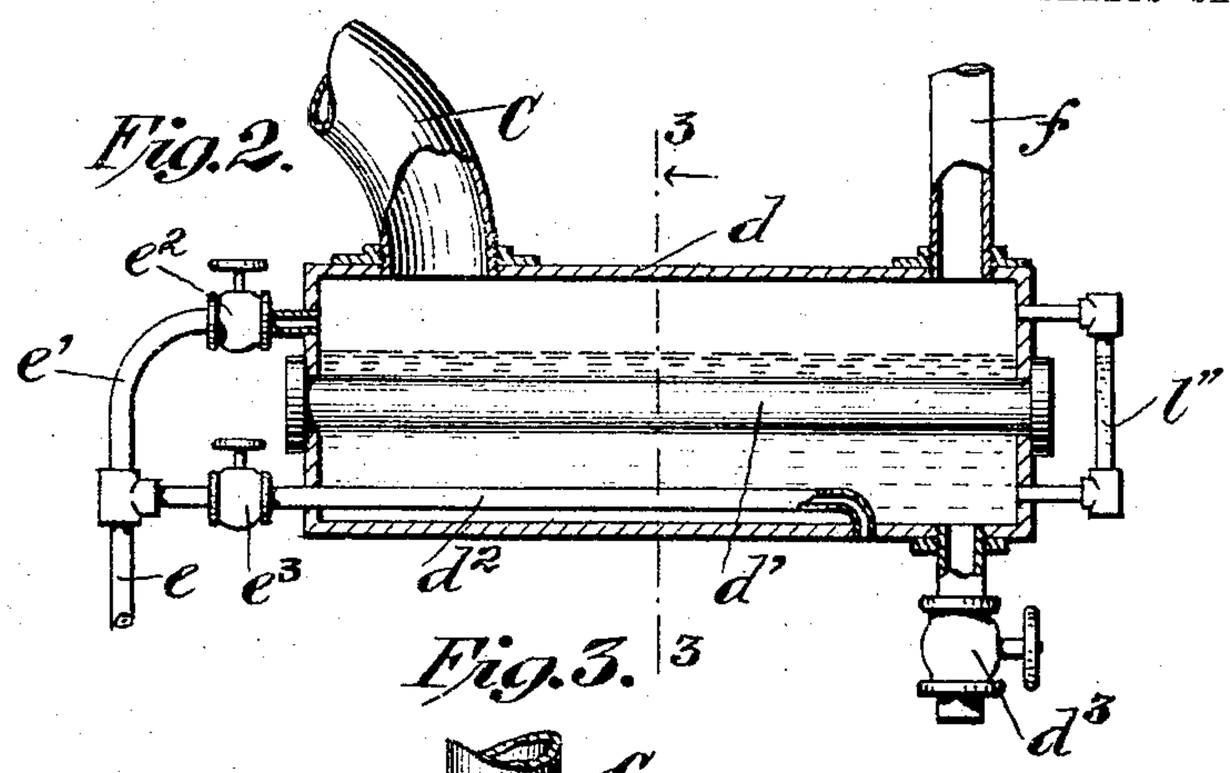

Fig. 3.

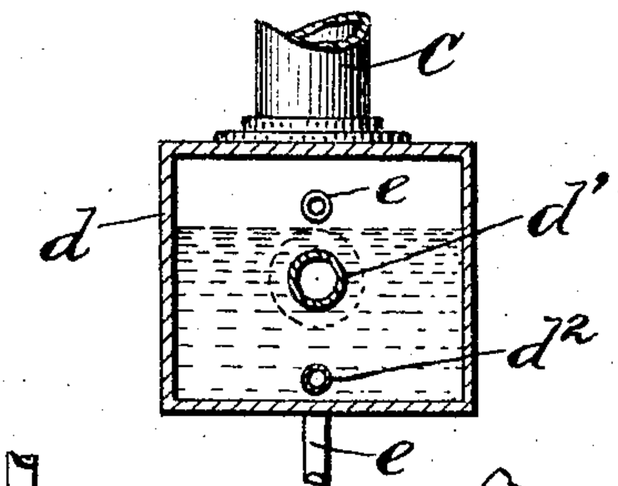

Fig. 4.

