



An attempt to separate from petroleum spray oils the portion which is injurious to plants
by Jesse R Green

A THESIS Submitted In partial fulfillment of the requirements for the Degree of Master of Science In
Chemistry Montana State College
Montana State University
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Abstract:

The purpose of this Investigation Is stated In the title. It has been conducted on the hypothesis that some portion of petroleum spray oils is especially injurious to plants. On account of the great number of compounds in petroleum and their close similarity, the identification and separation of any portion la difficult. The complexity of the reactions of the compounds of petroleum with those of the plant has made it almost impossible to solve the problem by purely scientific method#. Thus, in the absence of strictly scientific means, the cut and try method was used with the aid of whatever scientific knowledge or methods that were available.

There has been considerable speculation regarding the compounds that cause plant injury. The blame has largely been placed on the unsaturated compounds, but there are other possibilities. Sulfur and nitrogen compounds may be responsible for injury, but it has been shown in a former Investigation that the part that nitrogen plays must be very small(1). The oxygen compounds in petroleum are also among those that may be considered. Hoerner(2) has proposed the use of sulfonated oxidation products as insecticides and gives data showing practically no injury to typical plants. It la generally conceded that these compounds are efficient insecticides, but their effect on plants is still an open (1)Green, Jesse, Chemical and Physical Properties of Petroleum Spray Oils. Accepted for publication by J. of Agr. Res. 1932.

(2)Hoerner, John L., A Report of Progress on the Testing of Sulfonated Oxidation Products of Petroleum for Their Insecticidal Properties. Vd.

Agr. Expt. Sta. Bui. 310, 1929.

question. Until more Knowledge Is gained regarding petroleum compounds and their exact physiological effect it is best to with-hold opinions.

The causes and nature of plant injury have been discussed by Kelley (1), Swingle end Snapp(2) and Knight, Chamberlin and Samuels(3).

In the course of the work oils were treated by over 120 different processes and then applied to barley seedlings to determine the Injury they would cause. The barley seedling method of testing spray oils was devised and used in a previous work(4). It is carried out by applying the oil to be tested to 10 barley seedlings that have been grown in quarts send with nutrient solution In a small earthenware jar. several more than 10 seeds are planted and when the seedlings are 6 to 8 cm. high they are thinned out leaving 10 that are uniform and that are near the height of the seedlings in the other jars.

The oil ie applied to both sides of the seedlings with a camel's hair brush. At the end of 3 days the seedlings are cut and weighed.

Their weight Is subtracted from the same number of control seedlings and the difference in weight is

computed to percentage of the weight of the controls and called injury.

(1) Kelley, Victor K., Effect of Certain Hydrocarbon Oils on the Respiration of Foliage and Dormant Twigs of the Apple. 111. Agr. Expt. at. Bui. 348, 1830.

(2) Swingle, H.S., and Snapp, O. I., Petroleum Oile and Oil Emulsions as Insecticides, and Their Uae Against San Jose scale on ,each Trees of the South. U. S. Deptl of Agr. Pul. 253, 1831.

(3) Knight, Hugh, Chamberlin, Joseph C., and Samuels, C. D., Some Limiting Factors in Uie Use of Saturated Petroleum Oile as Insecticides. Plant Physiology, 4 : 288-381, 1928.

(4) Green, Jesse, Chemical and Physical Properties of Petroleum Spray Oils. Accepted for publication by J. of Agr. Res. 1832.

AN ATTEMPT TO SEPARATE FROM PETROLEUM SPRAY OILS THE
PORTION WHICH IS INJURIOUS TO PLANTS

BY

JESSE R. GREEN

A THESIS

Submitted in partial fulfillment of the requirements
for the Degree of Master of Science in Chemistry

MONTANA STATE COLLEGE

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AN ATTEMPT TO SEPARATE FROM PETROLEUM SPRAY OILS THE
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question. Until more knowledge is gained regarding petroleum compounds and their exact physiological effect it is best to with-hold opinions. The causes and nature of plant injury have been discussed by Kelley⁽¹⁾, Swingle and Snapp⁽²⁾ and Knight, Chamberlin and Samuels⁽³⁾.

In the course of the work oils were treated by over 120 different processes and then applied to barley seedlings to determine the injury they would cause. The barley seedling method of testing spray oils was devised and used in a previous work⁽⁴⁾. It is carried out by applying the oil to be tested to 10 barley seedlings that have been grown in quartz sand with nutrient solution in a small earthenware jar. Several more than 10 seeds are planted and when the seedlings are 6 to 8 cm. high they are thinned out leaving 10 that are uniform and that are near the height of the seedlings in the other jars.

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(3) Knight, Hugh, Chamberlin, Joseph C., and Samuels, C. D., Some Limiting Factors in the Use of Saturated Petroleum Oils as Insecticides. Plant Physiology, 4 : 299-321, 1929.

(4) Green, Jesse, Chemical and Physical Properties of Petroleum Spray Oils. Accepted for publication by J. of Agr. Res. 1932.

Consideration of Error in Method

There is obviously a large error in the barley seedling method, but it has served a useful purpose in estimating the injurious qualities of the oils to plants.

Figures 1 and 2 show the effect of processed oils. They represent tests Nos. 73, 74, 75 and 76 considered in the discussion of table VIII. The first three are extreme cases in which there was complete killing of the plants. A more typical example is shown in figure 3, which is a close-up view of test No. 76 and the control plants. The mere retardation in the growth of the treated seedlings as compared with the controls is the usual effect.

Figure 4 shows the samples reported in table VI after they were cut and ready to weigh. Figure 5 shows a close-up view of test No. 55 in which there was severe injury.

The largest error is, of course, the lack of uniformity of samples. In order to show the limits of this error the weights of 8 average samples of 10 seedlings each are reported in table I. The variation from the mean is given and in this trial the maximum positive variation was 12.7 per cent and the maximum negative variation was 8.4 per cent.

