disposal, driving motors or air engines of various kinds, clipping horses, coal or culm conveyors, lighting, agitating syrup in sugar refineries, beating eggs, raising beer, automatic fire-extinguisher service, propelling torpedoes and torpedo boats, sand-papering, aerating fuel, refining asphalt, excavating cesspools, finishing silk ribbon, for dry dock and canal lock service, agitating acids, ventilating in mines, cotton compresses, vulcanizing wood, temperature regulators, raising sunken vessels, driving printing presses and other individual tools, operating clocks, etc.

CHEMICAL SECTION.

Stated Meeting, held February 18, 1899.

THE LABORATORY PRODUCTION OF ASPHALTS FROM ANIMAL AND VEGETABLE MATERIALS.*

BY WM. C. DAY.

By carrying out operations of distillation at the ordinary atmospheric pressure upon animal and vegetable matter, both separately and mixed, I have succeeded during the past year in producing three different materials, all of which present in different degrees the properties characteristic of asphalts. Two of these materials quite closely resemble asphalts occurring in nature, namely, gilsonite and elaterite, as found in Utah.

Postponing for the present a consideration of the reasons which led to these experiments, I will first give a description of the work done and a statement of the results obtained since the publication last summer of a preliminary paper† on the same subject.

The first experiment was to distil from an iron retort a mixture of fresh fish (herring from the Delaware) and fat pine wood, partly in the form of sawdust and partly in

* Published by permission of the U. S. Geological Survey.

† "Proc. Amer. Philos. Soc.," **37**, 171.

sticks. The retort was connected with a short glass tube by means of a joint of plaster-of-paris and asbestos; this tube was connected at the other end by a similar joint with a small iron gas pipe four feet long, placed upon a combustion furnace, by which it could be maintained at a red heat. The retort was heated by gas furnaces and the distillation was carried to complete carbonization of the organic matter. An ordinary Liebig's condenser served to condense the mixed oil and water as it issued from the red-hot gas pipe. The distillation product consisted of water of a yellowish-red color, and a dark, nearly black, mobile oil, which for the greater part floated upon the water, although toward the close of the distillation a little oil would usually sink through the water.

Twelve operations of distillation consumed 9,882 grams of wood and 8,170 grams of fish, and yielded 3,010 cubic centimeters oil, of specific gravity 0.9837, and 8,240 cubic centimeters water. The average distillation shows, therefore, the figures 823.5 grams wood, 680.8 grams fish, 250.8 cubic centimeters oil and 686.7 cubic centimeters water; these average figures were approximated in each single distillation.

The oil was separated from the water and then dried by standing over chloride of calcium. A combustion of this oil, using copper oxide and lead chromate, gave the following results:

0.3104 gram oil gave 0.9593 gram CO_2 and 0.2794 gram H_2O , or

	Per Cent.
Carbon	84.28
Hydrogen	10.00

The dried oil was then subjected to distillation by itself in a hard glass retort provided with thermometer. A few drops of oil, accompanied by a little moisture, came over at 80°C .; the temperature rose rapidly to 120° , at which point distillation proceeded rapidly, giving a distillate lemon yellow in color and slightly turbid from moisture. The receiver was changed at 180° , when the distillate appeared darker in color but free from moisture. The receiver

was changed at 245° , 315° and 340° , at which last point the thermometer was removed; after this the distillation was conducted to about 425° as nearly as could be judged by the rate at which the temperature had been rising. At 315° a greenish fluorescence appeared. When the boiling was stopped the contents of the retort consisted of a mobile, homogeneous, black liquid containing no solid particles of any kind. When the retort cooled this oil solidified to a black, shining mass, showing conchoidal fracture, brittle and pulverizing to a brownish-colored powder slightly darker than the powder of Utah gilsonite, which, in appearance, it closely resembled; in fact, it was only by the rounded surface of the artificial product that the two could be distinguished by inspection. A number of distillations were made with essentially the same experience as just described, except that the material obtained the first time was slightly sticky to the touch and entirely soluble in carbon bisulphide, while the samples obtained subsequently were not at all sticky, and were not entirely soluble in the bisulphide.

