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FUNGICIDAL OILS

Edward F. English and Alexis Voorhies, Jr., Baton Rouge, La., assignors to Standard Oil Development Company, a corporation of Delaware

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This invention relates to fungicidal oils suitable for impregnating wood and methods of preparing the same from petroleum oils.

According to this invention highly toxic fungicidal oils are prepared from mineral oils. These fungicidal oils are preferably produced by the destructive hydrogenation of mineral oils, the mineral oil being either a straight run or cracked oil or an oil made by selective extraction of a straight run or cracked oil. The oils from which these fungicidal oils are derived may be of a boiling range including that of gasoline and extending up to 700° F. or somewhat higher. In addition to destructive hydrogenation, other methods of producing these fungicidal oils are high temperature cracking of liquid or gaseous hydrocarbons or mixtures thereof, or selective extraction of suitable base stocks. Fungicidal oils so produced are found to contain a substantial amount of aromatic, naphthenic and unsaturated hydrocarbons.

In the preferred destructive hydrogenation process these distillate oils as such or fractions separated by the use of selective solvents, are passed in vapor phase with the hydrogen over suitable catalysts at a pressure in excess of 20 atmospheres and preferably at a pressure of 100 to 200 atmospheres or higher and at a temperature above about 900° F. and preferably within the range of about 930°—1050° F. with a suitable partial pressure of hydrogen and time of contact to secure destructive hydrogenation without the formation of appreciable amounts of polymerized or coky material.

The hydrogen recycled with the oil is preferably within the range of 1,000–10,000 cubic feet per barrel of feed oil and the hydrogen consumed is preferably within the range of 500–1500 cubic feet per barrel of feed oil, the amount generally depending upon the gravity and boiling range of the charging stock.

A greater proportion of hydrogen may be used with suitable variation in feed rate, temperature and pressure as is known in the art. The feed rate depends upon the reaction temperature and other operating conditions, such as the partial pressure of hydrogen, and may be suitably about 1.5 to 4 volumes of oil per volume of catalyst filled reaction space per hour. The catalysts preferably comprise the oxides or sulfides of the metals of the VI group of elements with suitable promoters of the alkaline earth and earth oxides. Such catalysts are insensitive to sulfur poisoning and are suitably classified as sulf-active.

The product of such vapor phase destructive

hydrogenation of petroleum distillates or hydroforming process is called a "hydroformed oil" for the purpose of this invention and the claims.

This hydroformed oil is fractionated and the fraction having a low aniline point such as 20° F. to -80° F. and a gravity of about 8 to 20° A.P.I. has been found most suitable as a fungicidal oil. Extractives obtained by extracting suitable base stocks with selective solvents and having similar aniline points are also suitable for use as fungicidal oils. Highly cracked oils from suitable base stocks having similar aniline points are also suitable for use as fungicidal oils. Aniline points lower than the freezing point of aniline are determined by mixing the low aniline point oil under test with an oil of known and relatively high aniline point and calculating or determining by graphical extrapolation the unknown low aniline point from that of the mixture.

These fungicidal oils were found to be more toxic in concentrations between 0.01 and 0.02% when compared with the toxicity of coal tar creosote tested by the same method usually about 0.05% of coal tar creosote is required to produce a similar toxic effect. These fungicidal oils were therefore found to be more toxic than coal tar creosote by this method of test. The toxicity tests on the wood preservatives were made in nutrient agar medium with the standard fungus "fomes annosus". Of the fungicidal oil used in the above case, nearly 90% distills between 392° and 518° F. When all the oil is distilled up to 639° F. there is still a small residue but there are no strong indications of decomposition. The oil is completely sulfonated by sulfuric acid of the strength usually recommended for this test on creosote, that is, it shows no evidence of containing any large amounts of paraffin hydrocarbons.

