

## UNITED STATES PATENT OFFICE

2,363,243

PROCESS OF INDUCING TOXICITY AND  
PRODUCT THEREOF

Jacquelin E. Harvey, Jr., Washington, D. C., and  
Robert H. White, Jr., and Joseph A. Vaughan,  
Atlanta, Ga., assignors of one-half to said  
Harvey, Jr., and one-half to Southern Wood  
Preserving Company, East Point, Ga., a corpo-  
ration of Georgia

No Drawing. Original application November 18,  
1942, Serial No. 466,054. Divided and this ap-  
plication November 23, 1943, Serial No. 511,481

10 Claims. (Cl. 196—52)

The instant invention relates to the produc-  
tion of toxic oils employable as fungicides, in-  
secticides, and for any other service to which  
toxic oils may be put, being a division of our  
application Serial No. 466,054, filed November 18,  
1942, for Method of producing valuable materials  
and products thereof.

More especially the instant invention relates to  
the production of toxic oils from mixtures of  
petroleum fractions characterized by ring struc-  
ture content. Among such starting materials  
may be mentioned mixtures of petroleum frac-  
tions characterized by ring structure content re-  
covered from petroleum fractions by well known  
extraction methods including extractive distilla-  
tion and azeotropic distillation. Also may be  
mentioned mixtures of petroleum fractions char-  
acterized by ring structure content as flowing  
from thermal and/or catalytic treatment of cer-  
tain petroleum fractions which includes petro-  
leum 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 cata-  
lytic treatments of unusual length, as for ex-  
ample, for periods of from 1-10 hours or more.

An object of the instant invention is the pro-  
duction of toxic oils from the aforementioned petro-  
leum fractions or others whereby to provide oils  
of the preservative type, as for example preserva-  
tive wood impregnants conforming to specifica-  
tions extant or acceptable to the trade consum-  
ing such oil materials.

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

Another object of the instant invention is the  
reforming, modifying, converting and/or trans-  
forming of the mixtures of hydrocarbons where-  
by 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 petro-  
leum fractions having inherent but inhibited  
toxicity.

Another object of the instant invention is the  
maintenance of a preponderant proportion of the  
cyclic structures in the material undergoing tox-  
icity induction in at least a methylated condi-  
tion, it having been found that objectionable re-

action products are formed if this object is not  
adhered to.

Another object of the invention is the control  
of saturates in specific fractions of the material  
undergoing treatment.

Still another object of the instant invention is  
the control of the percentage of cyclic structures,  
as for instance aromatics, in specific fractions of  
the benefited material which is characterized  
by induced toxic properties.

Yet another object of the instant invention is  
the provision in the overall benefited 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  
change in specific gravity in the overall bene-  
fited material which is conducive to the in-  
duction of toxicity.

Another object of the instant invention is the  
coordination of process variables so as to provide  
specific gravities within definite limits in various  
fractions of the benefited material.

Another object of the instant invention is a  
coordination of process variables which will pro-  
vide in various fractional parts of the benefited  
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 a re-  
forming catalyst adapted to favorably influence  
the induction of toxicity. By the expression "a  
reforming catalyst" is meant a catalytic mate-  
rial adapted to exert catalytic influence whilst  
the starting material is being reformed, trans-  
formed, modified and/or converted. In the speci-  
fication and in the annexed claims, reformation,  
transformation, conversion and/or modification  
of the starting material whereby to induce tox-  
icity is specifically meant to include cracking,  
addition, and substitution reactions that are pos-  
sible within the limits of the process variables  
disclosed elsewhere herein.

Another object of the instant invention is the  
induction of additional toxicity into fractional  
parts of the once benefited starting material  
under specific controls of process variables.

In the past wood preservative oils of the high  
temperature coal tar derived type have been em-  
ployed 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 oils 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. 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 includes 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 structure 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 structure content produced (1940) at the Wood River Refinery of the Shell

Oil Company and which has the following inspection:

	Gravity	10.8
5	Flash, P. M. C. C.	295
	Flash, C. O. C.	290
	Fixed carbon	4.9 per cent
	Pour point	-10
	B. S. & W.	0.1 per cent by volume
10	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
15	Sol. in CS <sub>2</sub>	99.8
	Loss 50 grams, 5 hours, @ 325° F.	8.9
	Residue of 100 pene.	37.5 per cent
	A. S. T. distillation:	
	I. B. P., ° F.	518
20	10% rec. @ ° F.	565
	20% rec. @ ° F.	589
	30% rec. @ ° F.	614
	40% rec. @ ° F.	637
	50% rec. @ ° F.	660
25	60% rec. @ ° F.	1 675

<sup>1</sup> 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 structure 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 structure 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.

The following examples will serve to illustrate several modes of practicing the present invention.