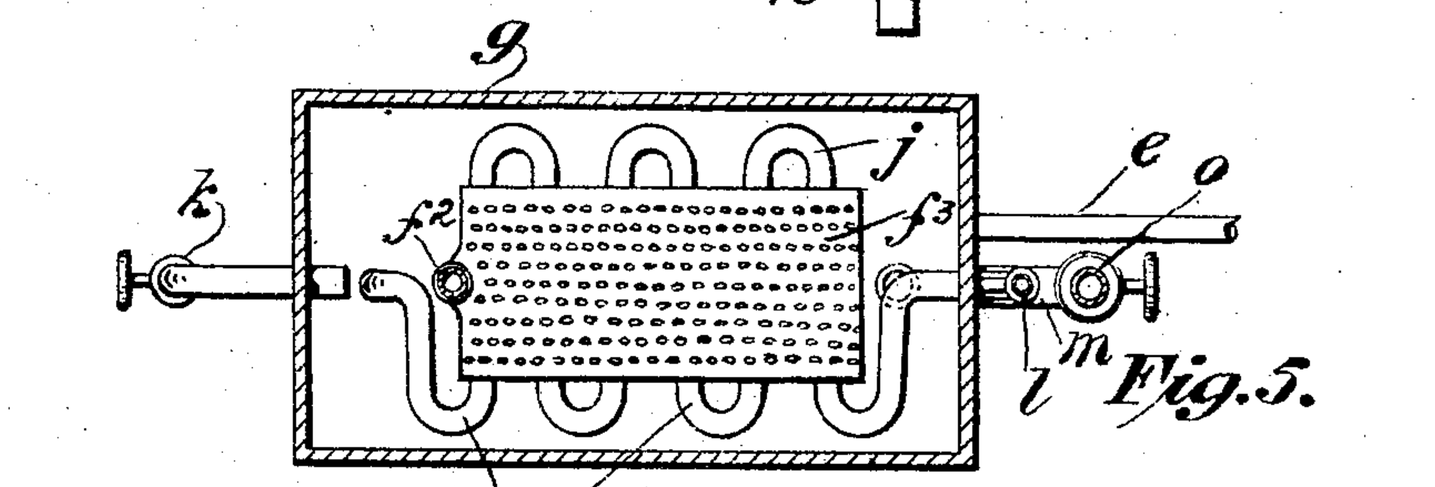

Fig. 5.

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PHOTO-LITHOGRAPHED BY SACHETT & WILHELMS LITHO. & PTG. CO. NEW YORK.

No. 771,859. Patented October 11, 1904.

UNITED STATES PATENT OFFICE.

FRANKLIN S. CLARK AND EDWIN ASCHER HARRIS, OF NEW YORK, N. Y., ASSIGNORS, BY MESNE ASSIGNMENTS, TO GEORGIA PINE TURPENTINE COMPANY OF NEW YORK, A CORPORATION OF NEW YORK.

PROCESS OF MANUFACTURING PINE-OILS FROM WOOD.

SPECIFICATION forming part of Letters Patent No. 771,859, dated October 11, 1904.

Application filed July 10, 1903. Serial No. 165,019. (No specimens.)

To all whom it may concern:

Be it known that we, FRANKLIN S. CLARK and EDWIN ASCHER HARRIS, citizens of the United States, both of the city, county, and State of New York, have invented a new and useful Process for the Manufacture of Pine-Oils from Wood, of which the following is a specification.

