T H E S I S

AN INVESTIGATION OF THE INSECTICIDAL VALUE OF EXTRACTS FROM COLORADO OIL-BEARING SHALE.

Submitted by

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Mr. Lee Jenkins

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INTRODUCTION

Colorado has, according to U. S. Geological Survey (1), 896,000 acres of oil-bearing shale. McKee (2) stated that combined deposits of Colorado and Wyoming could furnish 15 times as much oil as is now being supplied from oil wells of the country. This abundant source of oil furnishes a possibility of great industrial development in the region. Up till the present time oil has been produced from shale in the United States only on an experimental scale. The reason for this lack of development is the abundant supply of petroleum oil which can be obtained at a lower cost of production than oil from shale.

The oil shale furnishes valuable by-products not found in petroleum oil. McKee (2) reported that no nitrogen compounds of any value were found in petroleum oils, but from oil shale ammonia and basic nitrogen compounds related to pyridine can be obtained. The possibility of by-products has interested investigators. If by-products of sufficient value could be produced, the production of oil from shale could be put on a paying basis. Previous investigations of other workers (3 & 4) determined the presence of nitrogen base materials in the oil shale. The similarity in chemical composition of known nitrogen compounds in the shale oil to some of the vegetable alkaloids has aroused interest as to their insecticidal value.

Stauffer (3) investigated the nitrogen bases from the shale oils of Colorado and made a few tests on aphids. He reported favorable results. His results aroused the interest of Mr. J. W. Horne and Mr. C. P. Hopkins of the Bureau of Mines at Boulder. Arrangements were made to carry on an investigation of the insecticidal value of shale oil extracts at the Colorado State College, under the supervision of Dr. List, Station Entomologist. The various fractions of the shale oil were to be extracted at the Bureau of Mines at Boulder by Mr. Carl Hopkins, Junior chemist and Mr. J. W. Horne, Engineer in charge of the cooperative shale oil research laboratory at Boulder, Colorado.

Mr. Floyd Randolph made some tests with a few of the materials during the summer of 1931. He lost his life in an automobile accident during the summer.

The writer began work on the project in September of 1931 and continued till September 1932.

The purpose of this investigation was to test the various fractions of the shale oil as contact insecticides, including the margin of safety to plants, and to find a satisfactory method of emulsification.

LITERATURE CITED

Oil from shale has been produced in Scotland for about 80 years. In the earlier days the tar remaining after the oil had been removed was burned or discarded. In 1902 Garret and Smythe (4) became interested in the possibilities of recovering valuable nitrogen extracts as by-products. They were able to isolate the following nitrogen bases from the Scottish shale oils:

Pyridine B.P. 115 - 116°C

2-Methylpyridine B.P. 129.5°C (763 mm)

2: 6-Dimethylpyridine B.P. 142.5°C (760 mm)

2: 4-Dimethylpyridine B.P. 159-159.5°C

2: 5-Dimethylpyridine B.P. 154-155°C

2:4: 6-Trimethyl pyridine B.P. 170.5°C (763 mm)

Stauffer (3) isolated Symetrical collidine ($C_5H_2(CH_3)N$ and 2 methyl 5-ethyl pyridine ($C_5H_3(CH_3)(C_2H_5)N$) from the lower boiling fractions of the Colorado shale oil taken from De Beque, Colorado. He found that the nitrogen bases distilling below 300°C were primarily tertiary amines. From his tests he decided that the nitrogen bases from the Colorado shale oil which boil below 300°C are similar in physical properties to nitrogen bases from coal tar. The quinolines, isoquinolines and hydrogenated quinolines found in the coal tar are not present in the nitrogen bases from the shale oil, except possible traces.

Hopkins and Horne (5) decided that while only two nitrogen compounds have been definitely isolated from the Colorado shale oil, it is safe to assume that they are similar to materials extracted from the Scottish shale oils (4) and consist for the most part, of piperidine homologues with varying amounts of pyrrols and piperidines in the higher boiling point fraction.

