

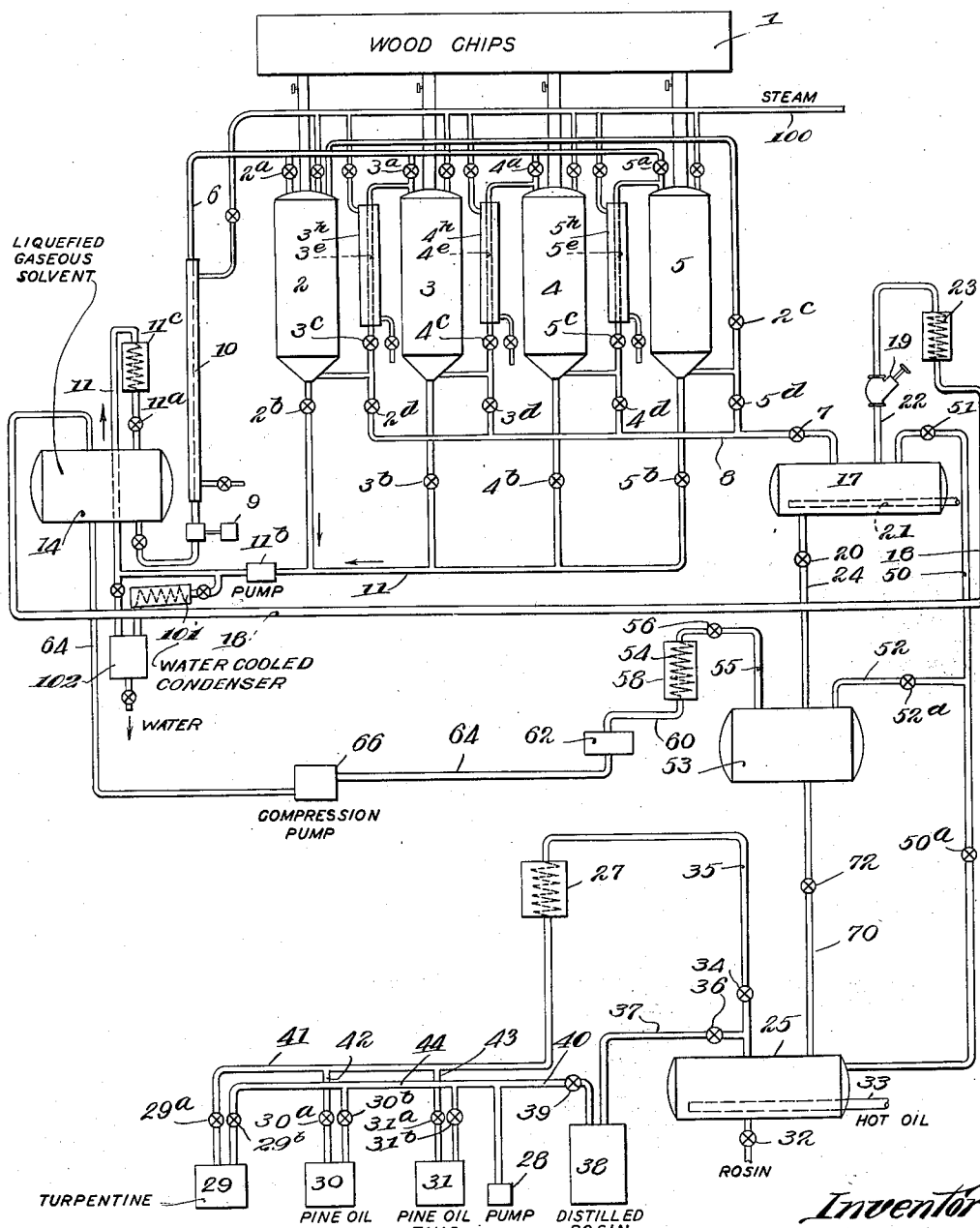
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PROCESS FOR THE SOLVENT EXTRACTION OF WOODS

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PROCESS FOR THE SOLVENT EXTRACTION OF WOODS

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My invention relates to a process for the solvent extraction of solutes from difficult or protective inclusions, and typically useful for removing from coniferous woods hydrocarbon-soluble extractives, preferably selectively.