This invention relates to a process of making water-white pine-oil directly from the wood in a continuous series of steps, this oil being immediately suitable for all the purposes to which spirits of turpentine may be applied. The process is further effective in that such oils as it produces which are not made water-white by the process are so improved that the process of refining the same thereafter is made simpler and easier. What we mean by "pine-oil" can perhaps be best explained by stating that the products of the dry distillation of pine and other similar woods as carried out in the herein process comprise, generally speaking, charcoal, tar, heavy oils, light oils, acetic acid, water, and gases, &c. The heavy oils are heavier than water and contain creosote, paraffin-like bodies, &c., together with more or less of the light oils and acetic acid. The light oils are lighter than water and consist of what we call "pine-oils," together with more or less of the heavy oils, acetic acid, &c. In the present application the name "pine-oils" has been used to designate the light oils after they have passed through the refining treatment described herein. In other words, we make the expression "pine-oils" substantially synonymous with "purified light oils." We are aware that the expression "pine-oil" has also been used to designate all of the liquid products of wood distillation collectively; but we have not so used it herein. Chemically speaking, pine-oil is a different individual from spirits of turpentine, although in its practical application it is an excellent substitute for turpentine. We recognize that pine-wood when distilled at a low temperature with steam will yield a small quantity of turpentine. These conditions, however, will not yield pine-oils, since the initial temperature at which these come over must be considerably higher and will vary from about 240° to 300° Fahrenheit. It is believed that turpentine is an educt of wood, whereas pine-oil is a product.

It has been the practice heretofore to produce from the wood direct only crude pine-oils. These oils have been too impure to be used for making varnishes or for the other purposes for which spirits of turpentine is used. It has therefore been necessary heretofore in order to obtain a pure and marketable product that the crude oil as made at the retort direct from the wood should be refined by further treatment, necessitating further expense, loss of time, loss of materials due to evaporation, together with the necessity of maintaining a refining and storage plant and other disadvantages incurred by the refining process.

The object of the present invention is to do away with all these detrimental features by reducing refined oils direct from the wood in one continuous process.

Our process may, for example, be carried out through the medium of the apparatus shown in the accompanying drawings.

Figure 1 shows a longitudinal sectional view of such an apparatus. In this the various pipes and other parts, such as coils and the suction-pump, are in elevation. Fig. 1ª is intended to show one form of heating means which can be used to heat the retort *a*, said heating means consisting of the furnace A, the flues B, and the chimney C. In Fig. 1 the retort *a* is only diagrammatically represented, but in practice will be furnished with heating means—for example, with the furnace and the other adjuncts shown in Fig. 1ª. Fig. 2 is a longitudinal sectional view of the air-condenser *d*. Fig. 3 is a transverse section thereof, taken along the line 3 3 of Fig. 2. Fig. 4 is a longitudinal sectional view of the tank *g*, and Fig. 5 is a horizontal sectional view taken along the line 5 5 of Fig. 4.