**Example 1.**—A mixture of petroleum fractions characterized by cyclic structure content having but slight growth inhibition to wood destroying fungi, as for example the Shell product shown in the foregoing tabular data, is charged to a vessel adapted to operate at superatmospheric pressure, as for instance at a pressure as high as several hundred atmospheres. The catalyst is a reforming catalyst. The oil is brought up to a temperature of 430° C. wherein it is held in the commonly accepted liquid phase at a pressure of 850 pounds for such a length of time as to provide 20% newly formed fractions boiling below 210° C.

At the end of the stated period the oil is withdrawn from the processing chamber, cooled and inspected. Upon inspection the oil is found to have toxic properties unveiled as the result of the treatment above named, and such induction of toxicity is accompanied and evidenced by the production of the named percentage of newly induced fractions boiling below 210° C.

In the induction of toxicity in accordance with the instant process, it has been determined that unless at least about 10% newly formed frac-

tions boiling below 210° C. are induced, latent toxicity is not unveiled to the desired extent. It has also been determined that if more than about 50% newly formed materials boiling below 210° C. are created, including fixed gases, reactions go forward that are prejudicial to the induction of toxicity, as for example there occurs inordinate gasification, inordinate production of undesired fugitive materials and/or polymerization of high boiling fractions of the starting material under treatment.

To approximate commercial operating conditions it is preferred to so control process variables as to provide about 15-35% newly formed materials boiling below 210° C., and in this manner of operation pronounced toxicity is induced.

In the induction of toxicity in accordance with the instant method, the process variables are so coordinated as to maintain a preponderant proportion of the cyclic structures of the materials under treatment in at least a methylated condition, it having been found that an attempt to totally dealkylate the cyclic structures of the starting material results in the formation of toxicity diluents, inordinate gasification and/or the formation of substantially non-toxic substances. The expression "in at least a methylated condition" refers to the number of carbon atoms in the ring appendages. Each fraction of the beneficiated material of induced toxicity, as for example and especially the materials boiling between 315° C. and 355° C., has a preponderant proportion of materials of cyclic structure present in at least a methylated condition.

Conditions that are prejudicial to the maintenance of a preponderant proportion of the cyclic structures of the starting material in at least a methylated condition are excessive temperatures and/or excessive time of treatment. Temperatures that are employable in the instant process which will provide the aforementioned end result are selected between the limits of 300-550° C., and preferably between 400-500° C., say 430° C. to 480° C. Using the preferred temperature whilst operating at superatmospheric pressure, as for example at pressures ranging between 400-3000 pounds, it will be found that when the treatment is carried on for a period of one to two hours the end product will have induced toxicity as flowing from, among other things, the maintenance of a preponderant proportion of the materials of ring structure content of the starting material in at least a methylated condition, and accompanied with and indicated by a percentage of newly formed fractions boiling below 210° C. falling between the limits of about 10-50%, and the induction of toxicity is enhanced by the specific inclusion of a reforming catalyst.

The pressure employed in the instant process may be autogenous due to the pressure of evolved vapors, or the pressure may be provided by any means well known to the art, as for example by pumping and/or valving arrangements.

The material of induced toxic properties as flowing from the process carried out under the controls above disclosed may be used in toto as a wood preservative or in the event it is desired to provide a preservative wood impregnant complying with specifications extant or of consumer preference, a wood preservative may be segregated from the overall beneficiated oil as a stabilized residual, distillate or extract and in the event the extract has non-permissible low boiling

ends, the extract may be stabilized to the necessary or desired extent.

As examples of wood preservative impregnants of the oil derived type that are meeting with consumer preference and which may be produced or paralleled by the process of the present invention, the following tabular data show several published specifications:

#### WOOD PRESERVATIVE IMPREGNANTS

##### Specifications

1. American Wood Preservers' Association
  - a. Up to 210° C., not more than 5%
  - b. Up to 235° C., not more than 25%
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%
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%
4. American Wood Preservers' Association
  - a. Up to 210° C., not more than 8%
  - b. Up to 235° C., not more than 35%
5. American Wood Preservers' Association
  - a. Up to 210° C., not more than 10%
  - b. Up to 235° C., not more than 40%
6. American Wood Preservers' Association
  - a. Up to 210° C., not more than 5%
  - b. Up to 235° C., not more than 15%
7. Prussion 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%
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.

If desired, the processing of the oil may be carried on in the presence of an extraneous gas whose partial pressure may vary over wide ranges, as for example the partial pressure of the extraneous gas may be 5-50% or more. Among the extraneous gases employable are hydrogen, carbon monoxide, carbon monoxide and water vapors, methane and its homologues, various refinery gases and inert gases such as nitrogen and carbon dioxide. Certain special benefits flow from carrying on the toxicity induction in the presence of an extraneous gas, among which may be mentioned the thermal protection of the material under treatment, as for example when employing hydrogen or a hydrogen containing gas the material under treatment is not so susceptible to polymerizing reactions. This provision, in one mode of operation is to be specifically read into the foregoing example, and in the event it is elected to carry on the process in the presence of a reactive gas, as for instance hydrogen, the suppression of polymerizing reactions is more pronounced and is especially beneficial.