The amount of oil applied to the seedlings influences the amount of injury. It is believed to be of less importance than it might appear to be. The amount of oil remaining on the seedlings when they are weighed is of greater importance. With a very viscous oil a great deal is required to completely cover the seedlings and there is practically no volatilization or run-off during the test.

HAMMERMILL
BOND

Table I. Showing Variation of Control Samples Used in Barley

Seedling Test

Controls	Weight of 10 seedlings	Variation from average	Percentage varia- tion from average
	grams	grams	
1 (no treatment)	0.790	+0.004	+0.5
2 " "	0.720	-0.066	-8.4
3 " "	0.790	+0.004	+0.5
4 " "	0.720	-0.066	-8.4
5 " "	0.890	+0.104	+12.7
6 " "	0.790	+0.004	+0.5
7 " "	0.780	-0.006	-0.8
8 " "	0.810	+0.024	+3.1
Average	0.786		

Ordinary methods of observation are perhaps just as useful as a comparison of the weights of the plants, and have been used in estimating the injury in every case. There is, however, practically no means of recording and presenting the data of analyses made by observation.

A study of the various tables will show that there is a wide variation in the degree of injury reported. This is due largely to the growing conditions which prevailed during the test. If conditions were good the control plants made rapid progress and left the injured ones far behind, thus showing a large amount of injury. If growing conditions were poor a smaller amount of injury would be caused by the same oil. For these reasons it is necessary to examine the data in each table as a unit. All the tests made in any single table were made at the same time and are comparable with each other.

Oils Used

A series of 13 oils were used in a former investigation, and

from this group the oils for this work were selected. Considerable data were obtained in the earlier study and are attached to this report as an appendix. The relative injury as determined in the former work is also given in the appendix. The laboratory numbers of the original oils are 3, 4, 5, 8, 12, 13, 15, 16, 20, 21, 22, 24, and 28. These numbers should not be confused with the barley seedling test numbers, or the processed oils which bear the same number as the test in which they were used. The original or non-treated oil is designated as "normal oil".

Distillation of Oils

The first attempt to separate the injurious portion from the oil was by distillation. A bead tower was used and was wrapped with an electrical heating element and asbestos insulation. The complete apparatus is shown in figure 6. A certain amount of fractionation was accomplished in the bead tower, and all the distillations were made at an absolute pressure of approximately 10 cm. of mercury.

The different oils were distilled into 3 fractions each. A given amount of oil was placed in the still and the first fraction consisted of one-third of the total, the second fraction one-third, and the residue remaining in the still of one-third. These samples were applied to barley seedlings and the results reported in table II.

There was more or less cracking or breaking down of the oils during distillation. Darkening of the residue, sudden changes in temperature and increases in sulfonatable portion are the evidences supporting this statement. The variations in temperature from one fraction to another were caused by the releasing of the vacuum and cooling down of the still to change the receiver between fractions.

All the fractions were analyzed for the sulfonatable portion by the method used by Marshall⁽¹⁾.

General trends can hardly be cited from a study of the distillation and sulfonation values found. There is a slight tendency for the first fractions to cause the greatest injury. In figure 7 the distillation data are presented graphically. The sulfonatable portion of the fractions has little, if any, relation to injury. In the case of oil No. 3 the sulfonatable value of the residue is very low and the injury caused by this fraction is also very low. With oil No. 24, the sulfonatable portion of the residue is high, but still the injury produced is low. These two residues were both very viscous and it has often been observed that very viscous oils fail to cause the injury that would be expected. They do not appear to penetrate the plant as do the oils of lower viscosity.

From the graphs in figure 8 it is quite evident that distillation is a very poor means of separating the sulfonatable materials from the remainder of the oil. The sulfonatable portion of all the fractions of any given oil runs fairly close together. It is also evident that distillation causes the formation of sulfonatable materials in the oil. Most of the fractions are higher in sulfonatable material than the normal oil. Oils Nos. 22 and 4 show a great increase in sulfonatable material during distillation. Oils Nos. 5 and 21 do not show an increase of sulfonatable materials, but an increase was the trend in most cases.

(1) Marshall, Warren G., Economic Poisons. Special Pub. 94, State of Calif. Dept. of Agr. 1929.

Table II. Injury to Barley Seedlings Caused by Distillates

Test number	Oil number	Fraction	(single determinations)		Sulfonatable Portion	
			Temperature range	Injury	distilled oils	normal oils**
			degrees	per cent	per cent	per cent
1	3	first	180 - 228	24.9	24.0	6.0
2	3	second	215 - 255	26.2	24.0	
3		residue*	272 -	27.8	4.0	
4	4	first	147 - 210	52.3	28.0	12.0
5		second	200 - 265	51.1	34.0	
6		residue	265 -	13.9	32.0	
7	5	first	155 - 215	51.8	42.0	41.6
8		second	205 - 230	36.5	42.0	
9		residue	230 -	21.8	46.0	
10	12	first	110 - 220	37.4	26.0	27.5
11		second	220 - 250	33.4	32.0	
12		residue	250 -	17.2	28.0	
13	15	first	100 - 229	31.2	20.0	26.4
14		second	210 - 250	30.5	26.0	
15		residue	250 -	43.2	30.0	
16	15	first	140 - 200	55.2	12.0	---
17	paraffin	second	200 - 225	35.2	12.0	
18	added	third	220 - 240	23.6	12.0	
19	20	first	155 - 192	34.5	26.0	1.0
20		second	185 - 190	25.2	28.0	
21		residue	190 -	20.0	30.0	
22	21	first	145 - 180	45.1	14.0	15.6
23		second	125 - 196	30.5	10.0	
24		residue	196 -	30.5	26.0	
25	22	first	165 - 208	24.1	28.0	2.0
26		second	175 - 196	24.9	28.0	
27		residue	196 -	28.1	30.0	
28	24	first	200 - 257	31.3	2.0	none
29		second	230 - 270	17.6	4.0	
30		residue	270 -	13.1	32.0	
31	28	first	190 - 222	44.6	42.0	35.2
32		second	220 - 250	48.9	42.0	
33		residue	250 -	28.1	48.0	

*In this case a third fraction was taken, by distilling off one-half of the residue, thus there is a break in the temperatures between the second fraction and the residue.