A retort *a* is provided with a suitable charg-

ing-door at the top and a suitable charcoal-door at the bottom, these being too evident to need detailed illustration, but are indicated by x and x'. The retort a has a bottom a', preferably conical, and a discharge-pipe a^2, leading from the lowermost point thereof for conducting the tar out of the retort, a steam-coil b being applied to the said discharge-pipe for the purpose of preventing the tar from congealing and to keep it on the move. At the top of the retort there is provided a pipe c for the passage of the vaporized products of distillation from the retort. This pipe c is in the form of a gooseneck and delivers the vapors from the retort a into an air-condenser, such as d. This air-condenser is a drum or chamber of copper, preferably, having a central flue d' leading therethrough for the passage of the air. From the air-condenser d the vapors pass as hereinafter to be described. Arranged in the lower part of the air-condenser d is a closed steam-pipe or coil d^2, which communicates with the steam-supply pipe e, with which the steam-coil b is connected. Also leading from the steam-supply pipe e is a short pipe e', which conducts the steam directly into the air-condenser. Pipes d^2 and e' are respectively provided with valves e^3 e^2. The purpose of the condenser d is to fractionate the products and to thereby separate them for application to different commercial uses, and, further, to more effectively relieve the vapors of heavy oils, acetic acid, &c., in order to secure a finished product of finer quality. The bottom of the condenser d is provided with a valve-controlled discharge d^3 or other suitable discharge device for drawing off the heavy oils, acetic acid, and water which have been condensed in the condenser d. Said condenser d is provided with a gage l'' to indicate the liquid-level therein. Leading from the condenser is a pipe f, which is of suitable length and which is preferably formed into a condensing-coil f', from which leads a pipe f^2. The purpose of the condensing-coil f' is to further fractionate the vapors and still further relieve them of heavy oils, acetic acid, &c., the same being condensed and returned from the said coil down the pipe f into the first condenser d. The pipe f^2 enters a tank g and is at its lower end provided with an enlarged portion f^3, having in its upper part a great number of minute perforations, so that the vapor may issue therefrom in numerous small streams, and thereby be more intimately brought in contact with suitable alkali, which is contained in the tank. A cheap alkali, like lime, is most advantageously used in the tank g; but otherwise any alkali would be just as effective. From the tank g the vapors pass through the pipe h, which leads into a second tank, i, which pipe is likewise formed at its lower inner end with an enlarged portion h', provided with minute perforations, so as to cause the vapor to intimately contact with the alkali in said tank i, which alkali is one of the caustic alkalies, meaning thereby either "caustic soda" or "caustic potash." In order to prevent the condensation of the vapors in the alkali-bath and in order to help the vapors through, and thus prevent the tanks g and i from filling up with water, &c., it is desirable to provide, as shown in the drawings, closed coils or pipes $j\,j'$ in said tanks, respectively, and short pipes or nozzles $k\,k'$, respectively, which open into the tanks g and i. The pipes $j\,j'$ and $k\,k'$ lead from the steam-supply pipe e and are provided with suitable valves, as shown, for separately controlling the steam through said pipes. It should be added that the tanks g and i are preferably covered on the outside with some non-conducting material I, so as to still further guard against condensation. Each of the tanks is provided with gages (indicated by $l\,l'$, respectively) for the purpose of indicating the liquid-level. Furthermore, each of the said tanks is provided with a two-branched pipe. The two-branched pipe m for the tank g is provided in each of its branches n o with valves for separately controlling them. The branch n is directed downwardly and o upwardly, the latter being for the purpose of receiving the alkali and the branch n for discharging the by-products which are formed in the tanks. The tank i has the pipe m', with branches n' o' for the same purpose.

From the chamber or tank i leads a pipe p, which is provided at its upper end with a downwardly-turned portion p', that is formed into a coil q, forming a condenser, at the lower end of which is an outlet q' and an intermediate trap q^2. The products of condensation are barreled off from the discharge q'. Connected with the downturned portion of the pipe p is an upwardly-extending pipe r, which is formed at its upper end with a coil r', having at its lower end a discharge r^2 and an intermediate trap r^3. This pipe r serves as a condenser.

A suitable vacuum-pump s is provided for the purpose of creating a suction in the apparatus and for drawing off the incondensable gases, for which purpose a pipe t leads from the pump by means of branch t' and a valve-controlled branch t^2 to the condensing-coil r'. This pipe t is furthermore connected by means of branches u and u', the latter being valve-controlled, with the condensing-coil q. Not only does this pump insure the constant passage of the vapors away from the retort and through the apparatus, but it obviates any back pressure on the retort. When not in use for the above purposes, the vacuum-pump also serves for forcing air into the products contained in suitable receptacles in order to aerate them, or another pump may be kept on hand and used for this purpose. The vacuum must not be so strong that it overcomes the liquid seals in the traps q^2 and r^3. The

vacua in the two condensers q and r' can be varied relatively to each other by manipulating the valves in the pipes u' t^2.