Broadly speaking I find that the dissolving properties of a solvent and its diffusion into the pores of a cellular material containing the solute vary inversely in respect to the molecular weight of the solvent. I have found that a solvent of such low molecular weight and low boiling point as under normal conditions of temperature and pressure to be gaseous, is when liquefied an ideal solvent, for the above reasons.

My invention includes in one aspect a treatment exemplified by the solvent extraction of a solute from the narrow cellular or intra-cellular spaces of solute-containing materials by treatment with the liquid state of a normally gaseous solvent; for further example, by a process for the treatment of coniferous woods for recovery therefrom of the contained extractives by the use of a hydrocarbon solvent substantially consisting of hydrocarbon materials which under normal conditions of pressure and temperature are gaseous and which due to its physical properties of fluidity and lack of resistance to penetration of minute voids, which qualities are an accompaniment if not a consequence of a low average molecular weight, possesses the property of rapid diffusion into and through the small ducts of the wood in which the resins and terpenes are contained. A typical process according to this invention is particularly designed for the extraction of rosin and the terpenes from the stump wood of the long-leaf yellow pine. I have found that if a solvent of low specific gravity and low average molecular weight is employed it more efficiently dissolves the rosin, turpentine and pine oil out of the coniferous woods without substantially dissolving any of the darker rosin-discoloring impurities in the wood such as are now removed by solvents in use.

Heretofore all commercially practical processes for the recovery of rosins and ter-

penes from coniferous woods by means of solvents have required that the wood be quite finely reduced as by shredding with the result that the residual wood after extraction has not been well adapted to the manufacture of paper pulp and is of little value except as fuel. One purpose of the present process is to make unnecessary such fine mechanical reduction of the wood prior to extraction, and to make it possible to efficiently extract chips of a size that are well adapted to standard pulp mill operations. This is accomplished by the use of a solvent of the physical properties associated with a relatively low average molecular weight to insure a rapid diffusion rate into and through the chips.

A further advantage of my invention is to provide a suitable chip of coniferous wood for use in paper making from which the rosin has been substantially extracted without any substantial degeneration of the cellulose therein, as occurs when the wood is steamed. By employing my invention I am enabled to substantially extract the rosin from chips of standard paper making size which chips produce a higher grade paper than the small chips or shreds.

One advantage of this process from the point of view of conserving useful fiber for paper making lies in the avoidance of any temperature causing the loss of tensile strength of cellulosic fibers in after treatment for paper making, such as the sulphite process particularly, and the avoidance of contributing degenerating treatment with superheated steam. In respect to the sulphite process relative completeness of extraction of resins is important to successful use of the paper pulp for making paper.

Another advantage of this process is its availability for treatment of relatively moist materials without damaging or expensively thorough pre-drying. Normally gaseous solvents of the type herein described contain components, notably butane, capable of solution in considerable amounts in water; either this capacity or the possible solubility of water in the liquid phase of the normally gaseous solvent may contribute to

the observed capacity rapidly and effectively to dissolve resins in the presence of capillary inclusions of water in amounts which would inhibit treatment with ordinary solvents. For example, moisture contents of from 15% to 20% by weight have little or no effect on the operation of the herein described solvent on the rosin solute.

Another object is the simultaneous extraction of resins and terpenes without the necessity of first pre-heating to remove the latter, as by distillation with superheated steam or otherwise, which partially breaks down the resins into bodies that are undesirable in the ultimate resin product, and at the same time lowers the value of the residual wood for pulping by degeneration of the cellulose. The simultaneous extraction of the resins and terpenes is made feasible by the use of a solvent that boils substantially below that of the terpenes contained in the wood, but forms therewith no constant boiling mixture with any of the constituent terpenes, thus making it possible to readily separate and recover the solvent from the extractives for reuse.

A further object of my invention is the recovery of a lighter colored resin than has so far been obtained by the solvent extraction of woods rich in resins, such as the stumps of the long-leaf yellow pine. An example in support of this statement is the fact that wood rosin, as the trade knows the product of solvent extraction of long-leaf yellow pine, is generally of an F grade, as referred to the color standards of the United States Department of Agriculture, according to which rosin is graded progressively by letter designation from B to X as the color lightens from a dark reddish amber to a light amber. By the process of this invention it is possible to produce much lighter grades of wood rosin than heretofore obtainable, rosin of N and even higher grade being readily attained.