In the event it is elected to employ carbon monoxide and water, the total pressure may vary over wide limits, as for example from 200 to 5,000 pounds, or higher. In like manner the carbon monoxide partial pressure may vary over wide limits, as for instance, from 5 to 50 percent, or higher. The water may represent from 5 to 50% or higher based on the oil under toxicity inducing conditions, and in some instances may represent more than twice the amount of the charged oil. In one mode of operation, this definite teaching concerning the employment of carbon monoxide and water is to be specifically read into all examples. The carbon monoxide and water may be introduced simultaneously with the feed stock, or at other times, separately or jointly.

*Example 2.*—A liquid sulfur dioxide extract is charged to a high pressure autoclave and hydrogen pumped into an upper pressure of 1,000 pounds. Three per cent of a reforming catalyst is employed. The material is heated to a temperature of 450° C. and held at that heat tone for a period of one hour and 10 minutes. A maximum pressure of 2050 pounds is attained when a heat tone of 425° C. is reached.

At the end of the named processing period, the oil is discharged from its treating enclosure, cooled and inspected. It is found that 19.2% newly formed materials boiling below 210° C. have been formed, and the benefited oil requires a smaller concentration for a given growth inhibition of wood destroying fungi than the starting material. It is also determined that a preponderant proportion of the materials of cyclic structure content in the treated oil has been maintained in at least a methylated condition.

The overall benefited material may be used as a preservative impregnant of induced toxic properties, or a preservative impregnant of the desired boiling range may be segregated therefrom.

*Example 3.*—Another mode of practicing the instant process whereby to induce toxic properties resides in the control of saturates in the benefited material boiling above 270° C., as for example the material boiling between 270° C. and 355° C.

It has been determined that the materials boiling above 270° C. in the benefited oil have a relatively low toxicity as compared to materials boiling below that temperature. It is known that unsaturates are amongst the most toxic of oil substances. However, it is also determined that if an attempt is made to provide in the benefited oil of induced toxic properties, the entirety of the materials boiling above 270° C., as for example the materials boiling between 270° C. and 355° C., as unsaturates, adverse reactions occur that are prejudicial to the induction of toxicity as for example there occurs (1) inordinate gasification, (2) inordinate production of materials of relatively little toxicity and/or (3) polymerized high boiling materials.

When providing acceptable toxicity in the overall reformed, transformed, modified and/or converted oil, it has been determined that by holding the percentage of saturates in the materials boiling above 270° C., as for example in the materials boiling between 270° C. and 355° C., to less than 30% but more than 5%, and preferably not more than 10%, no operating ills such as above named will occur, or if said ills do occur they are minimized.

As an illustrative control of process variables which provides induced toxic properties whilst

yielding an oil having less than 30% but more than 5% saturates in the materials boiling between 270° C. and 355° C., the following operational procedure is given:

A petroleum oil characterized by cyclic structure content 15.1% boiling below 315° C., 45% residue above 355° C., inherent but inhibited toxicity and having 41% and 34% saturates, respectively, in the 270–315° C. and 315–355° C. fractions, is subjected to a liquid phase thermal treatment in the presence of a pelleted siliceous clay and hydrogen at a temperature of 445° C. for a period of one and one-half hours whilst under a pressure of 1800 pounds. At the end of the named period of treatment the benefited oil is discharged from its treating enclosure, cooled and inspected. The benefited oil has only 28.5% residue above 355° C. and it is determined that there are only 23.3% and 12% saturates, respectively, in the 270–315° C. and 315–355° C. fractions. The oil has toxic properties that are more pronounced than the parent feed stock. During the course of treatment 18.1% of newly formed materials boiling below 210° C. were formed. A further inspection of the benefited material discloses that a preponderant proportion of the cyclic structures of the starting material was maintained in at least a methylated condition.

A variation of the process described in Example 3 may be provided by carrying on the process in the absence of hydrogen, and certain toxicity benefits will flow therefrom. The provision of carrying on the process without protective gas of extraneous source is, in one mode of operation, to be specifically read into Example 3.

*Example 4.*—An oil of cyclic structure content produced by the petroleum industry having inherent but inhibited toxicity, an initial boiling point of about 270° C., about 50% residue above 355° C. and 52% and 54% aromatics, respectively, in the 270–315° C. and 315–355° C. fractions, is subjected to a liquid phase thermal treatment in the presence of a reforming catalyst and hydrogen at a temperature of 455° C. for a period of one hour and 30 minutes. At the end of the named period the treated oil is withdrawn from the processing enclosure, cooled and inspected. It is found that about 22% newly formed fractions boiling below 210° C. have been formed. The residual matters above 355° C. have been reduced by in excess of 45%. The fractions of the benefited material boiling between 270–315° C. and 315–355° C. have 71% and 80.5% aromatics, respectively. The overall benefited oil is characterized by a toxicity more pronounced than the starting material.