Schreiner and Reed (6) found the quinolines to be more toxic to wheat seedlings than the pyridine homologues. Since the quinolines are not found in nitrogen bases from the shale oil these extracts should not be so toxic to plants as the nitrogen bases from coal tar.

DeOng (7) suggested that insoluble nitrogen bases and chlorinated benzenes have some advantages over nicotine even though the nicotine is more toxic. This is due to the fact that insecticides soluble in both water and oil have a tendency to diffuse into the water when left standing in emulsion.

There has been some variation in the results obtained by different investigators in regard to the effectiveness of nitrogen bases as contact insecticides.

Theobald (8) found that pyridine was promising as a substitute for nicotine for some species of aphids. Richardson and Smith (9) investigating the toxicity of some organic compounds to *Aphis rumicis* Linneaus found the pyridines from coal tar to be of little value. The concentrations toxic to *Aphis rumicis* was sufficient to injure dwarf nasturtiums.

Richardson and Haas (10) reported nicotine at 25°C to be about 31 times as toxic as pyridine to *Tribolium confusium* Duval. Neither nicotine nor pyridine showed appreciable anesthetic properties. However, partial recoveries were greater with nicotine than pyridine.

Dingemanse and Wibaut (11) experimented with amino-pyridine on frogs, rabbits, and cats and found it produced a period of paralysis followed by spasms.

Stauffer (3) used the kerosene fraction of the shale oil emulsified with equal parts of fish oil soap on *Myzus persicae* Sulzer on cabbage and obtained fairly good results without injury to the plant. He had better results when he used soap chips (Proctor & Gamble) 22 grams, shale oil 25 grams and water 50 grams to make up the stock solution. This emulsion at 1.25% gave him 97 to 100% kill. He attributed a large part of the insecticidal value of the kerosene fraction to the presence of nitrogen bases and to the high percentage of unsaturates present.

Stauffer's (3) results indicate that the toxicity of various fractions of shale oil distillate is greatest in the distillate of about 250°C, but is of insecticidal value through the range of 200°C to 350°C.

PROCEDURE

The winter season was near at hand when work on the shale oil extracts was resumed in the fall of 1931. In order to have a supply of insects available for tests during the winter it was necessary to grow plants in the greenhouse and infest them. A portion of the greenhouse west of the entomology building on the campus of the Colorado State College was used for this work. A number of the common garden plants, such as cabbage, turnips, navy beans, peas, potatoes and tomatoes were started. Several hundred coleus cuttings were rooted. From time to time infested plants were obtained from commercial greenhouses. All these plants weregrown in pots for convenience in making spray tests.

The extracts were only available in small quantities at one time so a small atomizer was used to apply the sprays. Many of the applications were made on cuttings, placed in water to keep them fresh. The stem was inserted in a hole in a piece of paper placed over the top of a bottle. Each bottle was then placed on a pie plate around the edge of which was placed a ring of tanglefoot to prevent the escape of the aphids. This method was used especially for application on _Macrosiphum sanborni_ Gillette on chrysanthemum.

In tests on _Myzus persicae_ Sulzer on turnip the whole plant was sprayed and the pot containing it placed on a pie plate treated with a ring of Tanglefoot around the edge. Counts were made at intervals of 48 hours after spraying.

Applications on coleus for mealy bug control were made, using the whole plant and isolating the sprayed plant from any source of reinfestation. Counts were made 48 hours after spraying.

Dormant tests were made on European elm scale both in the laboratory and in the field.

During the summer tests were made on aphids found to be abundant on shrubs on the campus. The spirea aphis were found to be the most numerous and were located near the greenhouse, so were used for a number of tests.

Each material of shale oil origin was given a number for convenience in taking and tabulating the records. In some cases combinations of materials were given numbers to designate them.

MATERIALS

The various fractions of the shale oil used were extracted at the laboratory of the U. S. Bureau of Mines at Boulder by Mr. Carl Hopkins and Mr. J. W. Horne.

The shale oil all came from the experimental plant of the U. S. Bureau of Mines at Roulison, Colorado.