The process is carried out in the apparatus shown as follows: The retort is filled with pine or fir wood or other woods yielding oils in the nature of pine-oil and then heated gradually. The retort may be heated from a furnace underneath the retort or in any other suitable manner. The initial temperature at which the pine-oils come over varies from about 240° to 300° Fahrenheit, depending upon the conditions. During the distillation tar is formed and is best drawn off from the bottom of the retort before the heat has become sufficiently high to decompose the tar. This may be accomplished by having the tar-pipe a^2 always open, so that the tar runs off from the retort as fast as it is formed. As the wood is heated the vaporized products of dry distillation pass into the air-condenser d, into the bottom of which the heavy oils, acetic acid, water, &c., precipitate, and from here they can be drawn off through the passage d^3. It is advisable, however, to let them stay a short time in the bottom of the condenser in order that the heat of the vapors may re-evaporate any pine-oils contained therein, which would otherwise be carried off with the heavy products in case they were withdrawn immediately. However, the best way to guard against possible loss of pine-oil through condensation at this point consists in providing open and closed steam-pipes e' d^2 within the condenser d, whereby the temperature therein can be regulated to prevent condensation of the pine-oil vapors. The open steam-pipe e' also serves to help along the vapors and to clean out the apparatus when necessary. The condensate in the condenser d will in actual operations preferably be kept at such level that the live steam from the pipe e' will play over its surface. From the condenser d the vapors pass through the pipe f and preferably, as before stated, through another condenser, as f', for the purpose of further fractionating these vapors to secure a better finished product. Without the condenser f' a certain amount of pine-oil might come out dark at the end of the process and require refinement which by the use of said condenser would come out white and require no further refinement. This condenser f' serves to still further relieve the vapors of heavy oils, acetic acid, &c., which thereupon run back into d. The uncondensed vapors at this stage of the process and known collectively as the "light oils" consist of pine-oils contaminated with acetic acid, creosote, &c. The vapors passing from the condensing-coil f' are conducted by the pipe f^2 into the tank g, where they are treated with lime or other alkali, air-slaked lime, ash-lye, &c. This lime may be in the form of milk of lime, the vapors being bubbled through the same, or in dry form. The object of the lime is to absorb from the vapors acetic acid, &c. Acetate of lime is therefore one of the commercial by-products of this process. The lime further absorbs the carbonic-acid gas, and thus improves the quality of the gas, which is one of the final products of this process. The vapor from the tank g passes through the connecting-pipe h into the tank i, which is filled with caustic soda or caustic potash. The alkali in the chamber i is preferably in the form of a bath through which the vapors are bubbled. Where a solution of caustic alkali is used, the strength of the same may vary between wide limits; but a solution of 1.21 specific gravity has been found to give good results on the average. A by-product is produced in the tank i, the heavy oils therein combining with the caustic soda and making a fine soluble disinfectant. The vapors thence pass into the pipe p and going through the condensing-coil q come out white at the discharge end q' in liquid form. It is desirable to provide, by means of the pipe r or the like, an air-condenser which is of sufficient length to condense all the pine-oil vapors before said vapors reach the top of this pipe, but not to condense certain bad-smelling oils which are mixed with the pine-oils and which will contaminate the latter unless they are removed by fractional condensation at this point. These bad-smelling oils are condensed in the worm-condenser r' and are drawn off and separated at the discharge end r^2. It should be said, however, that it is one of the great advantages of this process over any other process known to us for producing pine-oils that when the same is properly carried out little or no bad-smelling oils are found. Ordinarily, therefore, the fractionating apparatus r r' can be dispensed with. It is desirable, however, to have same for use should these bad-smelling oils for any reason contaminate the pine-oil vapors in appreciable quantity. As the distillation proceeds and the oils become heavier in gravity it is found that the product drawn off at q' is less likely to hold its white color and tends to become less pure. We have therefore found it desirable at about this point in the process to collect the heavier oils in separate receivers, these heavier oils being of second quality. It may also be desirable to make a further separation between the oils of still higher gravity and to collect these separately as a product of third quality.

The following temperatures were observed in an actual instance of the operation of the process. The temperatures in the retort varied from 240° to 800° Fahrenheit, in the drum d from 184° to 220° Fahrenheit, in the lime-chamber from 198° to 212° Fahrenheit, and in the soda-chamber from 187° to 212° Fahrenheit. These temperatures in each instance were taken by thermometers suspended in the vapor, the retort temperature being taken by a thermometer in the gooseneck c.