It is well understood in the art that the aromatics, as for example aromatics having side chains not longer than the propyl group are amongst the most toxic of all substances. As stated in the foregoing, the feed stock in the instant example has slightly more than 50% aromatics in the 270–355° C. fraction. However, the aromatics present, due to their peculiar type, exhibit inhibited toxicity. It would then, therefore, appear reasonable to attempt to provide in the finally benefited oil total aromaticity in the materials boiling between 270° C. and 355° C. in order to induce toxicity of a high order, and more especially it would appear reasonable to attempt to provide total aromaticity of a type exhibiting satisfactory toxic values. It is discovered, however, that if an attempt is made to provide in the benefited material the entirety of

the materials boiling above 270° C., as for example the materials boiling between 270° C. and 355° C., as aromatics, either of the toxicity-inhibited or toxicity-uninhibited type, adverse reactions occur which are prejudicial to a satisfactory induction of toxicity, as for example there occurs (1) inordinate gasification, (2) inordinate production of materials of relatively low toxicity and/or (3) high boiling polymerized materials.

It is found that by holding the percentage of aromatics in the materials boiling above 270° C. in the beneficiated oil, as for example the beneficiated materials boiling between 270° C. and 355° C., to more than 70% but less than 95%, and preferably not less than 90%, toxicity is induced in a commercial manner with the added benefits that the operating ills above mentioned are minimized or eliminated.

The oil of the instant example, as stated in the foregoing, has toxic properties more pronounced than the parent feed stock, and may be used in toto as a preservative wood impregnant. This phase of the instant invention, in any and all examples, resides in the novel manner of inducing toxic properties without reference to the provision of specification oils. However, as also previously mentioned, specification oils may be segregated from the overall beneficiation.

In lieu of practicing the process as specifically provided in Example 4, the process, in one mode of operation, may be specifically carried on without the presence of a protective gas of extraneous source and an increase of toxicity will flow from this mode of practice. However, the increase of toxicity when provided by thermal treatment in the absence of a protective gas is not as satisfactory as when carried on in the presence of the protective gas.

**Example 5.**—Another mode of practicing the instant process resides in controlling the specific gravity of the overall beneficiated material remaining finally liquid after completion of impressed process variables.

It has been found that if an oil mentioned in the foregoing characterized by inherent but inhibited toxicity is subjected to thermal treatment in the presence of a reforming catalyst, with or without a protective gas of extraneous source, whereby to provide a beneficiated material remaining finally liquid having, as compared to the parent feed stock, an overall change in specific gravity between 0.015 and 0.15, and preferably between 0.020 and 0.10, the material of the changed specific gravity has toxic properties more pronounced than the parent feed stock. This change in specific gravity is a valid test for induced toxicity. The noted change in specific gravity which is conducive to the induction of toxic properties may be either up or down, as more fully disclosed and explained in the following.

An oil of induced cyclic structures produced by the petroleum industry having a specific gravity of 0.960, characterized by inherent but inhibited toxicity, boiling preponderantly above 315° C. and with substantial residual matter above 355° C., is subjected to a liquid phase thermal treatment in the presence of a reforming catalyst and a hydrogen containing gas at a temperature of 465° C. whilst under a pressure of 1500 pounds for a period of two hours. At the end of the named treatment period the oil is cooled and inspected and found to have a specific gravity of 0.940 or a reduction in specific gravity of 0.020%. The overall beneficiated ma-

terial has induced toxic properties and more than 10% but less than 50% newly formed fractions boiling below 210° C.

According to this specific mode of operational control and test in the instant example, the process variables are so coordinated as to cause a reduction in specific gravity falling between the limits of 0.015 and 0.15%, and preferably between 0.020% and 0.10%. Such a stated change in specific gravity has the effect of inducing and indicating the induction of toxic properties into materials previously having inhibited toxic values. The lowering of the specific gravity within the defines stated is critical within limits. Unless an overall specific gravity of the material under treatment is lowered by 0.015%, a certain unveiling of inhibited toxicity is sacrificed, and if the overall specific gravity is lowered by more than 0.15%, inordinate gasification, production of fugitive materials of relatively low toxic value and/or polymerization will occur. To avoid or minimize these ills, and/or others, the reduction of specific gravity is preferably held between 0.020% and 0.10%.

Certain toxicity benefits will flow from carrying on the process of Example 5 without the inclusion of the protective gas of extraneous source. In one mode of operation, this provision of carrying on the process without a protective gas of extraneous source is to be specifically read into that part of Example 5 which provides for the lowering of the overall specific gravity of the feed stock.

In connection with the change in specific gravity of the overall starting material which results in the induction of toxicity, a modification of the process resides in raising the specific gravity of the material remaining finally liquid after impressed process variables by a percentage falling between the limits of 0.015 and 0.15, and preferably between 0.020 and 0.10.