The extracts from the shale oil were tested as they were supplied and insects found available. It was necessary to add an emulsifer to the nitrogen base materials. Saponin was used in a number of the tests because it has been found by Richardson and Shephard (12) to have very little toxicity to Aphis rumicis at 1% concentration, while .3% fish oil soap, a common emulsifier, gave 44% kill. Some of the oils were made miscible at the laboratory at Boulder and required no addition of an emulsifying agent.

A number of other materials and combinations of materials were tested as emulsifiers for the nitrogen bases. The more generally used ones were ammonium oleate, potassium oleate and penetrol. The nitrogen base materials were checked against standardized commercial products on the market, such as nicotine, nicotine sulfate and commercially prepared miscible oils.

RESULTS

Miscible Shale Oils

A number of tests were made using miscible shale oil on Macrosiphum sanborni Gillette on chrysanthemum. Several miscible oils of various fractions containing a high percentage of unsaturated hydrocarbons were tested. These oils all showed a marked tendency to burn the plants when used at concentrations sufficiently high to kill the insects. These oils were compared with Verdol, a summer oil prepared by the Standard Oil Company.

The miscible kerosene Be'35 at 0.4% concentration gave 25% kill on Macrosiphum sanborni Gillette, with no apparent burning to the chrysanthemum leaves.

The miscible gas oil Be'28^{o} at 0.4% concentration gave only 12% kill on Macrosiphum sanborni on chrysanthemum.

The total kerosene gas oil fraction, Hempel distillation, at .4% concentration, gave no kill on Macrosiphum sanborni. The miscible kerosene gave better results than the gas oil or the total kerosene and gas oil.

A 1% emulsion of Verdol gave 50% kill and at 2% gave 100% kill on Macrosiphum sanborni. Verdol at 2%

gave 15% burn on navy bean leaves.

Miscellaneous Materials

The Napthenic separate from the gas oil was tested for use as an emulsifying agent for the nitrogen base materials. It was found to cause burn on cabbage leaves at .5% concentration. It was not used extensively because of the toxic effect upon plants.

The alkaline wash from the pressure distillate killed only 80% of *Macrosiphum sanborni* on chrysanthemum and caused 50% burn on cabbage when applied at a concentration of .5%.

The filtrate from the retort condenser water with oleic acid added was toxic to *Macrosiphum sanborni* at 12% and showed no burning on cabbage leaves at 100% concentration. The quantity of this material which was available for tests was limited so it was not tested as thoroughly as the other materials. This material gave promising results.

The filtrate from the retort condenser water killed 89% of *Macrosiphum sanborni* at 25% concentration and caused no burn on cabbage leaves. There was slight burning at a concentration of 50%.

The water from the steam distilled nitrogen bases condensed to 20% of the original volume, killed only 95% of *Aphis spiraecola* Patch.

The water soluble material from the nitrogen bases from the kerosene killed 100% of *Aphis spiraecola* Patch at 8% but caused 25% burn on spirea. The concentration necessary to kill aphids burned the plants.

Numerous tests were made of the materials in the miscellaneous group. All were discarded except the filtrate from the condenser water.

The Nitrogen Base Materials: Tables are submitted for the results secured with the various nitrogen bases. The most promising of these was tested in combination with a number of other materials to see if small amounts could be added to a carrier such as a miscible oil and increase the toxicity of the oil to insects without causing injury to plants.

Table No. 1 gives the results of tests of crude nitrogen bases from the pressure distillate on aphids. For convenience in tabulation this material is designated as No. 11 in the table. The napthenic separate from the gas oil was tabulated as No. 17 and was used to some extent as an emulsifying agent. The combination of No. 11 with oil and emulsifying agents is given the number 6.

No. 6 is composed of sulfonated compounds from the pressure distillate 50 grams; No. 11, 25 grams; shale kerosene 50 grams; alcoholic potash till neutral;

5 grams of oleic acid. No. 6 was tested on aphids, red spider and mealy bugs. Saponin was added in some tests to see if the toxicity to insects could be increased by using this material as a spreader.