Subjected to combustion, the sample resulting from the first distillation gave the following result: 0.2211 gram substance gave 0.7100 gram CO_2 and 0.1540 gram H_2O , or

	Per Cent.
Carbon	87.57
Hydrogen	7.74

Two combustions of the artificial gilsonite finally made in quantity gave the following results:

I. 0.2529 gram substance gave 0.8031 gram CO_2 and 0.1599 gram H_2O .

II. 0.3015 gram substance gave 0.9564 gram CO_2 and 0.1938 gram H_2O .

	I. Per Cent.	II. Per Cent.
Carbon	86.61	86.51
Hydrogen	7.02	7.10

Two nitrogen determinations by Kjeldahl's method, using in the first case 1.990 grams substance, and in the second 0.9824, gave nitrogen 1.95 and 1.86 per cent., respectively.

Two determinations of sulphur by Peckham's method* resulted as follows:

- I. 2.0218 grams substance gave 0.0136 gram BaSO_4 .
 II. 1.9988 grams substance gave 0.0114 gram BaSO_4 .

	I. Per Cent.	II. Per Cent.
S =	0.092	0.078

According to the figures obtained, the composition of the artificial gilsonite appears to be as follows: For the sake of comparison, the figures for natural Utah gilsonite are also given here, as well as elsewhere.

	Artificial. Per Cent.	Natural. Per Cent.
Carbon	86.56	85.83
Hydrogen	7.06	10.59
Nitrogen	1.91	2.59
Sulphur	0.08	0.26
Oxygen (by dif.)	4.39	0.63
		Ash, 0.10
	<hr/> 100.00	<hr/> 100.00

While the differences in composition between these two materials are not great, still they can by no means be regarded as insignificant, particularly as regards those in the cases of hydrogen and oxygen. It is true, however, that much greater differences between two natural asphalts taken from sources in the same neighborhood have been found.

Determinations of solubility in the following solvents were made: Carbon bisulphide, turpentine, ether, gasoline and absolute alcohol. The method employed was to treat a weighed portion of the substance with the solvent until no further action took place, and then weigh the undissolved residue on a tared filter.

CARBON BISULPHIDE.

I.

Weight of substance taken	0.5505
" " undissolved residue	0.1060
" " dissolved substance	0.4445
Per cent. soluble in CS_2 = 80.74.	

* *Journal Soc. Chem. Ind.*, **16**, No. 12, 1897.

II.

Weight of substance taken	0'6970
" " undissolved residue	0'1293
" " dissolved substance	0'5677
Per cent. soluble in CS ₂ = 81'44.	

TURPENTINE.

Weight of substance taken	0'9041
" " undissolved residue	0'4568
" " dissolved substance	0'4473
Per cent. soluble in turpentine = 49'47.	

ETHER.

Weight of substance taken	0'5776
" " undissolved residue	0'1901
" " substance dissolved	0'3872
Per cent. soluble in ether = 67'03.	

GASOLINE.

Weight of substance taken	0'5339
" " undissolved residue	0'2845
" " substance dissolved	0'2491
Per cent. soluble in gasoline = 46'71.	

ABSOLUTE ALCOHOL.

Weight of substance taken	0'5547
" " undissolved residue	0'2862
" " substance dissolved	0'2585
Per cent. soluble in alcohol = 48'40.	

All the solutions obtained were characterized by a more or less marked greenish fluorescence, which is also true of the natural gilsonite.

ACTION OF SOLVENTS.

Solvent.	Utah Gilsonite.	Artificial Gilsonite.
Carbon Bisulphide	99'50	100'00
		first product, 100'00
		second " 81'44
Turpentine	97'34	49'47
Ether	73'08	67'03
Gasoline	63'08	46'71
Alcohol	34'81	48'40

While the above table shows in some cases quite notable differences in solubility, every one of the solvents exercises

in each case a pronounced effect, all figures being above 30 per cent., and generally nearly 50 per cent. or more.