Yet another object is to recover rosin that is adapted to the present uses of so-called gum rosin, which is obtained by bleeding the living tree. For example, in one of the largest uses for rosin, which is in the manufacture of soaps, wood rosin as now obtained is entirely unsuited, for the reason that soaps made therefrom are either initially dark in color, or tend to darken on exposure to air during a comparatively short time. Rosin made by the process of this invention is entirely suited to manufacture of a high grade rosin soap. This product is also superior to present-day wood rosin in other important uses, such as in the manufacture of varnish and paper size, wherein gum rosin is today used almost exclusively.

The desirability of accomplishing the foregoing objectives which are now realizable has long been recognized, and much effort

has been expended, in particular, to improve the grade of wood rosin. For this purpose various solvents have been suggested from time to time, but gasoline, or a middle fraction thereof, has remained in general use. I have discovered that the desired results can be obtained by the use of a solvent comprising a hydrocarbon of comparatively low molecular weight, preferably comprising one or more of the lower members of the paraffin or olefine series of hydrocarbons. These exert a marked selective action on the rosins, failing to extract a substantial proportion of the bodies which are responsible for the dark color in wood rosin and leaving these bodies in a condition not detrimental to use of the wood for paper pulp. I have found that hydrocarbon solvents having an absolute vapor pressure at 75° C. (a preferred working temperature), in excess of one thousand mm. of mercury, and less than twenty thousand mm., are ideally suited for the purpose of my invention. Hydrocarbon substances coming within this range have a relatively low average molecular weight, and their use at the preferred working temperature involves extraction under pressure to keep said substances liquefied. I have found that propane, butane and pentane alone or in admixture comply with the above specification and are ideally suitable, though as stated other materials may be employed and I have also actually used amylene and butylene. A suitable mixture will in general be found to have an average molecular weight lying between 28 and 77. I have further determined that a portion of even the higher paraffin series can be tolerated, but that with increasing average molecular weight, the rate of extraction falls off, and the recovered rosin is of lower grade.

My preferred solvent, in part because of availability at a price lower than motor fuel, is a mixture comprising chiefly butane. Fractions from petroleum or natural gas containing large proportions of such a material may today be regarded as a waste product from the operation of casing-head gasoline plants, wherein they are the product of the fractional distillation of the originally "wild" casing-head gasoline. When casing-head gas is scrubbed with oil or otherwise processed for the recovery of condensibles, there is extracted from the gas a portion of the contained propane and butane, which for purposes of transportation and use for blending with heavy naphtha to make a motor fuel is generally "stabilized," by which step is meant the separation of the normally gaseous propane and of substantially all of the butane. From this operation there may be first separated by treatment satisfactory for stabilizing the remainder a mixture of butanes and propane containing also some pentanes, which mixture

without further treatment is satisfactory for use as an extractive solvent; but there is advantage in preparing from the butane-propane-pentane mixture for the present use a preferred material comprising a so-called butane fraction which can be prepared from the butane-propane mixture by fractional distillation, preferably under pressure. For example, a material so prepared of the following composition is entirely suited to the present purposes:

Propane, 9%; butane, 89%; pentanes, 2%.

Weathering: Initial boiling point, 15° F.

Test: Final boiling point, 32° F.; Sp. gravity, 0.573.

The present process thus provides a new solvent for resins, described herein in relation to its use with respect to the extraction of resinous woods, but the utility of this new solvent is wider than this described use and the advantages involved in its use will be apparent to those skilled in the art of extracting sundry materials with hydrocarbon solvents. For example, such a light hydrocarbon solvent can be employed with advantage to the extraction of vegetable oils, such as cocoa butter and corn oil, the degreasing of wool, the cleansing of fabrics, in rubber manufacturing, etc. This invention, in so far as it involves this solvent, is therefore not limited to extraction of any particular material from any specific environment.

So far as I am aware the only use for butane at present is as fuel. Since butane is normally found in gaseous form in gasoline plants, it is usually burned in the distillation plant in gaseous state as a fuel. So far as I am aware I am the first to provide a material containing available liquefied butane or to discover its special utility as a solvent or to observe the specially desirable solvent properties of such materials as applied to the treatment of coniferous woods.