Table No. 1

Material No.	Concentration	No. insects	% kill 48 hours	Insect
11 17	0.8% 0.2%	35	2.8	*Myzus persicae*
11 Saponin	0.8% 0.25%	30	70	" "
11 Saponin	0.4% 0.025%	26	100	*Macrosiphum sanborni*
11 Saponin	0.27% 0.025%	23	74	"
11 Saponin	.2% .025%	26	30	"
6	2%	30	100	"
6	2%	20	100	"
6	2%	130	100	"
6	1.5%	160	94	"
6	1.5%	18	84	"
6	1%	41	100	"
6	1%	20	75	"
6	1%	122	90	"
6	.75%	23	42	"
6	.5%	52	100	"
6	.5%	10	90	"
6	.5%	124	60	"
6	.25%	9	21	"
6 Saponin	.2% 0.025%	101	99	"
6 Saponin	1.5% 0.025%	163	92	"
6 Saponin	1% 0.025%	205	78	"
6 Saponin	0.5% 0.025%	98	5	"

Material No.	Concen- tration	No. insects	% kill 48 hours	Insect
6 Saponin	2% 0.025%	19	65	*Tetranychus telarius*
6	2%	35	3	*Pseudococcus citri*
Saponin	0.025%			
6	1.5%	26	0	"
6	1%	11	0	Codling moth eggs
Sunoco	1%	12	16	" "

No. 11, when used at .4% concentration on cabbage leaves caused 50% burn. While toxic to insects at a low concentration there was no margin of safety to the plant.

No. 6, at 2%, caused no burn on cabbage and was satisfactory in control of *Macrosiphum sanborni*. At 1% it had no ovicidal value on codling moth eggs.

The tertiary amines, No. 12, from the pressure distillate were extracted by Mr. Hopkins in an attempt to isolate the material in the crude product which was toxic to insects.

Table No. 2 indicates the results obtained from tests of material No. 12 on aphids.

Table No. 2

Material No.	Concen- tration	No. insects	% kill 48 hours	Insect
12 Saponin	0.8% 0.025%	50	70	*Myzus persicae*

Material No.	Concentration	No. insects	% kill 48 hrs.	Insect
12 Saponin	0.4% 0.025%	*60	100	*Macrosiphum sanborni*
12 Saponin	0.4% 0.025%	40	5	"
12 Saponin	0.27% 0.025%	23	80	"
12 Saponin	0.2% 0.025%	*	* 75	"

The tertiary amines (No. 12) gave almost exactly the same results as is shown in Table No. 1 with material No. 11. This was true both with regard to insect kill and plant injury.

The crude nitrogen bases from the kerosene (No. 13) were tested on *Myzus persicae* and *Macrosiphum sanborni*. Table No. 3 indicates the results obtained.

Table No. 3

Material No.	Concentration	No. insects	% kill 48 hrs.	Insect
13 17	0.8% 0.2%	*50	100	*Myzus persicae*
13 Saponin	0.8% .025%	*60	100	" "
13 Saponin	0.2% 0.025%	*75	100	" "
13 Saponin	0.8% 0.025%	*	*92	*Macrosiphum sanborni*

* Estimated numbers.

Material No.	Concentration	No. insects	% kill 48 hrs.	Insect
13 Saponin	0.4% 0.025%	27	85	*Macrosiphum sanborni*
13 Saponin	0.27% 0.025%	20	75	"
13 Saponin	0.2% 0.025%	42	85	"
13 Saponin	0.2% 0.025%	28	75	"

The crude nitrogen bases from the kerosene caused 100% burn on cabbage leaves at .2% concentration when emulsified with Saponin. There was severe burning at concentrations high enough to give satisfactory kills on aphids.

The steam distilled nitrogen bases from the kerosene (No. 14) were tested in combination with a number of different emulsifying agents including penetrol and ammonium oleate. Saponin produced an unstable emulsion which began to separate out in a few minutes unless kept well agitated. Penetrol, which is an oxidized sulfonated gas oil prepared by the Kay Frye Laboratories, for use as a contact insecticide in combination with nicotine, formed a satisfactory emulsion at the ratio of 1 part penetrol to 8 parts of No. 14. Other materials used in combination with No. 14.