**These values were determined in a former investigation.

The sample of oil No. 15, designated as "paraffin added", was made by dissolving 80 grams of paraffin in 400 cc of oil and distilling into 3 fractions. It was thought that possibly paraffin might hold back the sulfonatable portion during distillation. The indications are that this object was accomplished. All the distillates had a sulfonatable value of 12 per cent, while the normal had 26.4 per cent. Of course, a great deal of paraffin distilled over, but the amount was far greater in the third distillate than in the first, yet they had the same sulfonatable value. It is very difficult to interpret some of the results, especially the fact that the first, second and third distillates of the paraffin and oil combination gave injury values of 55.2 per cent, 32.5 per cent and 23.6 per cent, respectively. Three distillates were made from this oil and the residue was discarded on account of its high paraffin content.

Filtration of Oils

The filtering of the oils was accomplished with the apparatus shown in figure 9. A steam jacketed tube about 2 cm in diameter contained the filtering material. The length of the filter column varied, but was usually about 30 cm long. Suction was always used and in some cases pressure was also necessary.

Table III shows the results of filtering through a clay like material obtained near Anaconda, Montana and designated in this report as "Osborne's mine run". Two of the three oils used showed much less injury after filtering and a third was not affected.

The sulfonatable portion of the oils was determined before and after filtration. Sulfonatable material was removed in every case by filtration. It is, thus, highly probable that the decrease in injury produced by filtration is brought about by the removal of the sulfonatable compounds.

Table III. Injury to Barley Seedlings by Filtered and Normal Oils
(duplicate determinations)

Test number	Oil number	Treatment	Injury per cent	Sulfonatable portion per cent
34	15	normal	64.2	25
35	15	filtered	33.3	15
36	5	normal	60.9	44
37	5	filtered	35.2	38
38	12	normal	50.7	34
39	12	filtered	36.1	32
40	28	normal	58.8	52
41	28	filtered	58.5	46

The first attempts to filter oil were made for the purpose of removing color. From previous experience color had been thought to be related to injury. In most of the filtrations the first few cubic centimeters of oil coming through would be clear, but as the process continued the oil would rapidly become darker and darker, and in a very short time the ability of the filter to remove color was exhausted. If color and injury are positively related the first clear filtrate should be the least injurious and the later and darker portions more injurious. Oil No. 15 was filtered through 60 cm of Osborne's mine run earth and 5 successive filtrates collected. In table IV all the filtrates show a

decided decrease in injury below the normal oil. As the filtration progressed the samples became darker, but there was no increase in injury with increase in color.

Table IV. Injury to Barley Seedlings by Successive Portions
of an Oil Passing Through a Filter
(single determinations)

Test number	Oil number	Treatment	Injury per cent
43	15	first filtrate (least color)	18.4
44	15	second filtrate	16.4
45	15	third filtrate	26.8
46	15	fourth filtrate	21.9
47	15	fifth filtrate (most color)	16.8
48	15	normal oil	35.9

Several kinds of filters were tried. The results of these trials are given in table V. All the materials used were ground to pass a 60 mesh sieve. A great deal of the material was finer, but part of it was about the size of a 60 mesh and prevented too close packing of the filter. It was found impossible to force oil through filtering material ground to 100 mesh size with the pressures used. In carrying out the filtration tests the same amount of oil was put through the same length of filter column, and the temperature and pressure were kept constant.

The first filter was Osborne's mine run. This same material was tried in combination with Norit (activated charcoal), another sample of it was ignited and still another treated with acid. The acid treatment consisted of wetting the earth with sulfuric acid and heating until SO₃ fumes were rapidly given off. The mixture with Norit was made by combining 5 parts of earth, by weight, and 3 parts of Norit, and the ignited

portion was prepared by holding the earth at a red heat for two or three hours.

The commercial Fuller's earth used in these tests was purchased from E. H. Sargent and Company, as was also the hydrated silica (40 per cent moisture). The volcanic ash was a good quality of this material obtained from a local natural source near Whitehall, Montana.

Although the determinations of the injury caused by the oils after passing through these various filters were made in duplicate, the differences shown in table V are not significant. They do, however, again show the value of filtration. The high injury value shown by the oil filtered through volcanic ash can be accounted for by the fact that filtration through this material was very rapid and thus the forces of adsorption had little chance to select a portion of the oil. The correspondingly high injury value of the oil filtered through hydrated silica can not be accounted for by any known reason. This material appeared to have all the qualities of a good filter and it is extensively used in the oil industry.

Table V. Injury to Barley Seedlings by an Oil After Being Filtered
Through Various Materials

(duplicate Determinations)

Test number	Oil number	Treatment	Injury per cent
42	15	normal	54.7
43	15	filtered through Osborne's mine run earth	18.6
44	15	filtered through H ₂ SO ₄ treated Osborne's mine run earth	26.0
45	15	filtered through Osborne's mine run earth and Norit	17.1
46	15	filtered through ignited Osborne's mine run earth	26.8
47	15	filtered through commercial Fuller's earth	26.8
48	15	filtered through hydrated silica	33.3
49	15	filtered through volcanic ash	36.4

In table VI the results of other filtrations are given. The oil for test Nos. 50 and 51 was prepared from a standard miscible spray oil, containing 9 parts of oil No. 15 and 1 part of cresoap⁽¹⁾. Test No. 50 shows an injury of 48.6 per cent from the filtered miscible oil and 60.5 per cent from the normal oil. The oil used in test No. 51 was prepared by washing the miscible oil with water until about one-half of its volume had been carried away as soluble or emulsified material. The portion remaining caused an injury of 73.5 per cent.

The washing of the oil used for test No. 51 and also several other oils was done in the washer shown in figure 10. A layer of oil is floated on water and a small stream of water is allowed to fall on the oil and pass out below through an inverted syphon.

