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USEFUL PRODUCTS AND PROCESS OF PRODUCING THEM

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The instant invention relates to the production of toxic oils employable as fungicides, insecticides, and for any other service to which toxic oils may be put.

More especially the instant invention relates to the production of toxic oils from mixtures of petroleum fractions characterized by ring structure content. Among such starting materials may be mentioned mixtures of petroleum fractions characterized by ring structure content recovered from petroleum fractions by well known extraction methods including extractive distillation and azeotropic distillation. Also may be mentioned mixtures of petroleum fractions characterized by ring structure content as flowing from thermal and/or catalytic treatment of certain petroleum fractions which includes petroleum fractions having ring structures induced in the course of thermal and/or catalytic treatment, as for example having ring structures induced in the course of one or more thermal and/or catalytic treatments of unusual length, as for example, for periods of from 1-10 hours or more.

An object of the instant invention is the production of toxic oils from the aforementioned petroleum fractions or others whereby to provide oils of the preservative type, as for example preservative wood impregnants conforming to specifications extant or acceptable to the trade consuming such oil materials.

Another object of the instant invention is the provision of preservative wood impregnants having boiling ranges and residues in accordance with published specifications and/or in accordance with consumer preference.

Another object of the instant invention is the reforming, modifying, converting and/or transforming of the mixtures of hydrocarbons whereby to induce toxicity.

Still another object of the instant invention is the induction of usable toxicity in the presence of a gas or gaseous mixtures.

Another object of the instant invention is the unveiling of latent toxicity in mixtures of petroleum fractions having inherent but inhibited toxicity.

Yet another object of the instant invention is the provision in the overall beneficiated material of that percentage of newly induced fractions boiling below 210° C. which is conducive to the induction of toxicity in other fractions of the material under treatment.

Another object of the instant invention is a coordination of process variables which will provide in various fractional parts of the beneficiated material cyclic structures with specific gravities falling within the limits hereinafter stated.

Another object of the instant invention is the induction of toxicity in the presence of catalytic

materials adapted to favorably influence said toxicity induction.

In the past wood preservative oils of the high temperature coal tar derived type have been employed in quantities greatly exceeding the total of all other wood preservative oils. From the standpoint of availability of said coal tar as the parent product of wood preservative oils, it is annually produced in this country under normal conditions to the extent of five hundred million to six hundred million gallons. This quantity of coal tar is capable of yielding an amount of highly effective wood preservative oil which would make this country self-sufficient in its wood preservative requirements. However, due to the fact that when a wood preservative distillate (creosote) is recovered from coal tar there remains in the still a residue (pitch) which, at best, is a low priced product and which, at worst, is a seriously distress product to the end that at times it is placed in inventory rather than sold, this country cannot economically produce its creosote needs. The current method of processing coal tar leaves much to be desired. The net result of this situation obtaining is that the coal tar distiller usually confines himself to that distillation recovery of creosote which would correspond to the attending amount of pitch that he can market at a profit. Accordingly, over a period of years several hundred million gallons of creosote oil have been imported into this country. That such a situation should obtain is apparently a paradox in that we annually produce a quantity of high temperature coal tar which if processed to yield creosote would make us self sufficient in that requirement. A survey of this paradox is fully outlined in an address given by no less an authority than S. P. Miller, technical director, The Barrett Company, 40 Rector Street, New York city, before the Franklin Institute, Philadelphia, Pennsylvania, in December 1932. The economics of coal tar have not materially changed since that date.

In view of the apparent inability of the coal tar industry to provide national needs of wood preservative oils, a strong incentive is given to groups processing other types of oil to invade the lucrative wood preservative market. At the present time many types of aromatic oils are produced by the petroleum industry, and the high boiling oils of aromatic content produced by this industry have for several years been tested for their wood preservative efficiency.

By the term "petroleum aromatic" as used herein and in the appended claims is meant to include mixtures of petroleum fractions characterized by cyclic content and include specifically various forms and types of naphthenes found in various mixtures of petroleum fractions,

as for example monocyclic and polycyclic naphthenes.

The so-called petroleum aromatics which includes the monocyclic and polycyclic naphthenes and unsaturated hydrocarbon fractions have in the past been produced in very large quantities. However, very little work has been done on these materials. Such a fact is borne out on page 667, "Reactions of pure hydrocarbons," Gustav Egloff, Reinhold Publishing Corporation, 330 West 42nd Street, New York city, which states:

"Despite the fact that naphthenes or cycloparaffines are available in enormous quantities, as shown by an estimate of 100,000,000 barrels present in the 1,498,000,000 barrels of crude oil which was the world's production in 1934, comparatively little work of a pyrolytic nature has been performed on individual naphthene hydrocarbons or the cycloolefins."