To illustrate this modification of the instant process an oil of cyclic content produced by the petroleum industry having relatively little toxicity, as for example a flashed residuum having a specific gravity of 0.924 and a substantial percentage of materials boiling above 355° C. is subjected to a liquid phase thermal treatment in the presence of a reforming catalyst and a saturated hydrocarbon gas at a temperature selected between the limits of 450–525° C. whilst under a pressure of 1200 pounds for such a period of time as to provide an overall beneficiated material remaining finally liquid having a specific gravity of 1.015. When the stated specific gravity has been attained the beneficiated material will have substantial residual matter above 355° C. A period of from one to five hours dependent upon the temperature selected will illustratively serve for the stated increase of specific gravity.

The oil of the stated increased specific gravity is inspected and found to have toxic properties more pronounced than its parent feed stock. The beneficiation in toto may be used as a preservative wood impregnant or, as taught in the foregoing, an impregnant of induced toxic properties having a specification boiling range may be segregated therefrom.

In lieu of increasing the specific gravity whilst employing a gas of extraneous source, the process may, in one mode of operation, be practiced without the added gas. When increasing the specific gravity with the exclusion of an extraneous gas, the increase of the specific grav-

ity is held within the limits noted in the foregoing.

*Example 6.*—An oil containing materials of cyclic structure content produced by the petroleum industry, as for example a liquid sulfur dioxide or furfural extract, having inherent but inhibited toxicity, boiling 15% at 315° C., and about 45% residual matter above 355° C., is charged to a high pressure autoclave and subjected to a liquid phase thermal treatment in the presence of a reforming catalyst and water gas at a temperature selected between 435–485° C. whilst under a pressure of 1700 pounds for such a time as to jointly provide more than 10% but less than 50% newly formed fractions boiling below 210° C., and an overall specific gravity in fractional parts of the beneficiated oil falling within the limits noted in the following tabular data:

Fractions	Low limit	High limit
210–235° C. ....	0.801	1.0048
235–270° C. ....	0.850	1.0315
270–315° C. ....	0.914	1.0691
315–355° C. ....	0.973	1.1175

and preferably between the limits noted below:

Fractions	Low limit	High limit
210–235° C. ....	0.829	0.9898
235–270° C. ....	0.878	1.0165
270–315° C. ....	0.942	1.0541
315–355° C. ....	1.001	1.1025

When processing the named oil and operating at the stated pressure and a temperature of 455° C., a period of one and one-half hours will provide a specific gravity in fractional parts of the beneficiated material falling between the preferred stated limits, and will also provide the stated percentage of newly formed materials boiling below 210° C.

The overall beneficiated material is cooled and inspected and found to have induced toxic properties as attested by the fact that it requires a smaller concentration for a given growth inhibition of wood destroying fungi than the starting material.

The overall beneficiation may be used as a preservative wood impregnant, or there may be segregated therefrom an oil complying with specifications extant, as for example an oil complying with the boiling range of a carbolineum type preservative oil, which in some instances boils almost entirely above 270° C.

The specific gravities of fractional parts of the beneficiated material noted in the foregoing are critical within limits. Unless the lower limit is approximated toxicity unveiling will be sacrificed. If the high limit is substantially exceeded adverse reactions will occur, as for example there will be inordinate gasification and/or production of highly polymerized and objectionable materials.

Instead of practicing the process disclosed in the immediate example by employing a protective gas of extraneous source, this mode of operation may be carried on without a gas of extraneous source with the resultant approximation of the noted specific gravities. Induced toxicity will also flow from the practice of this process variation.

*Example 7.*—In lieu of inducing toxicity whilst providing operational control of the overall spe-

cific gravity of fractional parts of the beneficiated material as heretofore disclosed, the control may be gauged by the provision of predetermined specific gravities of materials of cyclic structure content in fractional parts of the beneficiated material.

As an example, an oil of cyclic structure content produced by the petroleum industry having inherent but inhibited toxicity, no substantial percentage of fractions boiling below 270° C. and with in excess of 30% residual matter above 355° C. is heat treated in the liquid phase in the presence of a reforming catalyst and hydrogen at a temperature selected between the limits of 435–475° C. whilst under a pressure of 1800 pounds for such a length of time as to jointly provide more than 10% but less than 50% newly formed fractions boiling below 210° C., and a specific gravity 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 between the limits noted below:

Fractions	Low limit	High limit
210–235° C. ....	0.941	1.0430
235–270° C. ....	0.963	1.0606
270–315° C. ....	1.001	1.0783
315–355° C. ....	1.055	1.1135

When processing the named oil at a pressure and temperature of 1800 pounds and 460° C., respectively, a period of about one hour and 15 minutes will illustratively provide a specific gravity of materials of cyclic structure content in fractional parts of the beneficiation falling between the stated preferred limits.

When the beneficiation is inspected it is found to have toxic properties more pronounced than the parent material.