The action of concentrated nitric acid upon the natural and the artificial material is peculiar, and of exactly the same character. This action consists in completely dissolving the material with copious evolution of brown fumes and the production of a dark-red solution, which, upon diluting with water, yields a flocculent precipitate much resembling freshly precipitated ferric hydroxide.

In the course of an investigation of Utah gilsonite,* carried out some years since, I separated from the oils distilled from the mineral certain basic compounds suggestive in odor of the pyridine or quinoline series. These bodies were obtained by the extractive action of dilute sulphuric acid upon the oils. From such solution they are thrown down by alkalies as flocculent precipitates.

The same kind of substances were obtained from the oil which, by distillation, yielded the artificial gilsonite. The method of treatment adopted to extract these basic substances was to shake the oil with dilute sulphuric acid and then pass steam into the mixture contained in a large flask until oil no longer distilled off with steam. On neutralizing the residual acid with caustic soda solution, a precipitate looking and smelling like that from gilsonite oil was obtained. The precipitate was alternately redissolved in sulphuric acid and reprecipitated by alkali a number of times, and then, after washing with water, was left on a filter to dry. On drying, however, the material largely disappeared, thus showing its volatility, which the solid appearance when freshly precipitated had failed to suggest. It is evident, however, that the presence of these basic compounds affords another element of similarity between the natural and the artificial product, and also between these bodies and California petroleum.

DISTILLATION OF FISH ALONE.

The interesting character of the product obtained by distilling a mixture of fish and wood, and the similarity

* *Journal Franklin Institute*, **160**, 221.

between this and Utah gilsonite, suggested the advisability of carrying out the same kind of experiments with fish alone and also with wood alone. Accordingly, a number of charges of the same kind of fish were distilled, using the same apparatus as was employed for the mixture of wood and fish.

In all 4,585 grams of fish were distilled, yielding 700 cubic centimeters of oil and 2,830 cubic centimeters water. The distillate consisted of a yellow emulsion difficult to break up; the distillate from the fish and wood mixed gave no emulsion at all, but presented a well-defined line of separation between the oil and water. The emulsion was separated into oil and water by heating upon the water-bath, the oil being eventually brought to the surface of the water. Much ammonia was produced during the distillation.

An attempt was made to dry the oil by allowing it to stand over chloride of calcium for a number of days, but it could not be perfectly dried in this way. Success in drying was finally attained only by aspirating a current of dry air through the oil while it was heated upon the water-bath.

On attempting to distil the fish oil from a retort, as was done with the oil from the mixture of fish and wood, such vigorous and explosive "bumping" was encountered as to carry the contents of the retort over mechanically so that it was found impossible to distil it in this way. The appearance of moisture during this attempt to distil an oil which had been thoroughly dried made it evident that the water was formed during the distillation. The oil was transferred from the retort to an iron crucible and heated cautiously until the stage of water formation was passed, and then heated more strongly. After heating for a time the contents of the crucible were allowed to cool, when a very sticky, thick semi-liquid mass remained. It looked and smelled more like a maltha from Montana that I had examined a few years since than anything else I could compare it to. The material was again heated in the crucible, boiling it freely; on cooling again a solid was obtained, black in color and elastic, so that if bent nearly double it would fly back to its original shape like a thick piece of India rub.

ber. It could be easily cut, but not pulverized, although if struck a blow with a hammer it would break with conchoidal fracture.

Determinations of carbon, hydrogen and nitrogen were made with the following results:

I. 0.2366 gram substance gave 0.6638 gram CO_2 and 0.1933 gram H_2O .

II. 0.2333 gram substance gave 0.6618 gram CO_2 and 0.1916 gram H_2O .

III. 0.2233 gram substance gave by Kejhldahl's method ammonia corresponding to 4.19 per cent. of nitrogen.

IV. 0.8896 gram substance gave ammonia corresponding to 4.27 per cent. nitrogen.

V. 2.0402 grams substance gave 0.0287 gram BaSO_4 .

VI. 1.9954 grams substance gave 0.0276 gram BaSO_4 .

	I.	II.	III.	IV.	V.	VI.
Carbon	76.51	77.36	—	—	—	—
Hydrogen	9.08	9.12	—	—	—	—
Nitrogen	—	—	4.19	4.27	—	—
Sulphur	—	—	—	—	00.19	00.19

This material, if cooled down, became harder and less susceptible of bending; the same kind of change seemed to result also as the material became older, as after some months it became harder and more brittle.