If filtration removes the injurious portion of an oil it should be possible to extract the filter with certain solvents and recover a material that would be very harmful to plants. With this idea in mind, a large portion of oil No. 15 was filtered through a long filter column and the filter washed with several portions of gasoline into another container. The gasoline was distilled from the washings until the product appeared to have approximately the same characteristics of the normal oil. This was applied to barley seedlings in test No. 53 and caused an injury of 59.5 per cent, as compared with an injury of 47.3 per cent for the oil that had passed through the filter (test No. 52).

(1) Melander, A. L., Spuler, Anthony, and Green, E. L., Oil Sprays, Their Preparation and Use For Insect Control. Wash. Expt. Sta. Bul. 184, 1924.

The effect of filtering sulfonated oil No. 5 is reported in tests Nos. 55 to 59. After sulfonation the oil was centrifuged, decanted off and filtered. The first filtrate had a slight acidity and a portion was washed. For some reason this washed portion of the oil gave a very high injury of 79.9 per cent. The remainder of the first filtrate was filtered three times more and applied in tests Nos. 56, 57 and 58, respectively, and each time a portion was saved. The injury values of these filtered oils are not consistent, but the products of the last two filtrations caused very low injury.

Filtered and non-filtered oil No. 21 was used in tests Nos. 60 and 61. This oil was refined by the manufacturer by the Edeleanu SO_2 process. The small amount of difference between the injury of the filtered and non-filtered oil is some evidence that SO_2 removes the same materials that are removed by filtration.

The theory of color removal from oil by filtration is somewhat indefinite. Haseman⁽¹⁾ concludes that the coloring matter in oil is colloidal and that it is of the nature of the humic acids. He states further that a part of the colored compounds in oil is precipitated by the di-silicic acids in the filtering earth and that the remainder are filtered out mechanically.

The theory of adsorption is summarized by Torney⁽²⁾ by the statement that the concentration of any dissolved substance is increased near

(1) Haseman, J. D., The Alleged Catalytic Action of Fuller's Earth on the Coloring Matter in Oil. J. of Phys. Chem. Vol. 33, 1514-1527, 1929.

(2) Torney, Harold, Notes on Adsorption. The Refiner, Feb., 78, 1931.

the interface of the solid and the liquid. This may be accomplished either by the formation of chemical complexes or by the action of physical attractive forces between the solid and the dissolved substance. Although these theories are not specific they are perhaps the most accurate generalizations that can now be drawn.

Gilpin and Cram⁽¹⁾ have found that the more dense portions and the sulfonatable materials are held back in the passage of oils through Fuller's earth, which would indicate that the most injurious portion of petroleum is of higher molecular weight than the rest of the oil.

Table VI. Injury to Barley Seedlings by Variouslly Filtered Oils
(single determinations)

Test number	Oil number	Treatment	Injury per cent
50	15	9 parts oil and 1 part cresoap, filtered	48.6
51	15	9 parts oil and 1 part cresoap, washed with water	73.5
52	15	Large portion oil filtered through 1 filter	47.3
53	15	Adsorbed material washed from above filter with gasoline	59.5
54	15	Normal	60.5
55	5	Sulfonated, filtered once, and washed	79.5
56	5	Sulfonated, filtered twice	48.8
57	5	Sulfonated, filtered three times	none
58	5	Sulfonated, filtered four times	16.3
59	5	Normal	51.0
60	21	Edeleanu SO ₂ processed oil, filtered	58.5
61	21	Edeleanu SO ₂ processed oil, normal	58.8

(1) Gilpin, J. Elliott, and Cram, Marshall P., The Fractionation of Crude Petroleum by Capillary Diffusion. U. S. Geol. Survey Bul. 365.

Some Chemical Treatments

Several chemical processes were tried on the oils. Oil No. 15 was treated with chlorine. In the first attempt wet chlorine right from the generator was used. A vigorous reaction took place, causing a rise in temperature and the product was much more viscous than the original oil. In a second attempt dry chlorine was passed through the oil. The reaction was much slower but the product was much the same as with the wet chlorine. The chlorinated oil was washed free of any dissolved chlorine or acidity and was then dried. The drying of all oils was accomplished by bubbling air through the oil while it was held in a container in a boiling water bath. Test No. 62 of table VII shows the injury of dry chlorinated oil No. 15 to be 53.6 per cent as compared with 64.2 per cent for the normal oil.

Oil No. 15 was also treated with sodium hypochlorite, according to a method described by Post and Besemann⁽¹⁾. A sample of the oil was shaken several times with portions of sodium hypochlorite in the presence of copper sulfate. The process was designed to remove color, but in this case very little color was removed. The barley seedling test No. 63 shows very little difference from the normal oil.

Oil No. 28 was chlorinated by a similar process as that used on oil No. 15. When the chlorination was complete the product was so viscous that it was thought best to distill it before applying it to barley seedlings. The first distillate was light colored and had a very low viscosity. It was used in test No. 65. A second fraction was very dark

(1) Post, Wilhelm, and Besemann, Franz, Bleaching Mineral Oil. U. S. Patent No. 1,788,204, Jan. 1931.

and was applied in test No. 66. The residue was too viscous to be used. The chlorinated oil, without being distilled, was applied in test No. 68. Although some of the chlorinated oils caused less injury than the normal oil the possibilities of improving spray oils by chlorination seem to be very poor from these showings.

Table VII. Injury to Barley Seedlings by Chlorinated Oils

(duplicate determinations)

Test number	Oil number	Treatment	Injury per cent
62	15	Treated with chlorine, washed and dried	58.6
63	15	Treated with sodium hypochlorite	60.1
64	15	Normal	64.2
65	28	Treated with chlorine and distilled - first fraction	64.9
66	28	Treated with chlorine and distilled - second fraction	64.0
67	28	Treated with chlorine, not distilled, but washed and dried	45.0
68	28	Normal	68.8

Nitration produced results very similar to chlorination, only they were more severe. The reaction was accomplished by treating 100 cc of oil with 40 cc of commercial nitric acid and maintaining the temperature at 100° C for two to three hours, with frequent shaking. The products are similar in appearance to those of sulfonation, and the reaction proceeds at about the same rate. A resinous precipitate is formed in the sludge which differs from the product of sulfonation. It is brown and is plastic at ordinary temperatures.