A further object of my invention is to provide a novel process for the continuous extraction of materials in solvents, which comprises continuously extracting said material in an extraction unit, preferably a continuous multiple counter-current (serially operative) extraction unit, continuously separating the solvent and solute from the material, continuously distilling the solvent from the solute, continuously condensing the solvent and returning it to the extraction unit in a closed system, while maintaining a sufficient pressure in the system to keep the solvent liquid in the extraction unit, and preferably in addition, substantially stripping the last traces of the solvent from the solute by flash vaporizing the solute bottoms, condensing the recovered solvent and returning it to the extraction unit. While this feature of my invention may be employed for the extraction of various types of

materials with various solvents, it is peculiarly useful for extracting rosin from coniferous woods. I have found in practice that with a distillation unit alone for distilling the solvent from the solute, it is substantially impossible to remove the last traces of solvent from the rosin and the terpenes without raising the temperature of the distillation tank so high as to disintegrate or discolor the rosin and terpenes. By flash vaporizing the bottoms from the distillation tank into a larger unit under the same heat, it is apparent that the pressure in said larger unit may be lowered sufficiently to permit the last trace of solvent to volatilize therefrom without any rise in temperature and that if desired the temperature in the distillation unit can thus be kept below the discoloring or disintegrating level.

Further objects of my invention are to provide various novel products produced at different stages in my improved process. First, a novel resin-containing extraction product, secondly, a novel resinous product produced when the solvent has been distilled therefrom which may be readily transported if desired in liquid form in tank line or tank car for the further purification treatment; purer initial turpentine and initial pine oil than has been produced hitherto without refining; and lighter grade wood rosins than have heretofore been produced by any process involving the use of a hydrocarbon solvent.

The application of my invention to the extraction of rosin, turpentine and pine oil from such resinous woods as the long-leaf yellow pine will now be described with reference to the accompanying flow chart:

I preferably employ a battery of pressure extraction tanks, 2, 3, 4 and 5, connected together to operate successively and preferably continuously in counter-current fashion on the coniferous wood being treated. Chipped or shredded wood is fed from hopper 1 to the first three of the battery of extractors, 2, 3, 4 and 5, which may be of any desired size or construction. Before introducing the solvent it is desirable to eliminate air from the system, and therefore the air is preferably evacuated. This step also reduces explosion danger to the minimum and avoids the introduction of air into the closed butane system. Valve 2^a in line 6 leading from the butane storage tank 14 is then opened to admit the solvent to the extractor 2. Unless definitely stated that a valve is opened, it is assumed to be closed. The valves 3^c and 4^c leading into the next adjacent tanks are opened, tank 5 being temporarily withdrawn from use for cleaning and refilling purposes. Valves 4^a and 7 in line 8 leading to the butane distillation tank 17 are then opened. The material thus is cir-

culated through line 6 by means of the pump 9 through the valve 2^a into extraction tank 2, out of filling line 3^e through the open valve 3^c into the extraction tank 3, out of filling line 4^e through the valve 4^c to the extraction tank 4, and out of extraction tank 4, through line 8 and through the valves 4^d and 7, to the distillation tank 17. If desired, as is shown, the solvent inlet pipe 6 may be provided with a heat interchanger 10 to preheat the solvent before entering into the extraction tanks. After the solvent has been circulated through the extraction tanks 2, 3 and 4 for a period of time sufficient to thoroughly extract the rosin and terpenes therefrom (in the unit described the time for extraction was four hours) the extraction tank 5 now refilled with chips and exhausted of its contained air is cut into the system by closing valve 2^a and the valve 3^c in the line 3^e. The valve 4^d is also closed. The solvent is now circulated through the line 6 through the valve 3^a to the extraction tank 3, from tank 3 through the filling line 4^e through valve 4^c into the tank 4; from extraction tank 4 through valve 5^c in the line 5^e to the extraction tank 5 and out of tank 5 through the valve 5^d in the line 8 through the valve 7 to the distillation unit 17. While a battery of only four extractors is shown, it is apparent that more may be employed in use if desired.