No. 39
(Potassium oleate 10 grams
(No. 14 20 cc.
(Water 25 cc.

No. 66
Oleic acid 40 cc.
Alcohol 10 cc.
Ammonium hydroxide 5 cc.

Dendrol, a miscible oil for dormant applications.

Sunoco, a miscible oil for dormant use.

B. L. 40 - Black Leaf 40 or 40% nicotine sulfate.

Nicofume - free nicotine 40%.

The samples of No. 14 provided at different times varied somewhat in color and in the amount of emulsifying agent required to form a satisfactory emulsion. There was also a difference in the appearance of the emulsion formed from the first sample. The first sample was dark brown in color when emulsified but later samples were milky in appearance after being emulsified.

Table No. 4 indicates the results obtained when No. 14, with the various combinations, was applied on aphids, mealy bugs, red spider, and as a dormant spray on European elm scale.

Tests were made on European elm scale both in the laboratory and in the field. Material for all tests was obtained from Boulder.

Table No. 4

Material No.	Concentration	No. insects	% kill 48 hrs.	Insect
14 Saponin	.8% .025%	38	100	*Macrosiphum sanborni*

Material No.	Concentration	No. insects	% kill 48 hrs.	Insect
14 Saponin	.4% .025%	56	98	<u>Macrosiphum sanborni</u>
14 Saponin	.4% .025%	78	97	"
14 Saponin	.24% .025%	11	36	"
14 Saponin	.2% .025%	61	97	"
14 Saponin	.2% .025%	59	91	"
14 17	.8% .2%		*98	<u>Myzus persicae</u>
14 Saponin	.8% .025%		*100	" "
14 Saponin	.4% .025%		*100	" "
14 Saponin	.2% .025%		*1	" "
14 Penetrol	.66% 1.33%	62	100	<u>Macrosiphum sanborni</u>
14 Penetrol	.5% 1 %	47	100	"
14 Penetrol	.5% 1 %	42	80	"
14 Penetrol	.125% .875%	102	99	"
14 Penetrol	.2% .8%	150	100	"

*Numbers estimated

Material No.	Concentration	No. insects	%kill 48 hrs.	Insect
14 Penetrol	.33% .666%	79	100	*Macrosiphum sanborni*
14 Penetrol	.33% .666%	200	96	"
14 Penetrol	.33% .66%	31	63	"
14 Penetrol	.5% .5%	110	100	"
14 Penetrol	.2% .5%		*85	"
14 Penetrol	.15% 1.5%	680	97	"
14 Penetrol	.06% .44%	130	95	"
14 Penetrol	.1% .4%	140	100	"
14 Penetrol	.166% .334%	37	100	"
14 Penetrol	.166% .334%	104	95	"
14 Penetrol	.166% .334%	36	11	"
14 Penetrol	.05% .2%	124	97.5	"
14 Penetrol	.08% .166%	114	98	"
14 Penetrol	.03% .119%	62	78	"
14 Penetrol	.08% .16%	100	94	"

*Numbers estimated.

Material No.	Concentration	No. insects	% kill 48 hrs.	Insect
14 Penetrol B.L. 50	.5% .03% .016%	*300	100	Aphis spiraecola Patch
14 Penetrol B.L. 50	.5% .03% .016%	*250	100	"
14 Oleic acid 66	.5% .06% .25%	115	75	Aphis spiraecola Patch
14 Nicofume 66	.5% 1-10,000 .065%	200	90	"
14 66 Nicofume	.5% .065% .016%	*325	100	"
14 66 Nicofume	.5% .06% .008%	142	80	"
14 66 Nicofume	.25% .03% .02%	88	92	"
14 66 Nicofume	.5% .125% .5%	3	100	Squash bugs
14 66	.75% .37%		* 100	Clavigerus smithiae
14 66	.75% .37%		* 95	"
14 66	1 % .2 %		* 25	Aphis spiraecola

*Numbers estimated.