The provision of specific gravities of materials of cyclic structure content in fractional parts of the beneficiation noted in the foregoing is critical within limits. Unless the lower limit is approximated toxicity induction is sacrificed. If the high limit is exceeded adverse reactions will obtain, as for example there will occur inordinate gasification and/or production of highly polymerized materials.

In the mode of operation which induces toxicity whilst providing the stated increase of specific gravities in the materials of cyclic structure content, this process variation may be specifically practiced without the protective gas of extraneous source.

*Example 8.*—Referring specifically to the overall beneficiated material of induced toxic properties produced by the process variations of the foregoing examples, it is found that the materials boiling below and above 270° C. have relatively high and low toxicities, respectively. It is discovered that additional toxicity may be induced into the beneficiated material by subjecting same to another toxicity inducing cycle at a higher temperature than obtained in the first cycle of toxicity induction provided the retreatment yet maintains a preponderant percentage



of materials of ring structure content in at least a methylated condition. Referring specifically to the overall once beneficiated material of Example 1, this beneficiation is subjected to another toxicity inducing cycle in the liquid phase in the presence of a reforming catalyst and hydrogen at a temperature of 450° C. whilst under a pressure of 850 pounds. The retreatment is continued for a period of 45 minutes. The stated period is illustrative only. The retreatment period is desirably that which provides in the finally rebeneficiated material less than 50% newly formed materials boiling below 210° C., including the fixed gas or gases, based on the starting material. At the end of the stated period the retreated material is withdrawn from its treating enclosure, cooled, inspected and found to have toxic properties in excess of the overall once beneficiated oil. It is also determined that the finally beneficiated material yet maintains a preponderant proportion of the cyclic materials in at least a methylated condition.

When retreating the overall once beneficiated material, the process may specifically be carried on without the inclusion of the protective gas of extraneous source, and toxicity benefits will flow from this practice.

**Example 9.**—In lieu of retreating the entirety of the once beneficiated material at a more elevated temperature, only a portion thereof may be retreated in the liquid phase in the presence of a reforming catalyst, with or without the presence of a protective gas of extraneous source, and certain definite toxicity increases and benefits will flow therefrom, as for example, by retreating in liquid phase only the materials of relatively low toxicity boiling above 270° C. Or, the retreatment of materials boiling above 270° C., or a portion thereof, may be effected at the same temperature as the initial treatment. When the materials of relatively low toxicity are retreated for added toxicity induction at either of the temperatures aforementioned, the retreated material when commingled with that portion of the starting material once beneficiated, will provide a comminglement having toxic properties in excess of those of the once treated oil.

Instead of commingling the entirety of the once treated materials and the twice treated materials, only a portion thereof may be commingled provided the comminglement furnishes an oil conforming in boiling range to consumer acceptance or provides a comminglement from which may be segregated an oil of consumer acceptance.

The retreatment temperatures are selected between the limits of 300–550° C. and preferably between 425–500° C.

**Example 10.**—Practice the process of Example 1 with a molybdenum oxide catalyst.

**Example 11.**—Practice the process of Example 2 with a chromium oxide catalyst.

**Example 12.**—Practice the process of Example 3 with a vanadium oxide catalyst.

**Example 13.**—Practice the process of Example 4 with a tin oxide catalyst.

**Example 14.**—Practice the process of Example 5 with a molybdenum sulfide catalyst.

**Example 15.**—Practice the process of Example 6 with a chromium sulfide catalyst.

**Example 16.**—Practice the process of Example 7 with a vanadium sulfide catalyst.

**Example 17.**—Practice the process of Example 8 with a tin sulfide catalyst.

**Example 18.**—Practice the process of Example 9 with the coprecipitated oxides of copper and chromium as catalytic materials.

**Example 19.**—Practice the process of Example 1 with tin chloride as catalytic material.

**Example 20.**—Practice the process of Example 2 with aluminum chloride as catalytic material.

**Example 21.**—Practice the process of Example 3 with iodine as catalytic material.

**Example 22.**—Practice the process of Example 4 with iodoform as catalytic material.

**Example 23.**—Practice the process of Example 5 with hydroiodic acid as catalytic material.

**Example 24.**—Practice the process of Example 6 with chlorine as catalytic material.

**Example 25.**—Practice the process of Example 7 with bromine as catalytic material.

**Example 26.**—Practice the process of Example 8 with a hydrogen halid as catalytic material.

**Example 27.**—Practice the process of Example 9 with ammonium chloride as catalytic material.

**Example 28.**—Practice the process of Example 1 with pelleted bentonite clay as catalytic material.

**Example 29.**—Practice the process of Example 2 with activated Atapulugus clay as catalytic material.

**Example 30.**—Practice the process of Example 3 with a silica hydrogel as catalytic material.

**Example 31.**—Practice the process of Example 4 with a silica hydrogel impregnated with an aluminum salt as catalytic material.

**Example 32.**—Practice the process of Example 5 with bentonite and an adsorptive clay as catalytic materials.

**Example 33.**—Practice the process of Example 6 with a siliceous material impregnated with a metallic oxide as catalytic material.