After the cycle of operations is first started, in order to successively employ the counter-current principle a new tank is cut in at the desired point in the extraction cycle. When any number n of tanks are employed and the extraction period occupies t hours, a new tank may be cut into the system every $\frac{t}{n-1}$ hours. It is obvious, however, that at

the starting point tanks 2 and 3 are subjected to less extraction than they will be subsequently subjected to when the whole system has been operating for t hours or more. It is thus apparent that counter-current extraction methods are employed as fresh solvent is pumped on to the wood which has been previously subjected to solvent more or less saturated with extractive, the freshly charged wood always being first extracted with a solvent more or less saturated with the extractives, and the partially extracted wood being treated with fresh solvent. If desired, 3^e, 4^e, 5^e may as shown be provided with heaters 3^b, 4^b, 5^b, etc., in order to compensate for radiation losses from the extraction tanks and maintain a desired temperature in the several extraction tanks.

Before removing the wood from the respective extraction tanks, caution should be taken to remove all the hydrocarbon by pumping out any remaining solvent, then applying a vacuum to draw any remaining

traces of solvent through the valves 2^b, 3^b, 4^b and 5^b respectively in the lines leading to the return line 11 to the tank 14 through the open valve 11^a therein by means of the pump 11^b in said line 11 followed preferably by a steam distillation under diminished pressure. For example, steam may be let into the respective extraction tanks through any suitable steam connection at 100. The solvent vapor as discharged in this manner can be recovered by compression or condensed at atmospheric pressure by means of an ammonia-cooled condenser 11^c and returned as a liquid to the storage tank 14. Preferably water taken up from the wood, if any, or condensed from the steam distillation, is condensed in the water cooled condenser 101, and separated at 102 from the hydrocarbon solvent whenever necessary.

I also provide a unit suitable for the continuous distillation of the solvent carrying the extractive, which separates the solvent by evaporation or distillation from the extractive, the solvents being distilled, condensed and returned as a liquid to the storage tank 14.

This unit comprises an evaporator and still 17 operated under pressure in a closed pressure circuit and continuously heated by the steam coils 21 and the vapors therefrom passing through the pipe 22 (valve 19 being opened), being condensed in condenser 23 and continuously returned through line 18 to the solvent storage tank 14. The evaporator or still is so designed that as much of the solvent as possible is removed from the extracted materials without a damaging rise of temperature. To maintain the solvent liquid in the still 17 and extraction tanks, I preferably insert the back pressure valve 19 in the exit line 22 forming a part of the closed pressure circuit.

Whereas the distillation of solvent in still 17 is conducted under pressure, it may be found inadvisable to recover all of the solvent at this stage owing to the necessity of either employing too high a temperature in the still 17 or resorting to a prolonged distillation period, either condition being apt to injure the rosin. It is therefore recommended that the distillation of solvent in still 17 be discontinued when the rate of distillation begins to fall off and that the contents of still 17 thereafter be discharged through line 24 to flash still 53 wherein the pressure is dropped, for example, to substantially atmospheric pressure. This latter operation will be found effective to release the remaining traces of solvent in the rosin-turpentine-pine oil mixture. The solvent vapors from still 53 are condensed in 54, 58, which may be ammonia cooled, and the resulting liquid collected in tank 62, from which it may be periodically discharged by

compression pump 66 into the main solvent storage tank 14.

The mixture of rosin, turpentine and pine oil substantially stripped in still 17, and stripped of the last traces of solvent in still 53 is discharged through line 70 into the rosin still 25, wherein the turpentine and pine oil are separated from the rosin by means of distillation into several cuts, preferably turpentine, pine oil and pine oil tails in the tanks 29, 30 and 31, respectively.

A stated, I preferably provide a flash stripping still 53 and condenser unit 54, 58 having means 52, 55, 64, 66 to maintain a circulation therethrough to remove the last traces of the solvent from the extractives from the still 17, and operated under a lower pressure than the primary solvent still, the circulation means being connectable to the primary solvent still 17, and to the receiving tank 14.

When it is desired to remove the extractive through the line 24 to the still 53, the pump 9 will be completely stopped and valve 7 in the line 8 closed. Valve 19 in the line 22 is also closed and the valve 20 in the line 24 is opened. Vent lines 50 and 52 are provided to equalize the pressure between stills 53 and 17 to allow a free flow of the extractive to the stripping still 53, and when the extractive is being withdrawn from still 17 to still 53 valves 51 in said vent line 50 and valve 52^a in the line 52 leading from the line 50 to the still 53 are opened. At all other times these valves are closed. This allows the extractive to run from the still 17 through the valve 20 in the line 24 to the still 53. When sufficient extractive has been drawn to still 53 valve 20 is closed and valves 7 and 19 are opened and then the circulation of solvent is continued as before.