The following results of analysis were obtained upon a sample of elaterite from Utah. This material in lump form was hard and not at all capable of being bent; it was, however, quite flexible when sawed into thin slabs. The percentages of carbon and hydrogen found are not far removed from those of the asphalt from fish alone.

I. 0.2993 gram substance gave 0.8024 gram CO_2 and 0.2550 gram H_2O .

II. 0.1995 gram substance gave 0.5404 gram CO_2 and 0.1698 gram H_2O .

	I.	II.
Carbon	73.11	73.88
Hydrogen	9.46	9.45

Further investigation of this material is now being carried out. According to Dana's "Mineralogy," p. 734, elaterite analyzed by Johnston contains 84 to 86 per cent. car-

bon, and 12.3 to 13.2 per cent. hydrogen. I am unable to give the authority for calling the Utah material elaterite, but in composition it evidently resembles much more nearly the material obtained from fish than it does the elaterite described by Dana. The much lower percentage of carbon than is contained in gilsonite is noteworthy.

Treatment of oil obtained from fish alone with dilute sulphuric acid gave a solution of basic nitrogen compounds which could be precipitated by alkalies, just as in the case of oil from natural or artificial gilsonite. The odor of these basic substances was of the same character, whatever the source.

The following determinations of the solubility of the asphalt from fish alone were made:

CARBON BISULPHIDE.

Weight of substance used	0.2999
“ “ “ undissolved	0.0954
“ “ “ dissolved	0.2045
Per cent. soluble in $CS_2 = 68.19$.	

TURPENTINE.

Weight of substance used	0.3163
“ “ “ undissolved	0.1665
“ “ “ dissolved	0.1498
Per cent. soluble in turpentine = 47.36.	

ETHER.

Weight of substance used	0.2662
“ “ “ undissolved	0.1087
“ “ “ dissolved	0.1575
Per cent. soluble in ether = 59.17.	

GASOLINE.

Weight of substance used	0.3733
“ “ “ undissolved	0.2419
“ “ “ dissolved	0.1314
Per cent. soluble in gasoline = 35.19.	

ABSOLUTE ALCOHOL.

Weight of substance used	0.4239
“ “ “ undissolved	0.2074
“ “ “ dissolved	0.2165
Per cent. soluble in alcohol = 51.07.	

DISTILLATION OF WOOD ALONE.

The same kind of rich and heavy pine as was used in mixture with fish was subjected to distillation by itself. In all 4,588 grams were used, yielding 1,150 cubic centimeters of oil and 890 cubic centimeters water.

It is interesting to note here the much larger proportion of oil obtained than resulted from the distillation of fish alone. The distillation was accompanied by the production of a thick, white smoke, which could not be condensed. The distillate was strongly acid. The oil, after drying, showed a specific gravity of 0.992. It was subjected to distillation by itself, collecting the same fractions as were taken in the case of the distillation of oil from wood and fish. The first fraction, $90^{\circ} - 145^{\circ}$, was light-yellow in color, and slightly turbid from moisture; the second, $145^{\circ} - 180^{\circ}$, was darker yellow; the third, $180^{\circ} - 245^{\circ}$, was greenish-black; the last one showed green fluorescence. After distilling off somewhat more than half the oil, the black, but perfectly mobile liquid, was allowed to cool, when it solidified to a black shining mass, very brittle and showing conchoidal fracture. While the general color was black, inspection of a thin edge along a line of fracture showed a purple color, such as could not be seen with the material from wood and fish. The specific gravity was found to be 1.0825.

When pulverized, the powder, in the course of several days, would cement together and re-form a hard, rigid mass.

Determinations of carbon, hydrogen and nitrogen gave the following results:

0.2078 gram substance gave 0.6568 gram CO_2 and 0.1549 gram H_2O .

