UNITED STATES PATENT OFFICE.

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PRESERVED WOOD AND PROCESS OF MAKING SAME.

1,045,110. Specification of Letters Patent. Patented Nov. 19, 1912.

No Drawing. Application filed July 16, 1912. Serial No. 709,749.

To all whom it may concern:

Be it known that I, CARLETON ELLIS, a citizen of the United States, and a resident of Montclair, in the county of Essex and State of New Jersey, have invented certain new and useful Improvements in Preserved Wood and Processes of Making Same, of which the following is a specification.

This invention relates to a process of treating wood with preservatives and relates in particular to the impregnation of wood with a mixture of creosote and a pore-plugging body such as asphalt oil and to the product of said process.

It has been the custom heretofore to treat wood with creosote by what is known as the empty cell process which merely wets the fibers of the wood without introducing a saturating amount of the creosote oil. This reduces the cost of treatment without greatly reducing the preservative action.

Petroleum oils, and more particularly asphalt oils have been tried to some extent as wood preservatives. Among these are the so-called "timber asphalt," Bakersfield asphalt and Mexican Ebano oil. Oils of this character are used in a saturating amount for preserving wood, as for example railroad ties. The saturation of the tie calls for a large amount of oil and although the oil may be obtained near its source at a low cost per gallon in comparison to creosote yet the cost of saturating or full cell treatment of timber approximates that of creosote as applied in the empty cell process.

In the present invention oils of the creosote type may be used or mixtures of creosote oil and petroleum and asphalt oils, but the operation of the present process is more particularly intended for the treatment of wood with asphalt oils of rather heavy consistency preferably containing sulfur and given an impregnating consistency by reduction by creosote or Blaugas spent oil.

As I have set forth in U. S. Patents Nos. 871,392, 991,434, 1,017,636 and 1,028,201 and in my copending applications Serials Nos. 396,104 and 474,565 an oil-soluble compound of arsenic or copper such as copper oleate, resinate and the like, may be introduced into petroleum oils to furnish a high-powered fungicide and bactericide, so that the oil may be used advantageously for wood preservation. Copper compounds of this character are useful for preserving certain classes of woods while other oil-soluble compounds such as those of arsenic, lead, mercury, zinc and the like are useful on other types of wood. The asphalt oils are very effective water-proofing materials and in this respect at least are superior to the creosote. As a rule they have a greater consistency than the creosote oils and hence are somewhat more difficult to introduce into the wood. Conversely it is also somewhat difficult to remove from the wood any excess of the oil which may have been injected. These petroleum oils or residues have no pronounced antiseptic action and hence are not highly efficient preservatives. For example, they usually are not able to cope with *Merulius lacrymans* or dryrot, the mycelium of which secrete a considerable amount of a liquid substance, acting as a ferment and dissolving the fiber walls of some of the weaker cellulose structures and swelling and greatly weakening the harder varieties of cellulose tissues.

In addition to the high-powered preservative agents mentioned, certain other compounds of an organic character particularly the nitro compounds of the aromatic series may be used. Among these are dinitrobenzol, dinitrochlorbenzol, trinitrochlorbenzol, dinitrophenol, dinitro ortho cresol and their homologues. Of these dinitrophenol is especially effective. Four (4) ounces of nitro compound to a gallon of asphalt oil affords a very good preservative. One (1) ounce of dinitrophenol and 1¼ ounces of copper oleate to a gallon of petroleum oil affords an excellent tie preservative. In the case of preservatives to be used for treating piling to prevent the attack of teredo and limnoria special pains must be taken to have the oil properly proportioned as regards the character and amount of the high-powered preservative. Dinitro ortho cresol in combination with oil-soluble arsenic compounds and copper oleate forms a useful basis for the treatment of piling. For wood which is not to be exposed to extreme service conditions and especially for railroad ties which are to be treated in such a manner that their preservative life substantially coincides with their mechanical life sulfur compounds are useful. It has been proposed heretofore to make use of polysulfid of calcium for treating wood. The polysulfid is partially converted into

carbonate of lime and partly into thiosulfate and other oxysalts on exposure to air. Some of these compounds have an alkaline reaction and with the oxygen of the air convert cellulose into the friable oxycellulose. This causes tendering of the wood and loss of spike holding power.