Several oils of cyclic content produced by the petroleum industry have been inspected for their toxicity to wood destroying fungi, among which may be mentioned a high boiling oil of cyclic content produced (1940) at the Wood River Refinery of the Shell Oil Company and which has the following inspection:

Gravity	10.8
Flash, P. M. C. C.	°F 295
Flash, C. O. C.	°F 290
Fixed carbon	per cent 4.9
Pour point	°F -10
B. S. & W.	per cent by volume 0.1
S. U. vis. @ 100° F	151
S. U. vis. @ 210° F	41
S. F. vis. @ 77° F	34.5
Carbon residue	6.8
Per cent aromatics and unsaturates	82.4
Sol. in CS ₂	99.8
Loss 50 grams, 5 hours, @ 325° F	8.9
Residue of 100 pene	per cent 37.5
A. S. T. M. distillation:	
I. B. P.	°F 518
10% rec. @ °F	565
20% rec. @ °F	589
30% rec. @ °F	614
40% rec. @ °F	637
50% rec. @ °F	660
60% rec. @ °F	1 675

¹ Maximum.

In the foregoing tabular data P. M. C. C. means Pensky-Martin Closed Cup; C. O. C. means Cleveland Open Cup.

Upon evaluating the foregoing oil for its toxicity to wood destroying fungi (Madison 517), it was found that this oil did not inhibit the growth of the fungi named at a concentration of up to and including 10%.

It is now discovered that the oil above named or other oils of cyclic content produced by the petroleum industry can be increased in toxicity in accordance with the process of the instant invention.

According to the instant invention oils of cyclic content produced by the petroleum industry are reformed, transformed, modified and/or converted to oils of a more toxic nature having characteristics acceptable to consumers of wood preservative impregnant and/or conforming to wood preservative specifications extant.

It is a specific object of the instant invention to reform, transform, modify and/or convert mixtures of petroleum fractions characterized by cyclic structures having inherent but inhibited toxic properties in the vapor phase in the pres-

ence of an added protective gas or gases, to materials exhibiting a more pronounced toxicity than the parent feed stock.

In former attempts to provide a wood preservative oil of petroleum origin by processes analogous to that of the present invention, the feed stock utilized as starting material or the process adopted, or both, were such as to provide an oil boiling 90% at 270° C. or in another instance with only 0.6% residual matter at 315° C. These products have not been found acceptable in the art.

One of the petroleum oils hydroformed in vapor phase above noted had the following distillation range:

Distillation	Oil, per cent
Below 210° C.	0.0
210-235° C.	12.0
235-270° C.	68.0
270-315° C.	19.4
Residue	0.6

The oil above named after its impregnation into cellulosic materials to be preserved is entirely too volatile to provide an acceptable preservative impregnant.

It is, therefore, an object of the instant invention to provide a vapor phase process carried on in the presence of added gas or gases, which yields a reformed petroleum oil characterized by induced toxic properties having at least about 10-20% residual matter above 315° C.

By the expression "a reformed petroleum oil" as used herein and in the annexed claims is meant a beneficiated petroleum oil having induced toxicity as stemming from, among other things, a change in molecular structure which occurs during the practice of the present process. Thus, "a reformed petroleum oil" is a reformed, converted, transformed and/or modified oil, and includes an oil reformed by substitution and/or addition to the molecular structure, and/or subtraction from the molecular structure of the feed stock.

We have discovered that some of the mixtures of petroleum fractions have very substantial residual matter above 355° C. and inherent toxic properties inhibited by the complexity of the structure which structure is inherently unstable. Taking advantage of the lack of stability of the complex structure of these relatively high boiling oils that have substantial residual matters above 315° C. or 355° C., we are able by subjecting them to vapor phase reforming conditions in the presence of added gas or gases to simplify and stabilize the structure whilst providing in the finally beneficiated oil substantial residual materials above 315° C. or 355° C., at the same time unveiling the toxic qualities, and if the process is carried to an extent to provide specific gravities of materials of cyclic structure content in fractional parts of the beneficiated material falling between the limits noted in the following tabular data:

Fractions	Low limit	High limit
210-235° C.	0.913	1.0580
235-270° C.	0.935	1.0756
270-315° C.	0.973	1.0933
315-355° C.	1.027	1.1285

and preferably carried to the extent to provide specific gravities of materials of cyclic structure content in the fractional parts of the beneficiated material as noted in the following tabular data:

Fractions	Low limit	High limit
210-235° C.	0.941	1.0430
235-270° C.	0.963	1.0608
270-315° C.	1.001	1.0783
315-355° C.	1.055	1.1135

commercial toxicity is secured. By stripping from the beneficiated material the excess of fractions boiling below 210° C. as required by commercial specifications, (or specifically, whatever other low boiling temperature is specified) we are able to use the residue as a commercial wood preservative impregnant with acceptable toxic properties. In the event this material has too high a residue at 355° C. or has too high a coke residue for any particular service the desired preservative oil may be secured as an extract or distillate having no excess of the desired materials at 355° C. or an excess of coke residue.

The following examples will illustrate several modes of practicing the process of the instant invention.

Example 1.—A so-called petroleum aromatic oil, as for example a furfural or liquid sulfur dioxide extract, relatively non-toxic, having substantially no ends boiling below 270° C., materials boiling at about 355° C., and specific gravities of materials of cyclic structure content of 1.0166 and 1.0256 in the fractions 270-315° C. and 315-355° C., respectively, and about 50% residue above 355° C., is subjected in the vapor phase in the presence of hydrogen at a temperature of 510° C. whilst under a pressure of 1,000 pounds for such a length of time as to provide newly formed materials boiling below 210° C. and in fractional parts of the beneficiated oil materials of cyclic structure content having specific gravities falling between the limits noted in the following tabular data:

Fractions	Low limit	High limit
210-235° C.	0.913	1.0580
315-355° C.	1.027	1.1285

and preferably for such a length of time as to provide materials of cyclic structure content in fractional parts of the beneficiated oil having specific gravities falling between the following limits:

Fractions	Low limit	High limit
210-235° C.	0.941	1.0430
315-355° C.	1.055	1.1135

Operating under the conditions above named a period selected between the limits of one and three hours, say one hour and 15 minutes, will illustratively serve to provide a percentage of newly induced materials boiling below 210° C. and specific gravities of materials of cyclic structure content in fractional parts of the overall beneficiation falling between the preferred limits noted above.

The beneficiated oil flowing from the treatment named above had 18.9% materials boiling below 210° C., and the materials of cyclic struc-

ture content in the fractions 210-235° C. and 315-355° C. had specific gravities of 0.941 and 1.055, respectively. The residual matter above 355° C. in the beneficiation is about 34%.

5 When the period of treatment has been completed the oil is condensed and inspected and is found to require a smaller concentration for a given growth inhibition of wood destroying fungi (Madison 517) than the parent feed stock to such an extent as to be useful as a wood preservative. The induction and/or provision of the specific gravities of materials of cyclic structure content in the fractional parts of the beneficiated oil mentioned above is a valid test for the induction of toxicity in the overall fraction referred to, and further is an indication that toxicity has been induced in other fractions of the material under treatment.

The overall beneficiated material may be used 20 as a preservative or for any other purpose to which toxic oils are put. If desired, a preservative wood impregnant complying with specifications extant or of consumer preference, may be segregated from the overall beneficiated oil as a stabilized residual, a distillate or extract, and should the extract have undesirable low boiling ends, the extract may be stabilized to the desired extent by removal of low boiling ends.

As illustrative of wood preservative impreg- 30 nants that are meeting with consumer acceptance and which may be segregated from the overall beneficiated material of the instant process, the following tabular data show several published specifications:

WOOD PRESERVATIVE IMPREGNANTS

Specifications

- 40 1. American Wood Preservers' Association
 - a. Up to 210° C., not more than 5%
 - b. Up to 235° C., not more than 25%
- 45 2. American Wood Preservers' Association
 - a. Up to 210° C., not more than 1%
 - b. Up to 235° C., not more than 10%
 - c. Up to 355° C., not less than 65%
- 50 3. American Wood Preservers' Association
 - a. Up to 235° C., not more than 1½%
 - b. Up to 300° C., not more than 16½%
 - c. Up to 355° C., not less than 45%
- 55 4. American Wood Preservers' Association
 - a. Up to 210° C., not more than 8%
 - b. Up to 235° C., not more than 35%
- 60 5. American Wood Preservers' Association
 - a. Up to 210° C., not more than 10%.
 - b. Up to 235° C., not more than 40%
- 65 6. American Wood Preservers' Association
 - a. Up to 210° C., not more than 5%
 - b. Up to 235° C., not more than 15%.
- 70 7. Prussian Ry.
 - a. Up to 150° C., not more than 3%
 - b. Up to 200° C., not more than 10%
 - c. Up to 235° C., not more than 25%
- 75 8. National Paint, Varnish & Lacquer Association #220
 - a. 5% at 162° C.
 - b. 97% at 270° C.
9. Southern pine shingle stain oil
 - a. 5% at 137° C.
 - b. 95% at 257° C.
10. Neville shingle stain oil
 - a. I. B. P., 150° C.
 - b. 5% at 205° C.
 - c. 95% at 292° C.
11. Carbolineum----- 270° C., I. B. P.

By the nature of the process it is obvious that modifications of existing specifications, or other and more exacting specifications may be met.

As mentioned in the foregoing, the process variables are illustratively so coordinated as to jointly provide newly formed fractions boiling below 210° C. and a preferred limit of specific gravities of materials of cyclic structure content in the fractions 210-235° C. and 315-355° C. of the beneficiated oil.

In lieu of jointly controlling the process as to provide the aforementioned specific gravities of materials of cyclic structure content in the 210-235° C. and 315-355° C. fractions of the beneficiated oil, the proper control may be evidenced in accordance with the following example:

Example 2.—Select a material comparable in chemical analysis and boiling range to the feed stock mentioned in Example 1, as for example aromatic extracts, flashed residuums, or the like. Subject same in vapor phase in the presence of hydrogen at a temperature of 500° C. whilst under a pressure of 1800 pounds. Carry on the process for such a length of time as to jointly provide (1) newly formed materials boiling below 210° C. and (2) in the fractions 235-270° C. and 315-355° C. materials of cyclic structure content having specific gravities falling between the limits noted below:

Fractions	Low limit	High limit
235-270° C.....	0.935	1.0756
315-355° C.....	1.027	1.1285

and preferably between the following limits:

Fractions	Low limit	High limit
235-270° C.....	0.963	1.0606
315-355° C.....	1.055	1.1135

Operating under the conditions above named a period of about one hour and 15 minutes will illustratively serve to provide a percentage of newly induced materials boiling below 210° C. and specific gravities of materials of cyclic structure content in the fractional parts of the beneficiated oil falling between the preferred limits noted above.

At the end of the named treatment period the oil is condensed and inspected, and is found to have induced toxic properties. The induction and/or provision of the specific gravities of materials of cyclic structure content in the fractional parts of the beneficiation stated in the present example is a valid test for the induction of toxicity in the fraction referred to, and further is an indication that toxicity has been induced in other fractions of the material under treatment.

Example 3.—Select a liquid sulfur dioxide extract of a mixture of petroleum fractions, said extract boiling preponderantly above 260° C. and having residual materials boiling above 355° C. Subject same in vapor phase in the presence of hydrogen at a temperature of 515° C. whilst under a pressure of 2500 pounds. Carry on the process for such a period of time as to jointly provide and/or induce (1) newly formed materials boiling below 210° C. and (2) in the fractions 270-315° C. and 315-355° C. specific gravities of mate-

rials of cyclic structure content falling between the limits noted below:

Fractions	Low limit	High limit
270-315° C.....	0.973	1.0935
315-355° C.....	1.027	1.1285

10 and preferably between the following limits:

Fractions	Low limit	High limit
270-315° C.....	1.001	1.0783
315-355° C.....	1.055	1.1135

Operating under the conditions above named a period selected between the limits of one and two hours will illustratively serve to jointly provide a percentage of newly induced materials boiling below 210° C. and specific gravities of materials of cyclic structure content falling between the preferred limits in the fractional parts of the beneficiation as noted above.

When the period of treatment has been completed the oil is cooled, condensed and inspected. It will be found that the overall beneficiation requires a smaller concentration for a given growth inhibition of wood destroying fungi than the parent feed stock to such an extent as to be useful as a preservative wood impregnant. The induction and/or provision of specific gravities of materials of cyclic structure content in the fractional parts of the beneficiation mentioned in the instant example is a valid test for the induction of toxicity in the fractions referred to, and further is an indication that toxicity has been induced in other fractions of the material under treatment.