As the heated solute containing a portion of the solvent is drawn down the pipe 24 into the vaporizing still 53 the pump 66 is regulated to maintain a lesser pressure in the stripping still condensing unit than in the distillation still 17. It is apparent that with the drop in pressure all traces of the remaining solvent will be released out of the extractives in the vaporizing still 53, and led through the pipe 55, the valve 56 being opened, into the condenser 54 where they are condensed and pumped by the pump 66 through the line 64 into the receiving tank 14. It is thus apparent that by the introduction of this flash stripping still condensing unit into the closed system that it is possible to strip the last traces of solvent out of the extractives without raising the temperature high enough to degenerate or discolor the terpenes or rosins.

When it is desired to remove the solvent-free extractives through the line 70 to the rosin still 25, the pump 66 is completely stopped, the valve 20 in the line 24 closed,

the valve 56 in the line 55 closed and the valve 72 in the line 70 opened, and the valves 50^a and 52^a in the vent lines 50 and 52 opened, which valves are closed at all other times. This allows the substantially solvent free extractives to run from the vaporizer 53 through the valve 72 in the line 70 to the still 25. When sufficient extractive has been drawn to the still 25 valve 72 is closed.

It is recommended that vacuum be used according to the observed results and the degree of heat of the heating medium for still 25 supplied in heater coil 33 while distilling at least the pine oil fractions, and usually the turpentine fraction, in order to avoid overheating the rosin in still 25. For this purpose I provide a vacuum pump 28 connected to turpentine receiver 29, pine oil receiver 30 and pine oil tails receiver 31. When the last of the pine oil tails has been separated from the rosin, valve 32 may be opened for the discharge of the hot rosin, unless it is to be vacuum distilled, into receiver 38.

Thus in practice I raise the temperature in the rosin still 25 by means such as the hot oil coils 33 until substantially all of the turpentine is distilled therefrom through the open valve 34 in line 35, condensed in condenser 27, and led into the turpentine tank 29, with or without opening valve 29^b to line 44 and vacuum pump 28, if desired with no vacuum up to an end point of 150° C., valve 29^a then being opened the valves 30^a and 31^a being closed. After the turpentine has been taken off into the tank 29, the line 41 leading thereto is closed at valve 29^a, valve 29^b is closed and the valve 30^a in the line 42 leading to the pine oil tank 30 is opened. In order not to affect a decomposition of the pine oil and rosin by raising the temperature of distillation, the vacuum in the pine oil tank 30 may now be increased by operation of the vacuum pump 28 at a higher rate and by opening the valve 30^b in the line 40 leading thereto. When the pine oil has been substantially removed, while still maintaining the vacuum I then open the valve 31^a in the line 43 leading to the pine oil tails receiver 31, close the valve 30^a in line 42 and open the valve 31^b in the line 44 leading thence to the vacuum pump 28, after closing the valve 30^b, and then raise the temperature up to substantially 200° C. to remove the pine oil tails into their tank 31. This substantially strips the rosin in vacuo of all bodies which would tend to cause discoloring on exposure and more effectively removes and cleanly cuts the pine oil tails than has been possible in any method of rosin extraction of which I am aware.

The turpentine and pine oil recovered in the above manner may require a subsequent refining and redistillation to meet market

specifications. Usual operations for this purpose form no part of the present invention. When the process is operated in accordance with the foregoing preferred method of the rosin as delivered without vacuum distillation from still 25 is of marketable grade and of superior quality compared with the rosin heretofore produced by the solvent extraction of resinous woods.

10 Grades above H are readily obtainable, and the product is moreover suited to certain uses, such as the manufacture of soap, high grade varnishes and paper size, for which the present wood rosins are not well suited.