This fungicidal oil may be further treated to increase its efficiency, i. e. by the addition of small amounts of phenols, cresols, etc. which assists in fixing such oils in the wood and increases their effective life as preservatives. Alternately small amounts of caustic alkali solution emulsified in the above oils would serve the same purpose. This is due to the action of the phenolic compounds on the cellulose of the woody ligno-cellulose. Caustic alkalies may also serve the same purpose by a slight attack of the lignin in ligno-cellulose, this attack being insufficient to weaken the wood, though phenolic compounds are preferred for this purpose. These fungicidal oils may be further treated to increase the fungicidal

efficiency of the higher boiling fractions by addition of substances such as alpha-naphthol.

- These fungicidal oils may be further treated and part of the hydrocarbons converted into phenolic bodies by any of the well known methods such as fusion of the sulfonates with caustic potash or by the diazo reaction, and the resulting phenolic compounds may be isolated in a partially purified form and mixed with a residual highly cracked hydrogenated or unhydrogenated cycle stock to give a mixture that closely resembles coal tar creosote. Petroleum products or other products of a pitchy nature or merely of a high boiling range may also be added to the mixture in order to obtain a resultant mixture which is better retained in the impregnated wood, and resembling coal tar creosote in respect to the residue above 671° F., which varies between 5 and 50% of coal tar creosote.
- This fungicidal oil may be used for preserving wood or similar porous material by the methods ordinarily used for wood treating. Wood may be impregnated preferably with application of pressure of about 25 to 100 pounds per square inch and at a temperature of about 160° to 200° F. with the fungicidal oil or a mixture of the fungicidal oil and the phenolic or pitchy products as shown above.
- In impregnating wood with the above wood preserving oils 10 to 16 pounds per cubic foot for the full cell process and 6 to 10 pounds per cubic foot for the empty cell are found preferable though less weights even as low as 2 pounds or as high as 30 pounds of oils per cubic foot of the wood, may be used. These oils are also suitable for use in treating wood in combination with zinc chloride or other wood preservatives either before or after the wood is impregnated with the zinc chloride, etc.
- In impregnating cross-ties it is preferred that the penetration should be a minimum of $\frac{1}{4}$ inch and an average of about $\frac{1}{2}$ inch. To obtain good penetration it is preferred that "incising" be practiced on the cross-ties with parallel rows of longitudinal gouges, approximately $\frac{3}{4}$ inch

deep. The distance between rows is approximately $\frac{1}{4}$ inch and the holes are staggered. This practice makes available end penetration throughout the tie.

This fungicidal oil is especially useful in controlling termites either by killing the termites in wood already infested or avoiding the infection.

The foregoing description is merely illustrative and various changes and alternative arrangements may be made within the scope of the appended claims in which it is our intention to claim all inherent novelty in the invention as broadly as the prior art permits.

We claim:

1. A fungicide comprising a hydrogenated petroleum oil composed substantially of aromatic, naphthenic, and unsaturated hydrocarbons and having an aniline point of about 20° to -80° F. and a gravity of 8° to 20° A. P. I.
2. A fungicide comprising a liquid product having a gravity of 8° to 20° A. P. I. and an aniline point of 20° to -80° F. obtained by destructively hydrogenating a petroleum oil composed substantially of aromatic and unsaturated hydrocarbons in the vapor phase at a pressure in excess of 20 atmospheres and at a temperature of above about 900° F.
3. A fungicide comprising a liquid product having a gravity of 8° to 20° A. P. I. and an aniline point of 20° to -80° F. and nearly 90% volatile between 392° and 518° F. obtained by destructively hydrogenating the petroleum oil composed substantially of aromatic and unsaturated hydrocarbons in the vapor phase at a pressure in excess of 20 atmospheres and at a temperature of above about 900° F.
4. A fungicide comprising a hydrogenated petroleum oil composed substantially of aromatic, naphthenic and unsaturated hydrocarbons and having an aniline point of about 20° to -80° F., a gravity of 8° to 20° A. P. I. and nearly 90% volatile between 392° and 518° F.

EDWARD F. ENGLISH.
ALEXIS VOORHIES, JR.