Sulfur forms a very good antiseptic material under some circumstances. The proposal made hitherto to impregnate wood with sulfur alone, in a molten state, has certain disadvantages, one of which is the high temperature required to put the sulfur into a condition so fluid that it will penetrate readily. Another objection is the rather brittle condition of the wood after the sulfur has solidified within its interstices. If however sulfur is dissolved by heating in an oil such as petroleum in which it is not very soluble at ordinary temperatures and the hot saturated solution introduced into wood, a portion of the sulfur will separate on cooling, forming a fine precipitate in and around the fibers of the wood. In this state the sulfur is a good fungicide and greatly retards the development of wet and dry rot.

To illustrate, a petroleum oil of about 32 degrees gravity will dissolve at 100 degrees C. some 10% or so of sulfur. On cooling a 10% solution to about 60 degrees C. the sulfur separates to a very considerable extent forming a finely divided precipitate. If therefore wood, previously heated to a temperature of about 100 degrees is immersed in an oil bath containing about 10% of dissolved sulfur, pressure applied and the wood finally cooled a product is obtained carrying the fungotoxic sulfur quite uniformly distributed throughout the interior of the wood.

At 120 degrees, the melting point of sulfur, ordinary petroleum oil takes up considerably more than 10% of sulfur. With asphalt oils and other unsaturated oils, union of sulfur and oil takes place, more or less at 120 degrees C. and the oil becomes vulcanized, usually accompanied by thickening. A vulcanized asphalt oil, containing uncombined sulfur, may readily be thinned with creosote; twenty five or thirty per cent. of the latter sometimes being required. When using the volatile fractions between 210 deg. to 235 deg. only 15 or 18% is required. The fraction 210 deg. to 270 deg. should preferably not be used in excess of 25%. Preferably I vulcanize or heat a mixture of petroleum oil and creosote or Blaugas spent oil to form a sulfureted composite.

When creosote and petroleum oil are mixed it has been supposed that the bactericidal qualities of the creosote were greatly diminished or entirely suppressed by the palliative effect of the petroleum oil. This is not however strictly true. Petroleum has relatively slight antiseptic action and dilution of the creosote by it perhaps reduces the preservative action to an extent slightly greater than the degree of dilution would warrant. On the other hand creosote as compared to some of the petroleum oils and particularly the partially vulcanized asphaltic oils, is a poor waterproofing agent. An oil which thoroughly waterproofs is a great desideratum in wood preservation, hence the combination of creosote and partially vulcanized asphaltic oil fortified with an excess of uncombined sulfur offers a preservative having a number of valuable qualities. By adjusting the ratio of creosote and asphalt oil for each particular wood the requisite penetration and waterproofing qualities are secured. The antiseptic features of creosote are supplemented, when sulfur is used, by the fungo-toxic action of any precipitated interstitial sulfur, the amount of which is under regulable control, and the precipitation of sulfur in the pores of the wood tends to augment the resistance of the wood to the penetration of moisture. The asphalt oil obtained from the Bakersfield region is remarkably effective as a waterproofing agent but the supply of this useful oil is limited. The vulcanization of ordinary petroleum residues and semi-asphaltic oils affords a substitute for the Bakersfield oil at a very moderate cost.

Such a vulcanized oil can be properly fortified with a high-powered antiseptic to form a satisfactory preservative. By using an excess of sulfur over that required for vulcanization at any specific temperature the excess of the sulfur serves as an antiseptic and affords an oil which is very serviceable in many localities. Creosote may be used in the form of a miscible oil. If rosin is saponified with potash and introduced into creosote the mixture may be diluted with water to a very considerable degree and still persist as a clear homogeneous solution. On the further addition of water however the creosote is precipitated and forms a milky emulsion. Such mixtures as these may carry petroleum or asphalt oils and may be introduced into wood at such a dilution that the further addition of water causes precipitation of the creosote.

A copperized miscible oil may be made in accordance with Letters Patent on miscible oil, No. 993,827. Thus when the tie or other cellulose structure treated in this way is exposed to rain or earth moisture the creosote or other oily body precipitates and deposits on the wood fiber. Care should be taken in the case of green or unseasoned wood, as a moisture sensitive solution of this character would cause precipitation of the creosote or other oil, during the impregnating process. Seasoned wood is far more adaptable to this treatment than green

moisture containing wood. Of course it is not desirable to have a strongly alkaline soap present in large amount, because of liability of oxidation of the cellulose to oxycellulose. Rosin soap is somewhat inclined to alkalinity because of hydrolysis and is best used in conjunction with a small proportion of oleic acid, using a slight excess of the resinous acids and oleic acid so that the potash is well neutralized.