**Example 34.**—Practice the process of Example 7 with a silicious material impregnated with a metal sulfide as catalytic material.

**Example 35.**—Practice the process of Example 8 with coprecipitated alumina and chromia hydrogels as catalytic materials.

**Example 36.**—Practice the process of Example 9 with a synthetic silica-alumina gel as catalytic material.

The various catalysts mentioned in the foregoing assist in the reforming, transforming, modifying and/or converting of the starting petroleum oils whereby to provide materials of induced toxic properties. These catalysts are employable either in the material remaining liquid under process controls, or in the evolved vapors, or both. Other than the catalysts mentioned in the foregoing, also employable are the various metals and their carbonates, cellulosic materials and carbon, activated or otherwise. Especially effective as catalytic materials are the 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.

The temperatures of the instant process, in any and all steps, are selected between the limits of 300–550° C., and preferably between 425–500° C. The pressures employed in the instant process are in excess of atmospheric and are specifically those pressures required for operation in the liquid phase. The term "liquid phase" may not be technically correct, but as used herein and in the annexed claims is meant to distinguish from the

so-called vapor phase operation which employs vaporized materials only.

If desired, instead of subjecting the entirety of the feed stock to a single toxicity inducing operation, the parent material may be segregated into a plurality of cuts and these plurality of cuts subjected to separate 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.

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.

Many modes of practicing the instant process are possible. As for example the oils of inherent but inhibited toxicity mentioned in the foregoing may be subjected to a destructive distillation under pressure in the presence of a reforming catalyst, with or without the presence of a protective gas of extraneous source, and toxicity induced therein. The following disclosures will enable those skilled in the art to practice such a process, at the same time adding details which will immediately suggest themselves as routine and non-inventive improvements.

If desired, a mixture of petroleum fractions characterized by cyclic structure content, as for example the Shell product shown in the foregoing tabular data, having inherent but inhibited toxicity is charged to a still adapted to operate at superatmospheric pressure which communicates with a condenser. The catalyst is selected from the materials aforementioned. Intermediate the still and the condenser is an appropriate needle valve adapted to regulate the pressure within the still due to the pressure of evolved vapors, or jointly due to the evolved vapors and the presence of an extraneous gas. The still is so arranged that evolved vapors are at least partially refluxed. The reflux ratio may vary over wide limits and different effects flow from varying percentages of reflux. Air is expelled from the still during the preliminary heating period and the needle valve then closed so as to develop the desired pressure within the still due at least partially to the pressure of evolved vapors. It is preferred to carry on the destructive distillation in the presence of a protective gas of extraneous source, as for example hydrogen or a hydrogen containing gas. The needle valve is then partially opened, and the valve aperture, heat control and reflux so coordinated as to provide a relatively constant flow of evolved vapors through the needle valve aperture.

Operating at a pressure of, as an example a hundred pounds or higher, say many hundreds of pounds, it is found that the oil under distillation is reformed, transformed, modified and/or converted and toxicity induced therein. It is also found that the temperature necessary for the distillation of any given percentage of the feed stock is considerably higher than for the distillation of a comparable percentage under substantially atmospheric pressure.

As the distillation proceeds the temperature is

gradually raised so as to maintain a relatively constant flow of distillate. The distillation is carried to the desired extent, as for example for the distillation reforming of 80% or more of the feed stock, or the distillation may be carried to the greatest extent possible. The time necessary for the distillation of a given charging stock will be determined by the speed of firing, percentage of reflux, etc., and the process may be illustrated by recovering 3-10% of the still charge per hour as materials of induced toxic properties.

If desired, the distillate may be redistilled under a similar destructive distillation to provide additional toxic properties.

In the event it is elected to employ hydrogen as the protective gas of extraneous source, in this or other examples, the hydrogen may specifically be secured from carbon monoxide and water in a well known manner.

While Examples 10 to 36 disclose the use of definite catalysts with definite ones of the Examples 1 to 9 inclusive, it is to be understood that these catalysts are interchangeable with the definite controls of the early examples, and any of the named catalysts or their equivalents are usable in any of the Examples 1 to 9. The examples given, and the catalysts linked therewith are for purposes of illustration only.

A very attractive form of carrying out a modified mode of the instant process is by inducing toxicity into the starting material in the presence of nitrogen or carbon dioxide. Thus, one mode of operation specifically provides for nitrogen and/or carbon dioxide as the protective gas or gases of extraneous source.

Minor changes within the scope of the annexed claims may be made without departing from the spirit of the invention.