15 Also the rosin may be vacuum distilled in order to produce the highest grades. In case it is desired to subject the rosin remaining in the rosin still 25 to a vacuum distillation, the valve 34 in line 35 leading to condenser 27 is closed, and valve 36 in line 37 leading to pure rosin receiver 38 is opened. Receiver 38 is connected with vacuum pump 28 by means of valve 39 in line 40, which is then opened. The temperature in the oil

20 coil 33 is then raised a sufficient amount over 280° C. to sufficiently distill the rosin residue from still 25 over to the receiver 38, the desired reduction of pressure being maintained therein through the open system by

25 means of the vacuum pump 28.

I have further discovered that the rosin produced by this process can be refined by vacuum distillation to yield the highest grade X.

35 As previously stated, it is possible by means of a solvent containing butane, or its equivalent in use, to secure a very rapid extraction. While extractions can be made at ordinary temperatures, it is advantageous

40 to employ a moderate degree of heat. For this purpose the extraction battery as shown may be equipped with interstage heating units as above mentioned. The recommended temperature range may be between

45 50° and 100° C., but this range may be extended for some purposes, depending upon the conditions of the material operated upon and the qualifications of the solvent in use. Under some conditions it may be desirable

50 to resort to higher temperatures. As a rule, the higher the temperature the more rapid and complete is the extraction. Use of higher temperatures than 100° C. is recommended to be avoided. At 50° C. the working pressure for the butane fraction, which is recommended, is of the order of 60 to 70 pounds; at 75° about 120 pounds. The time required for the extraction depends upon the size of the wood, whether chips or

60 shredded wood, the circulation and the temperature. With good circulation and chips of 1/2" mean size a period of 1 1/2 hours will be substantially effective for each extraction stage, but it will be understood that

65 longer periods of extraction for chips of

larger size may be resorted to without detriment, leaving the wood in good condition for paper manufacture. The time for extraction necessarily varies with the condition of the material to be extracted, but is substantially shorter than usual treatments of which I am aware.

As an example of yields, the following results of practice can be cited:

Yields per ton of stump wood (long-leaf yellow pine)

Rosin-----	410 pounds
Turpentine-----	6.3 gallons
Pine oil-----	3.3 gallons

It is thus apparent that I have provided a novel process particularly adapted to the efficient extraction of resins from woods and producing an extracted chip wholly suitable for use in paper manufacture; various novel intermediate products and wood rosins of high grades suitable for uses not available for wood rosins heretofore produced.

When the process is carried out on moist or damp wood chips, the water substantially remains entrained with and is removed with the extracted wood. From time to time the circulating solvent may be treated to remove water in solution, for example by subjecting the solvent in gaseous or liquid state to a water-freezing temperature and removing the ice formed.

The examples of practice and product hereinabove described are offered by way of illustration and exemplification of the invention and not by way of limitation, and variations of practice and different products are contemplated within the definitions of the appended claims.

I claim:

1. Process for the treatment of coniferous woods to recover therefrom hydrocarbon soluble extractives which comprises the step, subjecting such woods to extraction in a liquid hydrocarbon solvent of low average molecular weight, said solvent having a vapor pressure at 75° C. in excess of 1000 and less than 20,000 mm. of mercury under conditions of time, temperature and pressure suitable for the solution of said extractives, during maintenance of the solvent in liquid phase.

2. Process for the treatment of coniferous woods to recover therefrom hydrocarbon soluble extractives which comprises subjecting chips of such woods to immersion in a liquid hydrocarbon solvent having a molecular weight of less than 78 and more than 28 under conditions of time, temperature and pressure suitable for the solution of said extractives during maintenance of said hydrocarbon solvent in liquid phase.

3. Process for the extraction of coniferous woods to recover therefrom hydrocarbon-soluble extractives which comprises subjecting the wood to the solvent action of a nor-

mally gaseous hydrocarbon solvent chiefly comprising butane and held liquid under pressure in a suitable vessel.

4. A process for the extraction of coniferous woods to recover therefrom hydrocarbon soluble extractives which comprises subjecting such woods while in a moist state to wetting with a normally gaseous hydrocarbon solvent chiefly comprising a mixture of butane and propane held liquid under pressure.

5. Process for the extraction of hydrocarbon soluble extractives comprising subjecting wood containing resinous bodies in a moist state to contact with a normally gaseous hydrocarbon solvent held in liquid phase and effective to dissolve the resinous bodies in the presence of water.