In the instance given both closed and live steam were used in the drum *d*. Closed steam was also used in the lime and soda chambers. Different temperatures from the foregoing will be shown by different workings of our process, depending upon the conditions. Thus the temperatures of the different parts of the apparatus will vary, depending upon the kind of wood used and its quality—for example, whether it is comparatively wet or dry; also, upon the size of the retort, the arrangement of the flues about the retort, and the variations in firing; also, upon the location of the thermometers used to measure the temperatures; also, upon whether the tar is removed in liquid form or distilled from the retort; also, upon whether an extra fine grade of charcoal is to be produced, in which event the final temperature in the retort will be run considerably higher than that specified—say from 1,000° to 1,200° Fahrenheit; also, upon the amount of live steam introduced, similarly with reference to the amount of closed steam used; also, upon the degree of vacuum in case a vacuum-pump is employed, &c.

It has been found that by pumping air by means of a suitable pump, such as *s*, into the various final products of our process contained in suitable receptacles any remaining traces of bad-smelling oils are removed. Aeration, furthermore, oxidizes these pine-oils and makes them a still more perfect substitute for turpentine.

It should be understood that caustic alkali alone without the use of lime (or its equivalent) can be employed in our process with entire effectiveness. However, as a matter of economy it is desirable to use, as described, lime (or its equivalent) in connection with the caustic alkali, thereby preventing the caustic alkali, which is expensive, from being used up to remove from the vapors impurities like acetic acid, &c., which can be quite as effectively removed by the lime, &c. In other words, in our process the use of successive lime (or its equivalent) and caustic-alkali treatments may be substituted for a treatment with caustic alkali alone, and it is to be so understood with reference to all the claims herein calling for caustic alkali alone.

Without restricting ourselves to the apparatus shown or to the process as described or enumerating all equivalents, as some steps in the process may be used without or replaced by others, what we claim is—

1. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation and treating the vapors containing said oils with caustic alkali under such temperature conditions that said oils are treated in vapor form.

2. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation and treating the light oil-vapors with caustic alkali under such temperature conditions that said oils are treated in vapor form.

3. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation, subjecting the vapors to fractional condensation thereby condensing vapors that are condensable without causing condensation of the pine-oil vapors, treating the residual vapors containing said pine-oils with caustic alkali under such temperature conditions that said oils are treated in vapor form, and condensing the ultimate vapors.

4. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation, removing the tar in liquid form from the retort, treating the vapors containing said oils with caustic alkali under such temperature conditions that said oils are treated in vapor form, and condensing the ultimate vapors.

5. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation, removing the tar in liquid form from the retort, subjecting the vapors to fractional condensation thereby condensing vapors that are condensable without causing condensation of the pine-oil vapors, treating the residual vapors containing said pine-oils with caustic alkali under such temperature conditions that said oils are treated in vapor form, and condensing the ultimate vapors.

6. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation, subjecting the vapors to fractional condensation thereby condensing vapors that are condensable without causing condensation of the pine-oil vapors, regulating the heat during such condensation to keep said pine-oils vaporized, treating the residual vapors with caustic alkali under such temperature conditions that said oils are treated in vapor form, and condensing the ultimate vapors.

7. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation, subjecting the vapors to fractional condensation thereby condensing vapors that are condensable without causing condensation of the pine-oil vapors, introducing live steam during such condensation, treating the residual vapors with caustic alkali under such temperature conditions that said oils are treated in vapor form, and condensing the ultimate vapors.

8. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation, removing the tar in liquid form

from the retort, subjecting the vapors to fractional condensation thereby condensing vapors that are condensable without causing condensation of the pine-oil vapors, introducing live steam during such condensation, treating the residual vapors with caustic alkali under such temperature conditions that said oils are treated in vapor form, and condensing the ultimate vapors.

9. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation, removing the tar in liquid form from the retort, condensing from the vapors the bulk of the heavy oils, treating the residual vapors containing said pine-oils with caustic alkali under such temperature conditions that said oils are treated in vapor form, and condensing the ultimate vapors.

10. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation, condensing the bulk of the tar and heavy oils from the vapors, treating the residual vapors containing said pine-oils with caustic alkali under such temperature conditions that said oils are treated in vapor form, and condensing the ultimate vapors.

11. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation, treating the vapors containing said oils with caustic alkali under such temperature conditions that said oils are treated in vapor form, and separating by fractional condensation the bad-smelling oils from the pine-oils.

12. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation, subjecting the vapors to fractional condensation thereby condensing vapors that are condensable without causing condensation of the pine-oil vapors, treating the residual vapors containing said pine-oils with caustic alkali under such temperature conditions that said oils are treated in vapor form, and separating by fractional condensation the bad-smelling oils from the pine-oils.

13. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation, treating the vapors containing said oils with caustic alkali under such temperature conditions that said oils are treated in vapor form, condensing the residual vapors, and aerating the condensed product.

14. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation, subjecting the vapors to fractional condensation thereby condensing vapors that are condensable without causing condensation of the pine-oil vapors, treating the residual vapors containing said pine-oils with caustic alkali under such temperature conditions that said oils are treated in vapor form, condensing the ultimate vapors, and aerating the condensed product.

15. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation and treating the vapors containing said oils with an alkali capable of removing from the vapors acetic acid and creosote, under such temperature conditions that said oils are treated in vapor form.

16. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation, treating the vapors containing said oils first with an alkali capable of removing acetic acid from the vapors and thereafter with another alkali capable of removing creosote from the vapors, the temperature conditions being such that said oils are treated in vapor form.

17. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation, subjecting the vapors to fractional condensation thereby condensing vapors that are condensable without causing condensation of the pine-oil vapors, treating the residual vapors containing said pine-oils with an alkali capable of removing from the vapors acetic acid and creosote under such temperature conditions that said oils are treated in vapor form, and condensing the ultimate vapors.

18. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation, subjecting the vapors to fractional condensation thereby condensing vapors that are condensable without causing condensation of the pine-oil vapors, treating the residual vapors containing said oils first with an alkali capable of removing acetic acid from the vapors and thereafter with another alkali capable of removing creosote from the vapors, the temperature conditions being such that said oils are treated in vapor form, and condensing the ultimate vapors.

19. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation and treating the light oil-vapors with an alkali capable of removing from the vapors acetic acid and creosote under such temperature conditions that said oils are treated in vapor form.

20. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation and treating the light oil-vapors with an alkali capable of removing acetic acid from the vapors and thereafter with another alkali capable of removing creosote from the vapors, the temperature conditions being such that the pine-oils are treated in vapor form.

21. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation, removing tar in liquid form from the retort, subjecting the vapors to fractional condensation thereby condensing vapors that are condensable without causing condensation of the pine-oil vapors, treating the vapors containing said pine-oils with lime under such temperature conditions that said oils are treated in vapor form, and condensing the ultimate vapors.

22. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation, subjecting the vapors to fractional condensation thereby condensing vapors that are condensable without causing condensation of the pine-oil vapors, treating the residual vapors containing said pine-oils with lime under such temperature conditions that said oils are treated in vapor form, and condensing the ultimate vapors.

23. The process substantially as herein described for preparing pine-oils and pine-like oils, which consists in subjecting the wood to distillation, subjecting the vapors to fractional condensation under such temperature conditions as to condense heavy oils and acetic acid from the vapors but not to condense the pine-oils, treating the residual vapors containing said pine-oils with lime under such temperature conditions that said oils are treated in vapor form, and condensing the ultimate vapors.

In testimony whereof we have signed this specification in the presence of the subscribing witnesses.

FRANKLIN S. CLARK.
EDWIN ASCHER HARRIS.

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