0.9362 gram substance gave ammonia corresponding to 0.26 per cent. nitrogen.

0.8884 gram substance gave ammonia corresponding to 0.33 per cent. nitrogen.

Determinations of sulphur gave only traces.

	Carbon.	Hydrogen.	Nitrogen.
I.	86.20	8.28	—
II.	—	—	0.26
III.	—	—	0.33

The following determinations of solubility were made:

CARBON BISULPHIDE.

I.

Weight of substance used	0.3664
“ “ “ undissolved	0.0050
“ “ “ dissolved	0.3554
Per cent. soluble in $CS_2 = 98.61$.	

II.

Weight of substance used	0.3868
“ “ “ undissolved	0.0003
“ “ “ dissolved	0.3865
Per cent. soluble in $CS_2 = 99.92$.	

TURPENTINE.

I.

Weight of substance used	0.4498
“ “ “ undissolved	0.0155
“ “ “ dissolved	0.4343
Per cent. soluble in turpentine = 96.55.	

II.

Weight of substance used	0.4218
“ “ “ undissolved	0.0167
“ “ “ dissolved	0.4051
Per cent. soluble in turpentine = 96.04.	

ETHER.

I.

Weight of substance used	0.3589
“ “ “ undissolved	0.0153
“ “ “ dissolved	0.3436
Per cent. soluble in ether = 95.45.	

II.

Weight of substance used	0.4084
“ “ “ undissolved	0.0130
“ “ “ dissolved	0.3954
Per cent. soluble in ether = 96.81.	

GASOLINE.

I.

Weight of substance used	0.5342
“ “ “ undissolved	0.0441
“ “ “ dissolved	0.4901
Per cent. soluble in gasoline = 91.74.	

II.

Weight of substance used	0.3582
" " undissolved	0.0412
" " dissolved	0.3170
Per cent. soluble in gasoline = 88.49.	

ALCOHOL.

Weight of substance used	0.5548
" " undissolved	0.2130
" " dissolved	0.3418
Per cent. soluble in alcohol = 61.60.	

High solubility is characteristic of this material in all cases.

A quantity of the oil from wood alone was treated with dilute sulphuric acid for the purpose of testing for basic oils. No trace of these oils could be precipitated, however, by neutralizing the acid with sodium hydroxide.

In connection with the present investigation a complete analysis of Utah gilsonite has been made with results that are somewhat lower in carbon and in sulphur than those obtained and published a few years since.* Instead of using finely-powdered lead chromate together with copper oxide, as was the case in the first analysis, a large quantity of coarse granules of lead chromate were employed with results that showed better agreement.

In this connection it should be remarked that the use of copper oxide in hydrocarbon combustions has not infrequently given trouble in the form of irregularities in the figures for carbon. Professor Peckham, in a recent conversation, called my attention to a remark made to him by Warren to the effect that copper forms carbides which are oxidized with difficulty, and hence, according as these are formed or oxidized in succeeding combustions, the figures for carbon will vary. This point is now being investigated. Certain it is, however, that asphalts are troublesome substances in elementary analysis. This statement is thoroughly borne out by a study of the literature of these bodies.

* *Journal Franklin Institute*, **160**, 221.

The following are the results of analysis of Utah gilsonite:

I. 0.2738 gram substance gave 0.2603 gram H_2O and 0.8631 gram CO_2 .

II. 0.2017 gram substance gave 0.1930 gram H_2O and 0.6336 gram CO_2 .

III. 1.0347 grams substance gave ammonia by Kejhl-dahl's method corresponding to 2.65 per cent. nitrogen.

IV. 0.9363 gram substance gave ammonia corresponding to 2.53 per cent. nitrogen.

V. 2.1651 grams substance gave 0.0390 gram $BaSO_4$.

VI. 2.0017 grams substance gave 0.0388 gram $BaSO_4$.

	Carbon.	Hydrogen.	Nitrogen.	Sulphur.
I.	85.98	10.56	—	—
II.	85.67	10.62	—	—
III.	—	—	2.65	—
IV.	—	—	2.53	—
V.	—	—	—	00.25
VI.	—	—	—	00.27

Taking the averages of these results, the percentage composition appears to be:

Carbon	85.83
Hydrogen	10.59
Nitrogen	2.59
Sulphur	00.26
Oxygen (by dif.)	7.3
Ash*	1.10
	100.00

*Quoted from paper on gilsonite, *Journal Franklin Institute*, 160, 221.