Exact measurements were not made during the nitration process, but 30 per cent of oil No. 15 and 65 per cent of oil No. 5 were removed by the nitration process as it was carried out. According to these fig-

ures nitric acid attacks a little more of an oil than does sulfuric acid under the same conditions. Tests No. 69 and 70 of table VIII show the injury caused by nitrated oils Nos. 15 and 5. In both cases the injury was about one-third greater than that of the normal oil.

Table VIII. Injury to Barley Seedlings by Nitrated Oils

(single determinations)

Test number	Oil number	Treatment	Injury per cent
69	15	Nitrated	30.1
70	15	Normal	19.2
71	5	Nitrated	26.3
72	5	Normal	19.8

Three samples of oil No. 15, that had been sulfonated and treated under slightly different conditions as described in tests Nos. 91, 80 and 79, were nitrated. They were applied in tests Nos. 73, 74 and 75, with No. 76 for the sulfonated oil (see table IX). Very high injury was caused by the sulfonated and nitrated oils. Figure 1 shows the seedlings before treatment and figure 2 after treatment. Figure 3 shows the effect of the sulfonated, but not nitrated, oil. It is test No. 76 beside the control samples.

Table IX. Injury to Barley Seedlings by Nitrated-Sulfonated Oils

(duplicate determinations)

Test number	Oil number	Treatment	Injury per cent
73	15	Nitrated-sulfonated oil from test No. 91	66.7
74	15	Nitrated-sulfonated oil from test No. 80	62.3
75	15	Nitrated-sulfonated oil from test No. 79	71.1
76	15	Sulfonated, but not nitrated, oil from test No. 91 as check	14.6

Sulfonated and Other Chemically Treated Oils

Some combinations of sulfonation and filtration were tried and reported in Table X. All the sulfonated oils show an improvement over the normal oil. The slight variations in treatment are probably of little significance.

Two portions of oil No. 15 were refluxed violently for 45 minutes with an excess of PbO (litharge) and CuO. The oils were decanted off, filtered and used in tests Nos. 81 and 82. It was thought that there was a possibility of removing sulfur compounds by treatment with these oxides as is done in the Frasch process⁽¹⁾. The results indicate that in any event there was deterioration of the oil as regards its value as a spray oil. The high temperature and violent refluxing may have promoted oxidation, or the formation of injurious compounds, in the oil.

Table X. Injury to Barley Seedlings by Sulfonated Oils and Oils Heated With Copper and Lead Oxides

(single determinations)

Test number	Oil number	Treatment	Injury per cent
77	15	Sulfonated and filtered, first filtrate, no further treatment	21.9
78	15	Sulfonated and filtered, first filtrate, treated with NaOH, washed and dried.	20.1
79	15	Sulfonated and filtered, second filtrate, treated with NaOH, washed, dried and filtered	15.5
80	15	Sulfonated, treated with NaOH, washed and dried	14.7
81	15	Refluxed with CuO and filtered	34.0
82	15	Refluxed with PbO and filtered	31.4
83	15	Normal	29.3

(1)Gruse, William A., Petroleum and Its Products. McGraw Hill Book Co., New York, 1928.

One hundred cc of oil No. 15 were treated with 20 grams of copper sulfate and an equal amount was treated with 20 grams of potassium permanganate. The two samples were held at 100° C on a steam plate for 36 hours with occasional shaking, after which the oils were decanted off and filtered. The filtrates were divided into three portions by distillation, that is, a first and second distillate and a residue. The injury they produced on barley seedlings is reported in tests 84 to 89 in table XI.

Table XI. Injury to Barley Seedlings by Oils Treated With
Copper Sulfate and Potassium Permanganate

(single determinations)

Test number	Oil number	Treatment	Injury per cent
84	15	CuSO ₄ treated and distilled, first fraction (140° - 196°)	53.8
85	15	CuSO ₄ treated and distilled, second fraction (186° - 174°)	45.1
86	15	CuSO ₄ treated and distilled, residue (174°)	44.5
87	15	KMnO ₄ treated and distilled, first fraction (138° - 170°)	53.0
88	15	KMnO ₄ treated and distilled, second fraction (160° - 177°)	53.5
89	15	KMnO ₄ treated and distilled, residue (177°)	37.8
90	15	Normal	50.0

Some further work was done on sulfonation. Oil No. 15 was treated according to the method of Steik and Cassar⁽¹⁾. One hundred cc of the oil were treated with 25 cc of fuming sulfuric acid and allowed to stand at room temperature for 3 hours with frequent shaking. The sludge

⁽¹⁾Steik, Karl, T., and Cassar, Harold A., Colorless or White Mineral Oil. U. S. Patent 1,803,140, April, 1931.

was centrifuged off and the oil treated again with 88 per cent acid at a temperature of 75° for a few hours. It was centrifuged again, filtered twice, and used in test No. 91 of table XII. A low injury was obtained from this oil, but it is probably not superior to the same oil sulfonated by the ordinary method

Oxidation Effects on Oils

In order to show the effect of heating and oxidation, oils No. 15 and 5 were heated in a refluxing still for 8 hours, and at the same time air was drawn through the oil. The products were very dark. A portion of each was filtered and tested in comparison with the non-filtered oil in tests Nos. 92, 93, 95 and 96. Oil No. 15 did not show any marked change due to oxidation, but oil No. 5 showed increased injury because of this treatment. Both treated oils gave much lower injury after being filtered.

