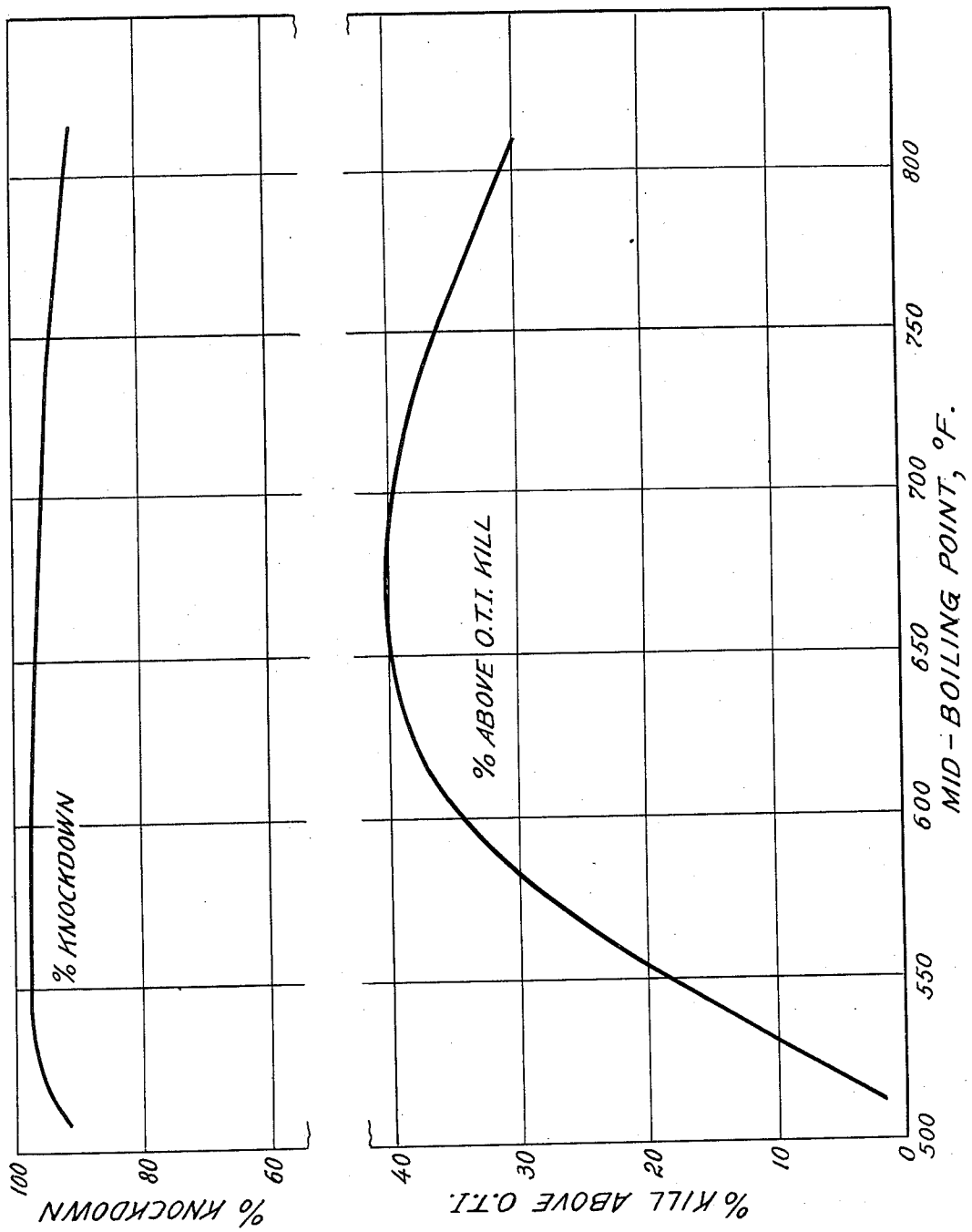
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TOXICANT PETROLEUM PRODUCTS