We claim:

1. 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 liquid phase cracking conditions in the presence of a reforming catalyst at a temperature selected between the limits of about 425-500° C.; unveiling toxicity in the materials under treatment by continuing the named cracking operation for a period not in excess of about two hours, the period being so selected with reference to the chosen temperature and pressure so as to provide a percentage of newly induced materials boiling below 210° C. falling between the limits of 10-50%; securing the unveiled toxicity in a relatively high degree by a coordination of time, temperature and pressure which provides less than about 30% but more than about 5% saturates in the beneficiated material boiling between 270° C. and 355° C. whereby to provide an overall beneficiated material having substantial residual matter above 315° C. and a toxicity in excess of the starting material; and segregating from the beneficiated material an oil of the wood preservative type having induced toxicity and an initial boiling point at least as low as about 270° C., substantial residual materials boiling above 315° C., and an end boiling point at least as high as about 355° C., the fraction 270-355° C. of the segregation having a percentage of saturates falling between the limits above named.

2. The process of claim 1 with inclusion of car-



rying on the cracking operation in the presence of a protective gas of extraneous source.

3. 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 liquid phase cracking conditions in the presence of a reforming catalyst selected from the group consisting of oxides and sulfides of heavy materials at a temperature selected between the limits of about 425-500° C.; unveiling toxicity in the materials under treatment by continuing the named cracking operation for a period not in excess of about two hours, the period being so selected with reference to the chosen temperature and pressure as to provide a percentage of newly induced materials boiling below 210° C. falling between the limits of 10-50%; securing the unveiled toxicity in a relatively high degree by a coordination of time, temperature and pressure which provides less than about 30% but more than about 5% saturates in the benefited material boiling between 270° C. and 355° C. whereby to provide an overall benefited material having substantial residual matter above 315° C. and a toxicity in excess of the starting material; and segregating from the benefited material an oil of the wood preservative type having induced toxicity and an initial boiling point at least as low as about 270° C., substantial residual materials boiling above 315° C., and an end boiling point at least as high as about 355° C., the fractions 270-355° C. of the segregation having a percentage of saturates falling between the limits above named.

4. The process of claim 3 with the inclusion of carrying on the cracking operation in the presence of a protective gas of extraneous source.

5. 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 liquid phase cracking conditions in the presence of a reforming catalyst selected from the group consisting of halogens, halides and derivatives thereof including substitution and addition products thereof and substitution and addition products of the latter at a temperature selected between the limits of about 425-500° C.; unveiling toxicity in the materials under treatment by continuing the named cracking operation for a period not in excess of about two hours, the period being so selected with reference to the chosen temperature and pressure as to provide a percentage of newly induced materials boiling below 210° C. falling between the limits of 10-50%; securing the unveiled toxicity in a relatively high degree by a coordination of time, temperature and pressure which provides less than about 30% but more than about 5% saturates in the benefited material boiling between 270° C. and 355° C. whereby to provide an overall benefited material having substantial residual matter above 315° C. and a toxicity in excess of the starting

material; and segregating from the benefited material an oil of the wood preservative type having induced toxicity and an initial boiling point at least as low as about 270° C., substantial residual materials boiling above 315° C., and an end boiling point at least as high as about 355° C., the fraction 270-355° C. of the segregation having a percentage of saturates falling between the limits above named.

6. The process of claim 5 with inclusion of carrying on the cracking operation in the presence of a protective gas of extraneous source.

7. 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 liquid phase cracking conditions in the presence of a reforming catalyst of silicious content at a temperature selected between the limits of 300° C. and 500° C.; unveiling toxicity in the materials under treatment by continuing the named cracking operation for a period not in excess of about two hours, the period being so selected with reference to the chosen temperature and pressure as to provide a percentage of newly induced materials boiling below 210° C. falling between the limits of 10-50%; securing the unveiled toxicity in a relatively high degree by a coordination of time, temperature and pressure which provides less than about 30% but more than about 5% saturates in the benefited material boiling between 270° C. and 355° C. whereby to provide an overall benefited material having substantial residual matter above 315° C. and a toxicity in excess of the starting material; and segregating from the benefited material an oil of the wood preservative type having induced toxicity and an initial boiling point at least as low as about 270° C., substantial residual materials boiling above 315° C., and an end boiling point at least as high as about 355° C., the fraction 270-355° C. of the segregation having a percentage of saturates falling between the limits above named.

8. The process of claim 7 with inclusion of carrying on the cracking operation in the presence of a protective gas of extraneous source.

9. A wood preserving impregnant consisting in its entirety of a mixture of cracked petroleum fractions having less than about 30% but more than about 5% saturates in the materials boiling between 270-355° C., an initial boiling point at least as low as about 270° C., a final boiling point above 355° C. and not less than about 45% boiling up to 355° C. and substantial residual material above 315° C.

10. A wood preserving impregnant consisting in its entirety of a mixture of cracked petroleum fractions having in the materials boiling between 270-355° C. less than about 30% but more than about 5% saturates, an initial boiling point not substantially above 270° C., a final boiling point above 355° C. and not less than about 65% boiling up to 355° C. and substantial residual material boiling above 315° C.

JACQUELIN E. HARVEY, JR.,  
ROBERT H. WHITE, JR.,  
JOSEPH A. VAUGHAN.