Table XII. Injury to Barley Seedlings by a Double Sulfonated Oil and Oils Subjected to Severe Oxidation

(single determinations)

Test number	Oil number	Treatment	Injury per cent
91	15	Double sulfonation and double filtration	23.0
92	15	Refluxed and air bubbled through for 8 hours	45.6
93	15	Refluxed and air bubbled through for 8 hours, and filtered	33.2
94	15	Normal	45.3
95	5	Refluxed and air bubbled through for 8 hours	44.6
96	5	Refluxed and air bubbled through for 8 hours, and filtered	30.3
97	5	Normal	36.5

The results of milder oxidation treatments are reported in tests 98 to 109 of table XIII. Three portions of each of oils Nos. 15, 5 and 24 were placed in 4 ounce bottles and each set of bottles was connected in series so that a current of air could be drawn through the oil. The first bottle of each set contained the normal dry oil, the second oil and water, and the third oil and water acidified with sulfuric acid. All the bottles were placed in a boiling water bath and air was aspirated through the oil for 8 hours.

The results show no significant differences in the injury caused by the different samples of the same oil. The low value in test No. 108 may be only experimental error. The injurious properties of the three original oils are well shown by the average values of 55.8 per cent, 44.5 per cent and 14.3 per cent for oils Nos. 15, 5 and 24, respectively. Oil No. 24 is considered the least injurious oil used and oil No. 15 the most injurious in this and the former investigation.

Treatment of Oils by Electrolysis

Several unsuccessful attempts were made to decrease the injury of spray oils by electrolysis. After finding that filtration decreased the injury caused by the oils it was thought possible to accomplish the same result in a more efficient way by electrolysis. The movement of materials colloiddally dispersed in liquids under the influence of an electrical potential has been observed to be analogous to the movement of dust particles in a Cottrell precipitator. There was also the possibility of separating out any electrolytes that might be present in petro-

leum. The high resistance of oil would, of course, indicate that the quantity of electrolytes, or charged particles suspended, in the oil was very small.

Table XIII. Injury to Barley Seedlings by Oils Subjected to Mild Oxidation Treatments

(single determinations)

Test number	Oil number	Treatment	Injury per cent
98	15	Air bubbled through dry oil	56.6
99	15	Air bubbled through oil and water	51.3
100	15	Air bubbled through oil, water and H ₂ SO ₄	55.1
101	15	Normal	60.3
		Average	55.8
102	5	Air bubbled through dry oil	49.6
103	5	Air bubbled through oil and water	49.1
104	5	Air bubbled through oil, water and H ₂ SO ₄	38.9
105	5	Normal	40.2
		Average	44.5
106	24	Air bubbled through dry oil	19.2
107	24	Air bubbled through oil and water	13.2
108	24	Air bubbled through oil, water and H ₂ SO ₄	5.6
109	24	Normal	19.2
		Average	14.3

Cell No. 1 in figure 11 was first tried in the electrolysis treatments. Oil was placed in a cellophane sack, which was immersed in a beaker of water. The negative carbon electrode was placed in the oil and the positive copper electrode in the water, and direct current of 140 volts was applied, but no action took place until the poles were moved close together. The action then became noticeable and a tar-like material collected on the cellophane sack. Copper was dissolved from

the positive electrode and a green salt settled to the bottom of the water compartment. The oil from this experiment was tried in test No. 101 of table XIV and shows no difference in injury from the normal oil. The tar-like material was perhaps somewhat analogous to the precipitate found on oil soaked insulation of electric cables studied by Schoepfle and Fellows⁽¹⁾. These authors attributed the deposition of a wax-like material in the insulation of electric cables to the action of cathode rays, and have found that several pure hydrocarbons break down under electrical influences, yielding unsaturated hydrocarbons and gases containing hydrogen and methane.

Cell No. 4 in figure 12 was constructed by putting two carbon electrodes in a (U) tube filled with oil. No apparent action could be observed but oil from the two compartments was tried in tests Nos. 112 and 113. Although there was no visible electrolysis it was thought that possibly there might have been a movement of particles which was not easily detected, however, the results are not considered significant.

A negative carbon electrode and a positive copper electrode were placed in oil in cell No. 2 of figure 11, but no apparent electrolysis could be made to take place on account of the high resistance of the oil. Then cell No. 3 was constructed. A layer of oil was placed on water in a beaker and a negative copper electrode was placed in the oil and a similar positive copper electrode in the water. They were brought very close together on each side of the oil-water interface. A considerable action took place with the evolution of gases and the

(1) Schoepfle, G. S., and Fellows, C. H., Gaseous Products From the Action of Cathode Rays on Hydrocarbons. Ind. and Eng. Chem. Vol. 23, p. 1396, 1931.

precipitation of a tar-like material and some copper salt in the water. After this treatment the oil was distilled. The residue from the first distillation was used in test No. 115, the distillate of the first distillation was redistilled into a distillate and a residue, which were used in tests Nos. 117 and 116, respectively. The results are not considered significant.

The electrolysis of a 4 per cent cresoap field emulsion of oil No. 15, prepared from the miscible oil used in tests Nos. 50 and 51, was tried in cell No. 4 (U-shaped type) and a slight movement of the suspended oil droplets from the positive to the negative pole was observed, indicating that the droplets were positively charged. An emulsion of oil No. 24 was also tried in this way and the same result was observed.

Carbon black was suspended in oil No. 15 and the combination placed in cell No. 4. It was thought that, as carbon black was an adsorbing material, it might be made to move under an electrical potential and carry with it a portion of the oil, but this was not the case. After several hours at a potential of 140 volts the slightest movement of carbon black could not be detected.

Cell No. 5 in figure 12 was designed to reduce resistance to a minimum. A thin layer of oil was separated from water on each side by sheets of cellophane. Carbon electrodes were placed in the water on each side of the oil with the idea that some material might be dialyzed with the aid of the electrical potential from the oil and into the water. No action could be made to take place even through a layer of oil 0.5 centimeter thick.

Another trial was made with the above cell by placing a thin sheet of aluminum in the oil layer. This was connected to the negative terminal and the carbon electrodes in the water compartments on each side were both made positive. An action similar to that obtained in Cell No. 1, in which the cellophane sack of oil was immersed in water, was obtained. Gases were given off from the oil near the negative aluminum electrode, a black precipitate collected on the cellophane, and a white precipitate, presumably some aluminum salt, settled to the bottom of the oil compartment. The oil from this electrolysis was applied in test No. 118, and, although the injury value obtained was somewhat lower than that produced by the normal oil, the electrolysis method of separating the toxic portion of spray oils was abandoned.