Example 4.—Select a furfural extract of a mixture of petroleum fractions, said extract boiling preponderantly above 250° C. and having substantial residual matter above 355° C. Subject same in vapor phase in the presence of hydrogen at a temperature of 515° C. whilst under a pressure of 1800 pounds. Carry on the process for such a length of time as to jointly provide (1) newly formed materials boiling below 210° C., as for example 15-35%, and (2) in the fraction boiling between 315-355° C. a specific gravity of materials of cyclic structure content falling between the limits of 1.027 and 1.1285, and preferably between the limits of 1.055 and 1.1135.

Carrying on the process under the conditions of the instant example, a period of about one hour and 30 minutes will illustratively serve to provide a percentage of newly induced materials boiling below 210° C. and a specific gravity of materials of cyclic structure content falling between the preferred limits in the 315-355° C. fraction of the reformed oil.

At the end of the processing period the oil is cooled, condensed and inspected. Find in the beneficiation a toxicity in excess of that of the parent feed stock. The induction and/or provision of the specific gravity of materials of cyclic structure content falling between the stated limits in the materials boiling between 315-355° C. is a valid test for the induction of toxicity in the fraction referred to, and further is an indication that toxicity has been induced in other fractions of the material under treatment.

As noted in the tabular data in the foregoing

giving boiling range specifications for oil wood preservatives, many preservative oils are possible of segregation from the beneficiated feed stock of induced toxicity. As for example, an oil boiling within the carbolineum preservative range, in which instance the segregation would have an initial boiling point of about 270° C., the fractions 270–315° C. and 315–355° C. of which, would illustratively contain materials of cyclic structure content having specific gravities falling between the limits of 1.001–1.0783 and 1.055–1.1135, respectively.

Example 5.—Practice the process of Example 1 with a hydrogen containing gas.

Example 6.—Practice the process of Example 2 employing hydrogen derived from carbon monoxide and water.

Example 7.—Practice the process of Example 3 with carbon dioxide, as for example with a combustion gas.

Example 8.—Practice the process of Example 4 with nitrogen.

Example 9.—Practice the process of Example 1 with water gas.

Example 10.—Practice the process of Example 2 with a molybdenum oxide catalyst.

Example 11.—Practice the process of Example 3 with a chromium oxide catalyst.

Example 12.—Practice the process of Example 4 with a vanadium oxide catalyst.

Example 13.—Practice the process of Example 1 with a tin oxide catalyst.

Example 14.—Practice the process of Example 2 with a molybdenum sulfide catalyst.

Example 15.—Practice the process of Example 3 with a chromium sulfide catalyst.

Example 16.—Practice the process of Example 4 with a vanadium sulfide catalyst.

Example 17.—Practice the process of Example 1 with a tin sulfide catalyst.

Example 18.—Practice the process of Example 2 with the coprecipitated oxides of copper and chromium as catalytic materials.

Example 19.—Practice the process of Example 3 with tin chloride as catalytic material.

Example 20.—Practice the process of Example 4 with aluminum chloride as catalytic material.

Example 21.—Practice the process of Example 1 with iodine as catalytic material.

Example 22.—Practice the process of Example 2 with iodoform as catalytic material.

Example 23.—Practice the process of Example 3 with hydriodic acid as catalytic material.

Example 24.—Practice the process of Example 4 with chlorine as catalytic material.

Example 25.—Practice the process of Example 1 with bromine as catalytic material.

Example 26.—Practice the process of Example 2 with a hydrogen halid as catalytic material.

Example 27.—Practice the process of Example 3 with ammonium chloride as catalytic material.

Example 28.—Practice the process of Example 4 with pelleted bentonite clay as catalytic material.

Example 29.—Practice the process of Example 1 with activated Attapulugus clay as catalytic material.

Example 30.—Practice the process of Example 2 with a silica hydrogel as catalytic material.

Example 31.—Practice the process of Example 3 with a silica gel impregnated with an aluminum salt as catalytic material.

Example 32.—Practice the process of Example 4 with bentonite and an adsorptive clay as catalytic materials.

Example 33.—Practice the process of Example 1 with a silicious material impregnated with a metallic oxide as catalytic material.

Example 34.—Practice the process of Example 2 with a silicious material impregnated with a metallic sulfide as catalytic material.

Example 35.—Practice the process of Example 3 with coprecipitated alumina and chromia hydrogels as catalytic materials.