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TOXICANT PETROLEUM PRODUCTS

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Petroleum products have been heretofore used in insecticides such as household fly sprays, cattle sprays, and the like, as carriers or bases for toxicant ingredients of non-petroleum origin. Certain petroleum fractions have been used for pest control, in handling pests such as mosquitoes, where the action is a physical one, such as smothering, rather than toxic. Other petroleum fractions have been used as orchard sprays, etc., where a relatively light toxicity sufficed. Certain products, such as ketones, and the like, of petroleum origin, but of greatly altered chemical nature have lately appeared as toxicants of higher potency for use in combinations such as household fly sprays. Some fractions derived from petroleum cracking are known to possess some toxicity in such use. One such product has reached a fairly high level of toxicity, being able to attain a Peet Grady rating of A, as hereinafter explained, when present to the extent of 40% in admixture with a non-toxic insecticide base oil.

This invention has for its object the provision of a process for the production of an insecticide toxicant of unusually and unexpectedly high potency, as well as the provision of that product. It is based upon the unexpected discovery that when gas oil is subjected to a certain sequence of catalytic cracking steps of a nature hereinafter described, substantial quantities of a toxicant having eight to twenty or more times the killing power of any previously known toxicant of petroleum origin may be recovered.

As is well known in the petroleum industry, petroleum fractions of gas oil nature boiling within the range 300–800° F. and more usually between about 500–750° F., may be cracked to lower boiling point products by bringing them into contact at temperatures of 800–900° F. with contact mass materials partaking of the general nature of clays. Such processes are well developed in patents issued to Eugene Houdry and others and are spoken of collectively as vapor phase catalytic cracking. In such processes when operating upon fresh stocks about 30–40% of the charge stock is converted to a material boiling below about 410° F., a small portion becomes permanent gases, a small portion becomes a solid cokey material which is deposited upon the catalyst or contact mass and the remainder is a material which in its generalized physical characteristics is not greatly different from the original charge stock. The catalytic contact mass used in such processes is of the nature of a clay, in quite general terms, in that it is usually a natural or synthetic association of alumina and/or silica, such as fuller's earth, or other natural clays, acid treated clays, clays treated by other processes, and synthetic materials arising from the precipitation and after-treatment of gels of varying compositions, any of which may or may not have other materials such as certain metallic oxides added to them to assist in their catalytic effect. These materials have in the art been designated generally by the term "adsorptive contact mass materials." It is also customary in the art to subject either the low boiling fraction produced by such cracking or higher boiling fraction apparently unaffected by its first exposure to such cracking to a second exposure to a contact mass of the same general nature for certain purposes. For example, a gasoline fraction from a first-pass cracking may be retreated for the purpose of rendering the gasoline more suitable for aviation fuel and this operation while charging a low boiling stock similarly gives rise to a portion of oil of boiling range much higher than that usual for gasoline. In some circumstances, heavier products from this operation may again be subjected to this kind of cracking giving rise once more to light products within the aviation gasoline boiling range and heavier products having a higher boiling range.

In the case of the re-cracking of heavier stocks from the first cracking operation, the general characteristics of the operation are quite similar to the first cracking operation from which the heavier stocks charged to the second cracking operation are derived.

This invention is based upon the discovery that there may be isolated from high boiling products resulting from multiple pass cracking in the presence of adsorptive contact masses an insecticide toxicant of unusually high killing power. The toxicant is specifically that portion of heavier products of multiple pass cracking in the presence of an adsorptive contact mass having a mid-boiling point between about 550 and 800° F., coupled with appropriate specific gravity, as hereinafter described, or any portion of the material boiling within that range having other properties specified, and coming from such a source. In connec-

tion with these materials, attention is called to the drawing attached to and made a part of this specification in which are is shown graphically the unusual high toxicity of this material.

The basis of the data presented in this drawing is the accepted commercial standard test for household insecticide, known as the Peet Grady method and described in a U. S. Department of Commerce Bulletin "Household Insecticide" (Liquid Spray Type) designated as "Commercial Standards CS72–38."