The impregnation of wood with emulsions is generally speaking difficult and unsatisfactory. Emulsions of zinc chlorid and creosote or petroleum oil for example, do not enter the wood very easily and one component is apt to penetrate more easily than the other. Damp wood will absorb the zinc chlorid solution from an emulsion leaving the particles of oil of the emulsion on the surface of the timber. Anhydrous zinc chlorid or zinc fluorid may be dissolved under certain conditions in asphalt oils to some extent to secure a moderately good antiseptic material. Timber treated with miscible oil containing water-soluble soap may be immersed in a solution of calcium chlorid, magnesium sulfate, barium chlorid, copper sulfate and the like so as to form a metallic water-insoluble soap in the superficial pores of the timber, thereby improving its resistance to the entry of moisture. The precipitation of the soap renders the oil vehicle of the miscible oil no longer soluble in water thus causing said oil vehicle to become fixed. Creosote solutions which are soluble in water may also be made by use of sulfonated oils. The manner in which compositions of this sort may be prepared has been set forth in Patent 879,375. Simply mixing a slightly alkaline concentrated sulfonated oil with creosote yields a useful product.

The copper and other compounds of naphthenic acids are useful with a certain limited number of oils for treatment of wood. Copper naphthenate is a very effective preservative. If present to the extent of 1% it prevents the development of the lower organisms. 1% or 2% of copper naphthenate in solution in gasolene is absorbed by dry wood readily, although so low a proportion of non-volatile material does not waterproof the wood. If however copper naphthenate is dissolved in fairly heavy Texas or Oklahoma asphalt oil a waterproofing and preservative composition is secured.

In carrying out the process of the present invention the compositions described in the foregoing may be used. In certain modifications of the process involving low impregnating temperatures, the sulfur and oil solution mentioned above is not as readily used.

For impregnation, I preferably employ wood which has been air or kiln dried. The treatment of green wood to remove the moisture by means of hot creosote oil for example, is undesirable because of the tendency to thereby weaken the fiber. Creosote combines to a certain extent with wood fiber, especially if heated to a high temperature. Its action is probably partly that of condensation with some of the aldehydic bodies present in the wood tissue and partly dissolution of lingin. Petroleum oils may be used at high temperatures without this same disadvantage but low temperatures, say 130 to 150 deg. F. are to be preferred to 212 deg. F. The present process embraces the specific procedure of treatment of wood with a preservative oil to cause partial impregnation, the wood used for these purposes being preferably previously dried so that moisture is not expelled to the detriment of the operation and in subjecting the partially impregnated wood to a very high gaseous pressure to properly distribute the oil. For this purpose I prefer a gas substantially free from or of reduced oxygen content to be used. The subjection of heated wood whose surfaces are coated with oil to ordinary air under high pressure carries with it the tendency to spontaneous ignition, which is avoided by the preferred procedure herein set forth.

In carrying out the specific procedure above mentioned I preferably use two impregnating cylinders and pass the gas from the one cylinder to the other, to and fro, alternating the operations so the gas may be used over and over again and in such a manner that it does not have to be compressed from atmospheric pressure up to the maximum pressure required each time a charge is applied, in accordance with the process of U. S. Letters Patent No. 1,028,201.

In the present invention the treatment of wood which is to be subjected to great mechanical stress such as paving blocks, railroad ties and the like, it is especially an objective to apply a preservative whose specific perservative action is carefully regulated to endure for a period substantially that of the mechanical life of the fibrous structure. Creosote may be and is used in such proportion that railroad ties, for example, show no signs of decay even after their mechanical effectiveness is lost. Ordinary petroleum oils, although having a waterproofing action, have not sufficient fungous resisting properties to preserve railroad ties under a moderately severe service condition up to the extent of their mechanical life. By the treatment of low grade petroleum residues including oils of the Pennsylvania type, as well as the asphaltic oils of Texas, Oklahoma, California and the like with sulfur or sulfurizing materials, especially in conjunction with creosote free from the higher boiling fractions (above 240 deg. C.) of Blaugas or Pintsch gas spent oils and tars, a sulfureted

oil is produced, which possesses two important features, namely, fluidity at high temperatures with consequent ease of impregnation, and a desirable degree of viscosity at low temperatures, which secures waterproof or water resistant qualities in a high degree. There is the further advantage of treatment with these sulfurized oils, that they may be caused to oxidize and dry in the superficial layers of the fibrous structure, so that the oil in the interior of the structure is fairly sealed within the wood. This is important, especially in making paving blocks which may be charged with oil in such a manner that the heat of the sun does not cause the liquid to exude from the interior of the block, a defect which has heretofore been observed in many of the compositions of the creosote and resin type.