Table XIV. Injury to Barley Seedlings by Oils Treated
by Electrolysis

(single determinations)

Test number	Oil number	Treatment	Injury per cent
110	5	Treated in cell No. 1 - positive carbon electrode in oil in cellophane sack and negative copper electrode in surrounding water	26.4
111	5	Normal	27.1
112	15	Treated in cell No. 5 - oil from positive pole	25.7
113	15	Treated in cell No. 5 - oil from negative pole	31.8
114	15	Normal	35.9

Table XV. Injury to Barley Seedlings by Oils Treated by Electrolysis and Distillation

(single determinations)

Test number	Oil number	Treatment	Injury per cent
115	5	Treated by electrolysis in cell No. 3 and distilled - residue from first distillation	28.9
116	5	Residue from redistillation of first distillate of above	39.5
117	5	Distillate from above redistillation	40.0
118	5	Treated by electrolysis in cell No. 6 with negative aluminum pole in oil	30.5
119	5	Normal	40.4

Extraction of Oils With Volatile Solvents

The extraction of oils with volatile solvents was suggested by Ferris⁽¹⁾ and Steinbrecher⁽²⁾. Some preliminary work was done to determine what solvents could be used. Oil No. 15 was found to be completely miscible with ether, chloroform, carbon disulfide, carbon tetrachloride and toluene. It was only partly miscible with acetone, 95 per cent alcohol and 40 per cent formaldehyde, thus these solvents were used to extract the oils. Apparently those solvents which are miscible with water are not completely miscible with oil and those which are not miscible with water are miscible with oil.

(1) Ferris, S. W., Birkhimer, E. R., and Henderson, L. M., Solvent Extraction of Lubricating Oils. Ind. and Eng. Chem., Vol. 23, 753-761, 1931.

(2) Steinbrecher, H., Refining Oils by Cold Fractionation. Braunkohlenarchiv, No. 30, 1-10, 1930.

One hundred cc of oil No. 15 was shaken with 10 successive portions of 95 per cent alcohol in a separatory funnel. About one-half of the oil was recovered. This amount was divided into three equal parts, one was not treated further, another was distilled with steam, and still another was distilled with dry heat to drive off the alcohol remaining in the oil. The distillation with steam was carried out in the apparatus shown in figure 13. The three products of alcoholic extraction were applied in tests Nos. 120, 121 and 122 of table XVI. While the average injury of these oils was only a few points below that of the normal oil, the seedlings appeared to stand the effects of the oil very well.

The same procedure was followed with formaldehyde as with alcohol. There was practically no loss of oil due to extraction with formaldehyde. The results are given in tests Nos. 123, 124 and 125 of table XVI.

The extraction with acetone had to be varied somewhat from the procedure followed with alcohol. It was so miscible with oil that it extracted too great a portion. The miscibility was decreased by adding 20 cc of water each time after shaking with acetone. The miscibility of acetone and water is greater than the miscibility of acetone and oil, hence more of the acetone would leave the oil for the water and the losses of oil were not too great. The injury of oils extracted with acetone is reported in tests Nos. 126, 127 and 128. A slight decrease in injury is shown.

Having observed some bad effects from steam distillation earlier in the study of spray oils, a sample of oil No. 15 was distilled

with steam for 8 hours and applied in test No.129. The injury caused was 29.5 per cent while that of the normal oil was 19.2. Two out of three samples of the steam distilled and extracted oils showed greater injury than the other extracted oils. All steam distillations were carried out at atmospheric pressure. In every case the residue, or portion not volatile with steam at atmospheric pressure, was recovered and used. A very small portion distilling off with the steam was not recovered and thus the term "steam distilled" is intended to apply, in this work, to the residue and not the distillate.

Table XVI. Injury to Barley Seedlings by Oils Extracted With Volatile Solvents and by Steam Distillation

(single determinations)

Test number	Oil number	Treatment	Injury per cent
120	15	Extracted with 95% alcohol in separatory funnel	6.3
121	15	Extracted with 95% alcohol and steam distilled	18.2
122	15	Extracted with 95% alcohol and distilled with dry heat	13.8
		Average	13.4
123	15	Extracted with 40% formaldehyde	27.4
124	15	Extracted with 40% formaldehyde and steam distilled	31.2
125	15	Extracted with 40% formaldehyde and distilled with dry heat	37.7
		Average	32.1
126	15	Extracted with acetone	13.2
127	15	Extracted with acetone and steam distilled	33.9
128	15	Extracted with acetone and distilled with dry heat	24.1
		Average	23.7
129	15	Distilled with steam for 8 hours	29.5
130	15	Normal	19.2



An extractor based on the principle that alcohol floats on oil was made for the purpose of getting better extraction (see figure 14). The idea of extracting heavier liquids with lighter ones was used by Fayolle and Lormand⁽¹⁾ and is described by Morrow⁽²⁾. Tests Nos. 131 to 136 of table XVII show some of the results of extracting oils with this apparatus. In tests No. 134 and 135 the oils were extracted with absolute alcohol.. Anhydrous lime was placed in the still to take up any water extracted from the oil and every precaution was used to carry out the extraction in such a way as to remove all the water from the oil. However, the results show that the oils prepared in this way were more injurious than the normal oil. No reason for the difference can be advanced.

Table XVII. Injury to Barley Seedlings by Oils Extracted with Alcohol, in an Extractor

(duplicate determinations)

Test number	Oil number	Treatment	Injury per cent
131	15	Extracted with 95% alcohol - 50% recovery	9.4
132	15	Extracted with 95% alcohol - 70% recovery	15.4
133	15	Extracted with 95% alcohol - 86 % recovery	32.6
134	15	Extracted with absolute alcohol - 50% recovery	25.2
135	15	Extracted with absolute alcohol - 82% recovery	36.4
136	15	Portion recovered from above alcohol extracts	52.4
137	15	Normal	24.4

(1)Fayolle and Lormand, Ch., Appareil de Performance Pour Epuisement des Liquides per les Liqueudes. Liqueudes non Miscible, Chemie and Industrie, 8, 273-274, 1922.