A short description of the method and test is that it consists of exposing two groups of house flies from the same culture in parallel chambers to the insecticide being tested and to an official test insecticide. The results of such a test are reported in terms of "knock down," that is, the number of flies which have fallen to the floor after a specified period of exposure and "kill" as compared with the official test insecticide. In rating an insecticide, the following rating is used:

Grade	Difference between 24-hour "percentage kill" of insecticide and that of O. T. I.
AA	+16 or greater
A	+6+15
B	−5+5

With this basis the meaning of the drawing will become clear. It was arrived at by selecting cuts of narrow boiling range from the heavy oils described hereinabove and making up a series of insecticides in each of which the narrow cut fraction was employed to the extent of 5% in admixture with a substantially non-toxic insecticide base oil of the kind usually used in the art, which insecticide base oil was a well treated light petroleum product boiling substantially between about 350° F. and 450° F. The drawing plots "knock down" and "kill" and compares the latter with the official test insecticide (O. T. I.), against the boiling point of the cut employed as toxicant.

From the drawing it will be noted that in all cases the "knock down" was substantially in excess of 90%. The "kill" plotted in the lower curve in the drawing shows the comparison between the insecticide composition so made and the official test insecticide. In other words, a mixture of 95% of insecticide base oil described, and 5% of the toxicant cut having a mid-boiling point of 550° F., killed 18½% more flies than did the official test insecticide and fractions having mid-boiling points of 650–700, used in the same concentration, killed 40% more flies than did the official test insecticide. In other words, an insecticide containing 5% of the materials herein described and having a mid-boiling point of about 550 or above, is a grade AA insecticide. These high toxicites are quite unusual for materials of petroleum origin.

The materials may be isolated from high boiling stocks resulting from multiple pass cracking in the presence of adsorptive catalysts by a comparatively simple process of distillation. They may be used in the form of a broad cut boiling between about 500° F. and 750° F. or more preferably, in the form of relatively narrow cuts having a boiling range of not over about 125° F. between the 10% over point and the 90% over point, and having a mid-boiling point of about 550° F. or higher. The preferable toxic component is a similar cut of narrow boiling range having a mid-boiling point lying between 600° F. and 750° F. These products possess physical properties quite different from virgin stocks of similar boiling range, as may be seen from the following:

Table I

	Cut from multiple pass cracking	Cut from virgin crude stock
Boiling range, °F	500–750	500–750
Gravity, °A. P. I.	9.5	32.5
S. U. V. @ 100° F. seconds	44	50
Visc. grav. const.	1.0038	.8371
Aniline point, °F.	−20	180
Pour point, °F.	Below zero	45

These differences are even more marked with narrow cuts, as follows:

Table II

	Cut from multiple pass cracking	Cut from virgin crude stock
Boiling range, °F	610–740	610–740
Gravity, °A. P. I.	1.9	30.5
S. U. V. @ 100° F. seconds	106	72
Visc. grav. const.	1.0574	.8370
Aniline point, °F.	12	188
Pour point, °F.	Below zero	60

These properties may be achieved by repetitive cracking of cracked products until that portion of the cracked products boiling from about 400° F. upwards, inclusive, has attained a specific gravity (compared with water upon the usual 20°/4° basis), of 1.000 or greater, preferably 1.010 or greater, after which it is fractionated to discard those portions boiling below about 550° F., and the remainder, or, preferably, selected portions thereof are utilized as the toxicant. The whole material does not have the relatively high toxicity of certain portions therein present, and is otherwise not of highly desirable nature as an insecticide, so that it is preferred to use selected cuts. It is in these selected cuts that the full force of the surprisingly high toxicity may be realized. Referring again to the drawing, a cut having a mid-boiling point of about 650° F. and a boiling range of about 125° F. between 10% over and 90% over, has a kill of +40 when present to the extent of 5% in admixture with a non-toxic base. With such narrow cuts the other physical properties lend themselves admirably to insecticide uses.

These physical properties are themselves of interest. A cut having a mid-boiling point of 550° F. will have a specific gravity of 0.990 or frequently somewhat greater, with higher boiling point cuts correspondingly heavier. All of these cuts will be of relatively light color, and will be fluid at ordinary temperatures. All but the heavier cuts will be fluid below 0° F. These cuts will have viscosity-gravity constants in excess of 1.000, increasing with boiling point. Considering all cuts from about 400° F. upwards, successive narrow cuts will have aniline points passing through a minimum of about −30° F. just as we enter into the lower end of the group of cuts herein claimed, with this property increasing numerically thereafter as boiling point of the cut increases.