Example 36.—Practice the process of Example 4 with a synthetic silica-alumina gel as catalytic material.

In the Examples 1–4 inclusive, instances have been cited wherein the feed stocks have very small percentages, if any, of materials boiling below 270° C. The instant process, as illustrated by Examples 1–4 inclusive, or others, is adapted to thermally treat in vapor phase in the presence of a protective gas of extraneous source, within the processing limits herein disclosed, a mixture of petroleum fractions characterized by relatively little toxicity, as for example the so-called aromatic extracts or other petroleum fractions of induced cyclic structures, having fractions boiling within the wood preservative range and thereby provide an overall treated oil or segregated fractions thereof requiring a smaller concentration for a given growth inhibition of wood destroying fungi than the starting feed stock to such an extent as to be useful as a wood preservative impregnant.

Various purposes appear to be accomplished by the vapor phase induction of toxicity in the presence of a gas or gases of extraneous source not accomplished by liquid phase treatment. Among the purposes accomplished may be mentioned the thermal protection of the material under treatment whereby to preclude or minimize undesirable polymerization, and in the event the gas or gases partake of, or in the reforming action, additional benefits are noted. It has been determined that various gases of extraneous source provide these desired and beneficial results in varying degrees. It has specifically been determined that included among these beneficial gases are hydrogen, hydrogen containing gases and substantially inert gases containing carbon. Also specifically employable are methane and its homologues, various refinery gases, carbon dioxide and nitrogen.

The gases above mentioned may be employed separately or in admixture, and this provision, in one mode of operation, is to be specifically read into all examples.

Various catalysts assist in the reforming, transforming, modifying and/or converting of the starting petroleum oil whereby to provide materials of induced toxic properties. Many catalysts other than noted in the foregoing are also employable as effective substances. Viewed broadly, the oxides and sulfides of metals may be used as well as the carbonates, sulfates and the metals themselves. Cellulosic materials and carbon, activated or otherwise, may be used with advantage. Especially effective as catalytic materials are the oxides and sulfides of metals, silicious materials, halogens, halids and derivatives thereof, including specifically substitution and addition products thereof, as for example and specifically, substitution and addition products of said derivatives, say a hydrogen halid, employed in well known manner.

The catalysts employed in the instant process are "reforming" catalysts. By the expression "a reforming catalyst" is meant a catalyst adapted

to favorably influence the reactions that are conducive to the induction of toxicity, be the reactions those of addition, substitution or subtraction.

The temperatures in the instant process may be selected over a wide range dependent upon the pressures employed. It is, of course, understood that when relatively low temperatures are employed the lower will be the pressure in order to provide vapor phase operation, and when operating at very low temperatures, pressures only slightly above atmospheric will suffice. Temperatures employable are selected between the limits of 400-650° C. and preferably between 425-550° C.

Various pressures are employable, as for instance 10, 50, 100 atmospheres or higher, and these pressures are so coordinated as to give total or substantially total vapor phase operation.

If desired, instead of subjecting the entirety of the starting feed stock to a single toxicity inducing operation in the vapor phase in the presence of an extraneous gas or gases, the parent material may be divided into a plurality of cuts and these plurality of cuts separately subjected to separate vapor phase toxicity inducing operations wherein the temperatures in each instance are dissimilar, as for example, but not as a restriction, subjecting the highest boiling cut to the lowest temperature, etc.

The hydrogen partial pressure, or the partial pressure of the gas or gases employed, may vary over wide limits, as for example it may represent a partial pressure of 5-50% or higher.

The time element is specifically selected so as to jointly provide and/or induce in the overall beneficiated material (1) newly formed materials boiling below 210° C. and (2) specific gravities of materials of cyclic structure content in the stated fractions falling between the stated limits, and preferably between the preferred limits. Using any given feed stock, a few trials will enable those skilled in the art to determine the correct period of treatment when employing definite selections of temperature and pressure.

The process of the instant invention may be practiced in an intermittent processing vessel or in a continuous manner as will become apparent to those skilled in the art after having read the foregoing disclosures.

In the examples shown in the foregoing, one or more phases, etc., of one example may be added to or substituted for other phase or phases in another example where the substitution or addition is obviously workable.

The evaluation of the materials of cyclic structure content and/or aromatics referred to in the foregoing is secured by recourse to the method disclosed under the caption "Neutral oils of coal hydrogenation—Action of sulfuric acid," Industrial and Engineering Chemistry, volume 32, page 1614 et seq., December, 1940.