(2)Morrow, G. A., Biochemical Laboratory Methods. John Wiley and Sons, New York, 1927.

Further tests were made with alcoholic extracted oils and reported in table XVIII. It was thought that alcoholic extraction in the extractor was not producing the desired result. The injurious portion of the oil may be volatile with alcohol and thus go round and round in the extractor without being eliminated. In fact a portion of the oil is volatile with alcohol as shown by the fact that when the alcoholic vapors from the still first hit the condenser an oily substance accumulated. A study of the data, however, indicate that at least some of the injurious portion of the oil is removed by either method of extraction. The decrease in injury caused by alcoholic extracted oils is probably due to the same reason that injury is reduced by sulfonation or filtration. Sulfonation values were determined on part of the alcoholic extracted oils of table XVIII. In every case alcoholic extraction removes the same materials that sulfonation does.

Extraction of Oils with Ammonia

A process described by Albright⁽¹⁾ for neutralizing acid treated oils with ammonia has suggested that it might be possible to improve spray oils by extraction with ammonia. The sulfur content of oils treated by this process is said to be decreased.

Fifty cc of oil No. 15 was extracted in a separatory funnel with 5 consecutive portions, of 50 cc each, of commercial ammonia and steam distilled to drive off the dissolved ammonia. About one-half of the oil extracted was recovered after extraction, and it was applied in tests No. 149 of table XIX. A sample of oil No. 15, that had been sulfonated, was also extracted with ammonia. The injury shown by this

(1) Albright, J. C., Ammonia for Neutralizing and Treating. The Refiner, September, 1931.

sample was less than that of the normal oil, possibly because of the effect of sulfonation. The sample that was not sulfonated, but was extracted with ammonia, showed practically no difference from the normal oil.

Table XVIII. Injury to Barley Seedlings by Oils Extracted with Alcohol by Two Different Methods

Test number	Oil number	Treatment	Injury per cent	Sulfonatable portion* per cent
<u>Triplicate Determinations for Injury</u>				
138	15	Extracted 10 times with 95% alcohol in a separatory funnel - 50% recovery	47.6	8
139	15	Extracted with 95% alcohol in an extractor - 40% recovery	53.2	--
140	15	Normal	62.8	18
141	5	Extracted 5 times with 95% alcohol in a separatory funnel - 50% recovery	46.0	34
142	5	Extracted with 95% alcohol in an extractor - 65% recovery	40.3	--
143	5	Normal	49.2	40
<u>Duplicate Determinations for Injury</u>				
144	28	Extracted with 95% alcohol in an extractor - 65% recovery	41.1	--
145	28	Extracted with 95% alcohol in an extractor - 40% recovery	37.7	34
146	28	Normal	49.4	44
147	8	Extracted with 95% alcohol in an extractor - 50% recovery	11.3	42
148	8	Normal	23.0	50

*The sulfonatable portion of the normal oils in this table differs from that found in the appendix because the same strength of acid was not available. However, all the values on this table were obtained with the same acid and under the same conditions.

Table XIX. Injury to Barley Seedlings by Oils Extracted

With Ammonia

(duplicate determinations)

Test number	Oil number	Treatment	Injury per cent
149	15	Extracted 5 times with ammonia in a separatory funnel - 50% recovery	36.0
150	15	Sulfonated and then extracted as above	23.3
151	15	Normal	37.7

Discussion

All the oils applied caused some retardation in growth of barley seedlings, but it was very evident that some are more injurious than others. The untreated oils were found, in the previous investigation, to cause a wide range of injury. This variation may be due to the formation of injurious compounds during the refining process, or to the original properties of the oil.

The data presented on the formation of sulfonatable compounds during distillation and on the influence of severe oxidation conditions show that the refining process may make an oil more injurious, but the properties of the original oil are also important. Several investigators (1, 2, 3) have pointed out the effect of the movement of the oil in the earth, or its filtration while in storage in the earth. They have shown that the paraffins, or lighter fractions of petroleum, diffuse

(1) Day, David T., Proc. Am. Philos. Soc., 1897.

(2) Gilpin, J. E., and Cram, M. P., The Fractionation of Crude Petroleum by Capillary Diffusion. U. S. Geo. Sur. Bul. 365, 1908.

(3) Gilpin, J. E., and Bransky, G. R., The Diffusion of Crude Petroleum Through Fuller's Earth. U. S. Geo. Sur. Bul. 475, 1910.

more slowly. The natural oils in storage in the earth may have thus been subjected to more or less fractionation during movements in geologic time.

Differences in the rate of diffusion of the various fractions may be governed by the same forces that apply to gases of different density. Graham's law states that the rate at which a gas diffuses through a small opening, or another space, is inversely proportional to the square root of the density of the gas. A close analogy seems to prevail between gaseous diffusion and the diffusion of oil through a filter. The above investigators have given extensive data showing that the lighter fractions of petroleum diffuse more rapidly through Fuller's earth and hence conclude that some of the differences occurring in natural oils have been caused by the filtration of the oil while in the earth and over long periods of time.

Maberry⁽¹⁾ has called attention to the remarkable similarity of petroleum oils in general, and states that petroleum is a mixture of a few homologous series, variations of which cause the differences found. Filtration in nature has apparently been an important factor in the separation of the injurious portions of some spray oils. Gilpin and Bransky have shown that sulfur compounds and materials that combine with sulfuric acid and with bromine are retarded in the passage of oil through earthen filters. The present investigation shows that sulfonatable materials are held back during filtration (see table III). It has also been shown that alcoholic extraction removes sulfonatable materials.

(1) Maberry, C. F., Pro. Am. Philos. Soc., 1903.