The toxicant cuts indicated may be used in admixture with such bases as that heretofore described for the production of non-staining, highly toxic household sprays having good odor char-

acteristics. They may be used with heavier oils as bases for other purposes, such as cattle sprays, horticultural sprays, and agricultural and industrial insecticides generally. The concentration of 5% mentioned hereinbefore is merely for purposes of defining the level at which tests were made and at which toxicity is defined. The actual concentration to be used may be widely varied, dependent upon purpose to be accomplished, and may well be as high as 50% of toxicant for certain purposes.

Additionally either the oils containing the toxicants, or in certain cases the toxicants themselves, may be utilized in emulsified form in aqueous dispersions, using dispersing agents usual in this art, such as petroleum sulphonic acid derivatives and other common emulsifiers for oils.

We claim:

1. An insecticide composition containing as a characterizing ingredient, a material derived from a petroleum fraction by a multiple pass cracking in the presence of adsorptive contact mass material having an initial boiling point of the order of 500° F. and a mid-boiling point of at least about 550° F. and not over about 750° F. and having a killing power when present in a concentration of 5% in a non-toxic insecticide base oil as measured by the official Peet Grady test of at least 16% greater than the official test insecticide under comparable conditions.

2. An insecticide characterized by the presence of a toxic ingredient derived from a petroleum fraction which has been subjected to multiple pass cracking in the presence of an adsorptive contact mass which toxic agent has a boiling range between the 10% over and 90% point of not over about 125° F., which has a mid-boiling point of at least 550° F. and not over about 750° F. and which when subjected to Peet Grady test as an insecticide composition having 5% of a toxic ingredient and 95% of a non-toxic insecticide base oil has a comparative killing power of at least 16% greater than the official test insecticide under comparable conditions.

3. An insecticide characterized by the presence of a toxic ingredient derived from a petroleum fraction which has been subjected to multiple pass cracking in the presence of an adsorptive contact mass which toxic agent has a boiling range between the 10% over and 90% point of not over about 125° F., which has a mid-boiling point lying between about 600° F. and 750° F. and which when subjected to Peet Grady test as an insecticide composition having 5% of a toxic ingredient and 95% of a non-toxic insecticide base oil has a comparative killing power of at least +30% greater than the official test insecticide under comparable conditions.

4. An insecticidal hydrocarbon oil derived from petroleum by multipass catalytic cracking boiling substantially within the range of from about 500° F. to 750° F., having a mid-boiling point of at least about 550° F., having a specific gravity of about 1.00 or greater, having a viscosity gravity constant of at least about 1.00 and having a pour point of not greater than 0° F., which, when subjected to Peet Grady test as an insecticide composition having 5% of toxic oil and 95% of a non-toxicant insecticide base oil has a comparative killing power of at least 16% greater than the official test insecticide under comparable conditions.

5. An insecticidal hydrocarbon oil derived from petroleum by multipass catalytic cracking having a boiling range between 10% over and 90% point of not over about 125° F., coupled with a mid-boiling point of at least 550° F. and not over about 750° F. and coupled with a viscosity gravity constant of at least about 1, which, when subjected to Peet Grady test as an insecticide composition having 5% of toxic oil and 95% of a non-toxicant insecticide base oil has a comparative killing power of at least 16% greater than the official test insecticide under comparable conditions.

6. An insecticidal hydrocarbon oil derived from petroleum by multipass catalytic cracking having a boiling range between 10% over and 90% point of not over about 125° F., which has a mid-boiling point line between about 600° F. and 750° F., coupled with a specific gravity of about 1.00 or greater, coupled with a viscosity gravity constant of at least about 1.00, which, when subjected to Peet Grady test as an insecticide composition having 5% of a toxic ingredient and 95% of a non-toxic insecticide base oil has a comparative killing power of at least +30% greater than the official test insecticide under comparable conditions.

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