While Examples 5-36 disclose the employment of definite catalysts and gases with definite ones of the Examples 1-4 inclusive, it is to be fully understood that these catalysts and gases are interchangeable with the definite controls of the early examples, and any of the named catalysts, gas or gases, or their equivalents are usable in any of the Examples 1-4 inclusive, and certain toxicity benefits will flow therefrom. The examples given, and the catalyst and gas linked therewith are for the purposes of illustration only.

Minor changes may be made within the scope of the appended claims without departing from

the spirit of the invention. In the claims affixed to this specification no selection of any particular modification is intended to the exclusion of other modifications thereof, and the right to subsequently make claims to any modification not covered by these claims is expressly reserved.

We claim:

1. In the induction of toxicity into a mixture of petroleum fractions boiling preponderantly above 270° C., characterized by inherent but inhibited toxicity and a substantial percentage of materials of ring structure content, the process which comprises: subjecting said material in vapor phase to a temperature selected between the limits of 400-650° C. whilst contacting a gas of extraneous source under superatmospheric pressure; unvelling toxicity in the material under treatment by carrying on the process for a period not substantially in excess of two hours, the period being so selected with reference to the chosen temperature and pressure as to jointly provide newly formed materials boiling below 210° C. and materials of cyclic structure content in the fractions 210-235° C. and 315-355° C. of the beneficiated material having specific gravities falling between the limits of about 0.913-1.0580 and 1.027-1.1285, respectively; and segregating from the beneficiated material an oil of the wood preservative type boiling preponderantly between 210° C. and 355° C., having at least 10-20% residual material boiling above 315° C., and in the fractions 210-235° C. and 315-355° C. a specific gravity in the materials of cyclic structure content falling between the limits above named.

2. In the induction of toxicity into a mixture of petroleum fractions boiling preponderantly above 270° C., characterized by inherent but inhibited toxicity and a substantial percentage of materials of ring structure content, the process which comprises: subjecting said material in vapor phase to a temperature selected between the limits of 400-650° C. whilst contacting a gas of extraneous source under superatmospheric pressure; unvelling toxicity in the material under treatment by carrying on the process for a period not substantially in excess of two hours, the period being so selected with reference to the chosen temperature and pressure as to jointly provide newly formed materials boiling below 210° C. and materials of cyclic structure content in the fractions 235-270° C. and 315-355° C. of the beneficiated material having specific gravities falling between the limits of about 0.935-1.0756 and 1.027-1.1285, respectively; and segregating from the beneficiated material an oil of the wood preservative type boiling preponderantly between 210° C. and 355° C., having at least 10-20% residual material boiling above 315° C., and in the fractions 235-270° C. and 315-355° C. a specific gravity in the materials of cyclic structure content falling between the limits above named.

3. In the induction of toxicity into a mixture of petroleum fractions boiling preponderantly above 270° C., characterized by inherent but inhibited toxicity and a substantial percentage of materials of ring structure content, the process which comprises: subjecting said material in vapor phase to a temperature selected between the limits of 400-650° C. whilst contacting a gas of extraneous source under superatmospheric pressure; unvelling toxicity in the material under treatment by carrying on the process for a period not substantially in excess of two hours, the period being so selected with reference to the cho-

sen temperature and pressure as to jointly provide newly formed materials boiling below 210° C. and materials of cyclic structure content in the 270-315° C. and 315-355° C. fractions of the beneficiated material having specific gravities falling between the limits of about 0.973-1.0933 and 1.027-1.1285, respectively; and segregating from the beneficiated material an oil of the wood preservative type boiling preponderantly between 210° C. and 355° C. having at least 10-20% residual material boiling above 315° C., and in the fractions 270-315° C. and 315-355° C. a specific gravity in the materials of cyclic structure content falling between the limits above named.

4. The process of claim 1 wherein the gas of extraneous source is hydrogen.

5. The process of claim 1 wherein the gas of extraneous source is a hydrogen containing gas.

6. The process of claim 1 with inclusion of carrying on the process in the presence of a reforming catalyst.

7. The process of claim 2 with inclusion of carrying on the process in the presence of a reforming catalyst.

8. The process of claim 3 with inclusion of carrying on the process in the presence of a reforming catalyst.

9. The process of claim 1 with inclusion of carrying on the process in the presence of a catalytic material selected from the group consisting of oxides and sulfides of heavy metals.