Material No.	Concentration	No. insects	% kill 48 hrs.	Insect
14 66	.75% .25%		* 50	*Aphis spiraecola*
14 66	.5% .25%		* 1	"
14 66	.5% .25%		* 98	*Clavigerus smithiae*
14 66	.5% .25%		* 95	"
14 66	.5% .25%		* 15	*Aphis spiraecola*
14 66	1 % .25%		* 25	"
14 Penetrol	.66% 1.33%	30	93	*Tetranychus telarius* Linne.
14 Penetrol	.33% .666%	18	78	"
14 Penetrol	.166% .334%	13	38	"
14 Nicofume 66	.5% 1-6000 .06%	8	0	"
14 Nicofume 66	.5% 1-10,000 .065	6	0	
14 30	.16% .5%	270	94	*Myzus persicae*
Volck 14	3 % .25%		Few small ones killed	*Pseudococcus citri* Risso

Material No.	Concentration	No. insects	% kill 48 hrs.	Insect
Volck Penetrol 14 B.L. 40	1 % 1% .125% .125%	Small ones killed		Pseudococcus citri Risso
Volck Penetrol B.L. 40	2% 1% .125	" "	"	"
Volck "	3% 3%	Few small ones killed		"
Dendrol	1%			"
Dendrol	1%			"
Laboratory Tests - No. 14 in combinations. Dormant				
Penetrol 14	6% .5%	42	100	Gossyparia spuria Modeer
Penetrol 14	4% .5%	50	100	"
Penetrol 14	2% .5%	50	90	"
Penetrol 14	1% 1%	60	100	"
Dendrol 14	4% .5%		*100	"
Dendrol 14	3% .5%		*100	"
Dendrol 14	2% .5%	100	100	"
Laboratory Test				
Sunoco 14	8% .5%		*100	"
Sunoco 14	4% .5%	33	100	"

Material No.	Concentration	No. insects	% kill 48 hrs.	Insect
Check		48	77	
Sunoco 14	2% .5%	30	84	<u>Gossyparia spuria</u>
Sunoco	15%		*100	"
"	10%	33	100	"
"	8%		*100	"
"	4%	40	92	"
Dendrol	8%		*100	"
"	6%		*100	"
"	5%		*100	"
"	4%	33	100	"
"	3%	12	33	"
		Field Tests - Dormant		
Dendrol 14	1.5% .5%	40	100	"
14 13 Oleic acid	.5% .5% .25%	44	66	"
Check		50	76	"
Dendrol 14	3% .5%	40	91	"
Dendrol 14	3% .5%	22	95	"
Dendrol 14	2% .5%	40	97	"
Check		40	82.5	"
Penetrol 14	1% 1%		* 66	"
Sunoco 14	2% .5%	40	100	"
Check		40	80	"

*Number estimated.

Material No.	Concentration	No. insects	% kill 48 hrs.	Insect
Penetrol	6%	40	100	<u>Gossyparia spuria</u>
Penetrol	5%	40	90	"
Check		40	80	"
Sunoco	4%	50	100	
Sunoco	3%	40	80	"

Table No. 4 shows the nitrogen bases from the kerosene to be toxic to insects at low concentration. There was no burning on cabbage leaves at 0.4% concentration when emulsified with Saponin. It was found to be less toxic to plants at concentrations sufficient to kill several species of aphids than any of the nitrogen base materials tested. However, the effects upon plants varied considerable. Some times there was no burning and at other times under apparently the same conditions and concentrations, there was severe burning.

When applied to mealy bugs, <u>Pseudococcus citri</u> L., with ammonium oleate there was a decided anesthetic effect. A high percentage of the insects would appear dead for about 2 hours and then many of them would recover. The mealy bugs had shiny appearance after being sprayed with combinations of No. 14, indicating that the waxy coating was penetrated by the spray. The toxicity of other oils to mealy bugs was increased by the addition of a small amount of No. 14 without greatly increasing plant injury. It was possible to kill a high percentage of mealy bugs on coleus without any immediate injury being apparent. After about 5 days following application of No. 14 combined with oil, to coleus, there was noticeable injury to the plants. They became pale and began dropping their leaves. The plants that were sprayed with concentrations sufficient to control mealy bugs never recovered from the harmful effects.