6. Process for the treatment of coniferous woods to recover therefrom rosin, turpentine and pine oil which comprises treating such woods during a sufficient time with a liquid hydrocarbon solvent of low average molecular weight, said solvent having a vapor pressure at 75° C. in excess of 1000 and less than 20,000 mm. of mercury under conditions of temperature and pressure suitable for the effective solution of the contained terpene and resinous contents and removing said extractives, the removal of said extractives ensuing without decomposition and without removal of discoloring impurities from the wood.

7. A process for the treatment of coniferous woods to recover therefrom hydrocarbon soluble extractives which comprises multiple countercurrent extraction in a closed system at temperatures between 50° C. and 100° C. and pressures suitable to maintain said solvent in liquid phase at said temperature said liquid hydrocarbon solvent being low average molecular weight, said solvent having a vapor pressure at 75° C. in excess of 1000 and less than 20,000 mm. of mercury.

8. A process for the treatment of coniferous woods to recover therefrom hydrocarbon soluble extractives which comprises treating such woods for a time of the order of from one to four hours with a hydrocarbon solvent comprising chiefly butane at temperatures between 50° and 100° C. under pressure.

9. A process for the treatment of coniferous woods to recover therefrom rosin, turpentine and pine oils which comprises treating such woods with a hydrocarbon solvent comprising chiefly butane at temperatures between 50° and 100° C. under pressure, separating the solvent and extractives from the woods, recovering the solvent from the extractives for re-use, distilling the residue to remove terpene oils from the rosin, and vacuum distilling the residual rosin.

10. A process for the treatment of coniferous woods to recover therefrom hy-

drocarbon soluble extractives which comprises treating such woods with a liquid hydrocarbon solvent of low average molecular weight, said solvent having a vapor pressure at 75° C. in excess of 1000 and less than 20,000 mm. of mercury under conditions of time, temperature and pressure suitable for the solution of said extractives, separating the solvent and extractives from the woods, recovering the solvent from the extractives for re-use, distilling the residue to remove terpene oils from the rosin, and vacuum distilling the residual rosin.

11. A process for the treatment of coniferous woods to recover therefrom rosin, turpentine and pine oils which comprises treating such woods with a hydrocarbon solvent comprising chiefly butane at temperatures between 50° and 100° C. under pressure, distilling the residue to remove terpene oils from the rosin and vacuum distilling the residual rosin.

12. Process for the extraction of naturally occurring solid inclusions in celulosic materials with normally gaseous hydrocarbon solvents having a vapor pressure at 75° C. in excess of 1000 and less than 20,000 mm. of mercury in a closed system under pressure comprising extracting said materials in an extraction unit, separating the solvent and solute from the materials, distilling a major portion of the solvent from the solute under pressure and condensing the solvent and returning it to the extraction unit under pressure, vaporizing the remaining solvent from the solute by reducing the pressure to strip the last traces of solvent from the solute, and condensing the recovered solvent and returning it to the extraction unit.

13. Process for the extraction of rosin from coniferous woods with a normally gaseous hydrocarbon solvent having a vapor pressure at 75° C. in excess of 1000 and less than 20,000 mm. of mercury, comprising extracting said materials in an extraction unit, separating the solvent and solute from the materials, distilling a major portion of the solvent from the solute under pressure and condensing the solvent and returning it to the extraction unit in a closed system under pressure vaporizing the remaining solvent from the solute by reducing the pressure to strip the last traces of solvent from the solute and condensing the stripped solvent under pressure sufficient to maintain the solvent in liquid phase during extraction of the material.

14. A process for the extraction of terpenes and rosins from coniferous woods with a hydrocarbon solvent, normally gaseous at extracting temperature, comprising extracting said terpenes and rosins in an extraction unit with a hydrocarbon solvent removing the solvent and extractives from the wood, distilling the solvent from the ter-

penes and rosins at a temperature below 100° C., condensing the solvent and returning it to the extraction unit in a closed system while maintaining a sufficient pressure in the system to keep the solvent liquid in the extraction unit, and flash vaporizing the solute terpene and rosin bottoms to strip the last traces of solvent therefrom by the retained heat of the solvent and solute liquid, condensing the recovered solvent and returning it to the extraction unit.

Signed by me at Cambridge, Massachusetts, this fourth day of October, 1927.

ARTHUR D. LITTLE.