10. The process of claim 2 with inclusion of carrying on the process in the presence of a catalytic material selected from the group consisting of oxides and sulfides of heavy metals.

11. The process of claim 3 with inclusion of carrying on the process in the presence of a catalytic material selected from the group consisting of oxides and sulfides of heavy metals.

12. The process of claim 1 with inclusion of carrying on the process in the presence of a halogen, halid or derivative thereof, including substitution and addition products thereof, as catalytic material.

13. The process of claim 2 with inclusion of carrying on the process in the presence of a halogen, halid or derivative thereof, including substitution and addition products thereof, as catalytic material.

14. The process of claim 3 with inclusion of carrying on the process in the presence of a halogen, halid or derivative thereof, including substitution and addition products thereof, as catalytic material.

15. The process of claim 1 with inclusion of carrying on the process in the presence of silicious material as catalytic agent.

16. The process of claim 2 with inclusion of carrying on the process in the presence of silicious material as catalytic agent.

17. The process of claim 3 with inclusion of carrying on the process in the presence of silicious material as catalytic agent.

18. A petroleum derived preservative wood impregnant consisting of in its entirety a destructively cracked product of petroleum fractions, said preservative characterized by a preponderance of materials boiling between 210° C. and 355° C., and at least about 10-20% materials boiling above 315° C., the fraction 210-235° C. of which contains materials of ring structure content having a specific gravity between about 0.941 and 1.0430; the fraction 235-270° C. of which contains materials of ring

structure content having a specific gravity between about 0.963 and 1.0606; the fraction 270-315° C. of which contains materials of ring structure content whose specific gravity falls between about 1.001 and 1.0783; and the fraction of which boiling between 315-355° C. contains materials of ring structure content having a specific gravity falling between about 1.055 and 1.1135.

19. A petroleum derived preservative wood impregnant consisting of in its entirety a destructively cracked product of petroleum fractions, said preservative characterized by a preponderance of materials boiling between 210° C. and 355° C., and at least about 10-20% materials boiling above 315° C., the fraction 235-270° C. of which contains materials of ring structure content having a specific gravity between about 0.963 and 1.0606; the fraction 270-315° C. of which contains materials of ring structure content whose specific gravity falls between about 1.001 and 1.0783; and the fraction of which boiling between 315-355° C. contains materials of ring structure content having a specific gravity falling between about 1.055 and 1.1135.

20. A petroleum derived preservative wood impregnant consisting of in its entirety a destructively cracked product of petroleum fractions, said preservative characterized by a preponderance of materials boiling between 210° C. and 355° C., and at least about 10-20% materials boiling above 315° C., the fraction 270-315° C. of which contains materials of ring structure content having a specific gravity falling between the limits of about 1.001 and 1.0783; and the fraction of which boiling between 315-355° C. contains materials of ring structure content having a specific gravity falling between about 1.055 and 1.1135.

21. The process of inducing toxicity into a petroleum derived material, which comprises: subjecting a mixture of petroleum fractions boiling preponderantly above 270° C., characterized by a substantial percentage of relatively non-toxic materials boiling above 315° C., ring structure content and inherent but inhibited toxicity to vapor phase cracking conditions whilst contacting a gas of extraneous source at a temperature selected between the limits of about 400-600° C. and a pressure in excess of atmospheric; unveiling toxicity in the materials under treatment by continuing the named cracking operation for a period not substantially in excess of two hours, the period being so selected with reference to the chosen temperature and pressure as to jointly provide newly formed materials boiling below 210° C., and an overall beneficiated material having fractional parts which contain materials of cyclic structure content having specific gravities falling substantially between the limits noted in the appended tabular data:

Fractions	Low limit	High limit
235-270° C.	0.963	1.0606
270-315° C.	1.001	1.0783
315-355° C.	1.055	1.1135

whereby to provide a material of induced toxic properties; and segregating from the overall beneficiated material an oil of the wood preservative type characterized by induced toxic properties, boiling preponderantly between 210° C. and

355° C. and having at least about 10-20% residual matter above 315° C., the fraction 270-315° C. of which contains materials of ring structure content which have a specific gravity falling between the limits of about 1.001 and 1.0783, 5 and the fraction of which boiling between 315-

355° C. contains materials of ring structure content which have a specific gravity falling between about 1.055 and 1.1135.

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