Tests with No. 14 combined with an emulsifier and nicotine were made in an effort to find a combination safe to the plant and that would give mealy bug control on greenhouse plants. There was considerable plant injury at concentrations strong enough to give control of the mealy bugs.

The dormant applications indicated a possible increase in the toxicity of dormant oils to Europen elm scale when combined with No. 14.

The nitrogen bases from the kerosene, lime separate, were compared with No. 14. The toxicity to plants was higher and toxicity to insects lower than with the steam distilled nitrogen bases from the kerosene.

The nitrogen bases from the kerosene, steam distilled and purified showed less toxictiy to aphids than No. 14.

The vacuum distilled nitrogen bases from the kerosene were less toxic to aphids and showed about the same toxicity to plants as No. 14.

No. 15, the crude nitrogen bases from the gas oil, was readily emulsified with Saponin but did not form a stable emulsion. Table No. 5 indicates the results of applications of No. 15 on <u>Myzus persicae</u> and <u>Macrosiphum sanborni</u>.

Table No. 5

Material No.	Concentration	No. insects	% kill 48 hrs.	Insect
15 Saponin	.8% .025%	56	100	(<u>Macrosiphum sanborni</u>)
15 Saponin	.4% .025%	51	98	"
15 Saponin	.4% .025%	59	100	"
15 Saponin	.27% .025%	50	80	"
15 Saponin	.2% .025%	30	67	"
15 Saponin	2% .2%	8	37	"
15 Saponin	.2% .025%		* 1	(<u>Myzus persicae</u>)
15 17	.8% .2%	*50	* 95	" "

*Number estimated.

Material No.	Concen-tration	No. insects	% kill 48 hrs.	Insect
15 Saponin	.8% .025%	63	100	(*Myzus persicae*)
15 Saponin	.4% .025%	* 58	*99	" "

The crude nitrogen bases from the gas oil were slightly more toxic to aphids and much more toxic to plants than the steam distilled nitrogen bases from the kerosene. Concentrations as low as .2% caused 25% burn on cabbage.

No. 16, the steam distilled nitrogen bases from the gas oil was tested on aphids on growing plants and dormant applications, in combination with other oils, were made on European elm scale.

Table No. 6 shows the results of these tests.

Table No. 6

Material No.	Concen-tration	No. insects	% kill 48 hrs.	Insect
16	2%		*50	*Myzus persicae*
16 17	.8% .2%		*100	" "
16 Saponin	.8% .025%		*100	" "
16 Saponin	.4% .025%		*100	" "
16	.8%	18	100	*Macrosiphum sanborni*

*Number estimated.

Material No.	Concentration	No. insects	% kill 48 hrs.	Insect
16 Saponin	.4% .025%	37	100	<u>Macrosiphum sanborni</u>
16 Saponin	.4% .025%	33	100	"
16 Saponin	.27% .025%	30	100	"
16 Saponin	.2% .025%	39	81	"
16 Saponin	.2% .025%	*	100	"

No. 16 in combinations - Field Tests - Dormant

Material No.	Concentration	No. insects	% kill 48 hrs.	Insect
Dendrol 16	3% .5%	58	100	<u>Gossyparia spuria</u> Modeer
Dendrol 16	2% .5%	50	98	"
16 13 Oleic acid	.5% .5% .25%	50	100	"
Check		50	76	"

No. 16 killed from 80 to 100% of <u>Macrosiphum sanborni</u> at 0.2% concentration when emulsified with Saponin but also caused 100% burn on cabbage at this concentration. This fraction appeared to have greater toxicity to European elm scale when combined with dormant oils than any of the materials tested.

The crude secondary amines from the gas oil, No. 31,

*Number estimated

caused 2% burn on cabbage at 0.25% concentrations and killed 99% of chrysanthemum aphids.