The present invention contemplates also the fiber coating of railroad ties, paving blocks and the like, adjusting the amount of the oil to this end and proportioning the amount of high powered antiseptic material with respect to the mechanical life of the railroad tie or other fibrous structure whereby the preservative life or action and mechanical life substantially coincide.

The treatment of petroleum oils and creosote with sulfur, with or without the introduction of oil soluble copper or arsenic salts or other high powered preservative, makes possible the manufacture from low grade petroleum oils, and oil which has the properties, to a very large extent, of the Bakersfield oil. As stated the supply of the latter is not very great, but it is in considerable demand, in connection with the preservation of wood largely because of its good waterproofing qualities, and the present invention in part is concerned with the conversion of low grade petroleum oils by sulfur treatment and the like, thereby producing an oil which has an even better waterproofing character than Bakersfield asphaltic oil.

This application is in part a continuation of Serial No. 474,565 as regards the use of creosote admixed with asphaltic or other suitable pore-plugging oil.

What I claim is:

1. The herein described process of preserving railroad ties, paving blocks and other fibrous material consisting in injecting thereinto at least a fiber coating amount of asphalt oil carrying creosote material; the said creosote material being present in predetermined amount whereby the preservative action substantially coincides with the life of the tie and the like, and in causing at least a major portion of the interior fibers of said tie or other fibrous material to be coated with said oil.

2. The herein described process of preserving railroad ties, paving blocks and other fibrous material consisting in injecting thereinto at least a fiber coating amount of a mineral oil carrying creosote material: the said creosote material being present in predetermined amount whereby the preservative action substantially coincides with the mechanical life of the fibrous material and in causing at least a major portion of the interior fibers of said tie or other fibrous material to be coated with said oil.

3. The herein described process of preserving railroad ties, paving blocks and other fibrous material consisting of injecting thereinto at least a fiber coating amount of oily material comprising low-boiling creosote and a waterproofing agent, the proportion of the creosote being adjusted with reference to the mechanical life of the wood structure and the proportion of waterproofing agent being adjusted with reference to the porosity of the wood.

4. The process of treating wood comprising subjecting same to a sulfureted composite of creosote and asphalt oil under pressure.

5. The process of treating fibrous material which comprises impregnating wood with oils containing a thin-bodied antiseptic oil and a heavy-bodied mineral oil of a waterproofing character, the proportion of the creosote antiseptic being adjusted with reference to the mechanical life of the fibrous material and the proportion of waterproofing agent being adjusted with reference to the porosity of the wood.

6. As a new article of manufacture wood impregnated with oils comprising thin creosote oil and a heavy-bodied asphalt oil of a waterproofing character; the proportion of the creosote antiseptic being adjusted to the mechanical life of the wood structure and the proportion of waterproofing agent being adjusted with reference to the porosity of the wood.

7. As a new article of manufacture, wood impregnated with a mixture of thin creosote and asphaltic oil, proportioned with respect to the mechanical life of the wood structure.

8. As a new article of manufacture preserved wood impregnated with a mixture of creosote, Blaugas spent oil and an asphalt oil.

9. As a new article of manufacture preserved wood impregnated with a mixture of creosote, Blaugas spent oil and asphaltic oil carrying sulfur bodies in solution therein.

10. As a new article of manufacture wood impregnated with sulfureted asphalt oil and sulfureted creosote oil.

11. As a new article of manufacture wood containing very volatile creosote or carbolic bodies sealed in with asphaltic oil.

12. As a new article of manufacture wood containing creosote bodies sealed in with asphaltic oil.

13. As a new article of manufacture wood containing creosote bodies and a quantity of an asphaltic pore-plugging compound proportioned with respect to the porosity of the wood.

14. As a new article of manufacture wood containing creosote bodies and a pore-plugging asphaltic oil.

Signed at Montclair in the county of Essex and State of New Jersey this 19th day of June A. D. 1912.

CARLETON ELLIS.

Witnesses:
BIRDELLA M. ELLIS,
ANITA B. FERRIS.