The crude nitrogen bases plus the alcoholic waste from the pressure distillate, gasoline fraction, were tested on _Myzus persicae_. At 1.5% concentration, from 40 to 75% kill was obtained.

The secondary and tertiary amines separated from the gas oil fractions were about equal in toxicity to both plants and insects, but neither was as effective as the steam distilled, nitrogen bases from the same fraction before separating.

SUMMARY

The miscible shale oils tested were toxic to growing plants at concentrations necessary to kill aphids.

The filtrate from the retort condenser water killed aphids at a concentration of 12% and caused no burning on cabbage at 100%.

Steam Distillation improved the insecticidal value of the nitrogen bases.

The steam distilled nitrogen bases from the gas oil were toxic at low concentrations, to both plant and insects. Concentrations that killed aphids gave severe burning to the plants.

The steam distilled nitrogen bases from the kerosene gave high percentages of kill on different species

of aphis at concentrations which caused only occasional burning to the growing plants.

Material No. 6, which was a combination of nitrogen bases and oil with an emulsifier, gave good results on chrysanthemum aphids, at concentrations which caused no injury to cabbage.

Different samples of steam distilled nitrogen bases from the kerosene varied in color and in the amount of emulsifying agent required.

Penetrol and ammonium oleate both gave good results as emulsifying agents for the nitrogen bases.

CONCLUSIONS

1. The miscible shale oils tested were not safe to use on growing plants.

2. The nitrogen bases from the various fractions of shale oil vary in toxicity both to plants and to insects.

3. The steam distilled nitrogen bases from the kerosene were the most promising of the nitrogen base materials for use on growing plants.

4. Concentrations of nitrogen base materials necessary to kill aphids were often injurious to the plants.

5. Results indicated that the nitrogen bases have an anesthetic effect upon mealy bugs.

6. The nitrogen bases appeared to be wax solvents,

readily penetrating and wetting the waxy coating of mealy bugs.

7. The toxicity of miscible dormant oils was apparently increased by the addition of nitrogen bases.

8. Material No. 6, consisting of sulfonated compounds from the pressure distillate, crude nitrogen bases, shale kerosene, alcoholic potash and oleic acid gave promising results on aphids.

9. These tests have indicated that the shale oils show promise of being a source of valuable insecticides.

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ABSTRACT

Abstract of investigations of the insecticidal value of extracts from Colorado Oil-bearing shale.

Colorado has 896,000 acres of oil-bearing shale. This abundant source of oil furnishes a possibility of great industrial development in the region.

Workers at the Bureau of Mines became interested in determining the insecticidal value of the extracts from the shale oil. They were interested in obtaining by-products of value to help develop the shale oil industry. The chemical work was done at the Bureau of Mines.

Arrangements were made to carry on an investigation of the insecticidal value of shale oil extracts at the Colorado State College.

The purpose of the investigation was to test the various fractions of the shale oil as contact insecticides, including toxicity to plants and to find a satisfactory method of emulsification.

Several miscible shale oils were tested as contact insecticides on aphids on growing plants. A number of miscellaneous materials were tested to determine their toxicity to both insects and plants.

The nitrogen bases from the various fractions of the shale oil were also tested.

The miscible shale oils tested were toxic to growing plants at concentrations necessary to kill aphids.

The filtrate from the retort condenser water killed aphids at a concentration of 12% and caused no burning on cabbage at 100%.

Steam Distillation improved the insecticidal value of the nitrogen bases.

The steam distilled nitrogen bases from the gas oil were toxic at low concentrations, to both plants and insects. Concentrations that killed aphids gave severe burning to the plants

The steam distilled nitrogen bases from the kerosene gave high percentages of kill on different species of aphids at concentrations which caused only occasional burning to the growing plants.

Material No. 6, which was a combination of nitrogen bases and oil with an emulsifier, gave good results on chrysanthemum aphids, at concentrations which caused no injury to cabbage.

Different samples of steam distilled nitrogen bases from the kerosene varied in color and in the amount of emulsifying agent required.

Penetrol and ammonium oleate both gave good results as emulsifying agents for the nitrogen bases.