TABLE GIVING ANALYTICAL RESULTS.

Name of Substance.	Carbon.	Hydrogen.	Nitrogen.	Sulphur.	Oxygen.	Ash.
Oil from fish and wood	84.28	10.00	undtm.	undtm.	undtm.	none
Artificial gilsonite from first preparation	87.57	7.74	"	"	"	"
Artificial gilsonite made finally	86.56	7.06	1.91	0.08	4.39	"
Utah gilsonite	85.83	10.59	2.59	0.26	0.63	0.10
Asphalt from fish alone	76.93	9.10	4.18	0.19	9.60	none
Utah elaterite	73.11	9.45	1.90	3.17	12.37	trace
Asphalt from wood alone	86.20	8.28	0.29	trace	5.23	none
Utah nigrite	83.33	8.69	undtm.	0.42	undtm.	0.12

	Fixed Carbon.	Volatile Matter.	Ash.
Utah nigrite	36.33	63.55	0.12

The specific gravities of various substances, determined in the course of the present investigation, are given in the following table:

SPECIFIC GRAVITIES.

Oil obtained from primary distillation of fish and wood, temperature 26° C.	0.9837
First fraction of above oil, 80-145° C. when distilled by itself, temperature 25.8° C.	0.842
Last fraction in same distillation, 340° C., temperature 25.9° C.,	1.002
Utah gilsonite, temperature 26° C.	1.0354
Artificial gilsonite, temperature 26° C.	1.1713
Asphalt obtained from wood alone, temperature 26° C.	1.0825
Asphalt obtained from fish alone, temperature 26° C.	1.0590
Oil from wood and fish, volatile with steam, temperature 26° C.,	0.8940
Oil obtained in primary distillation of wood, temperature 26.4° C.	0.9920

TABLE OF SOLUBILITIES IN VARIOUS SOLVENTS.

Name of substance.	Carbon Bisulphide, all.*	Turpentine.	Ether.	Gasoline.	Absolute Alcohol.
Artificial gilsonite	81.09	49.47	67.03	46.71	48.40
Utah gilsonite	99.50	97.34	73.08	63.08	34.81
Asphalt from fish alone :	68.19	47.36	59.17	35.19	51.07
Asphalt from wood alone	99.26	96.29	96.13	90.12	61.60

* This determination involved no weighings, as when the solution was filtered nothing insoluble remained behind on the filter.

The foregoing experiments suggested themselves as the result of a number of years of experimental work upon asphalts from a number of natural sources in the Western part of the United States and a study of the literature of natural hydrocarbons, solid, liquid and gaseous, and the synthetic experiments which have been carried out by Warren, Engler and Sadtler. From the chemical-geological standpoint the writings of Peckham have been very suggestive, advocating, as they have done, the idea that bitumens are distillates together with water of organic matter, which has accumulated in strata of all ages in the earth.

Utah gilsonite is the natural material to which the writer has given most experimental study. This mineral contains very little oxygen and sulphur, almost no ash, but a notable quantity of nitrogen, which shows itself in distillation pro-

ducts in the form of basic substances similar in a general way to the pyridine and quinoline series, and of the same character as the basic substances obtained by Peckham and Salathé from California petroleum, and freely commented upon by Peckham in a number of papers by him.

These nitrogen compounds suggest animal origin of the bodies containing them. It seemed, however, to the writer that a material having exclusively animal origin would be likely to contain a larger proportion of oxygen than is contained in such material as natural gilsonite, and that in laboratory experiments to reproduce asphalts low in oxygen, vegetable material should be present at the same time, and that opportunity should be afforded for the oxygen containing distillates from oils and animal substances to react at a fairly high temperature with the abundant gaseous hydrocarbons produced by distilling wood or in general vegetable material. The result of such reaction between bodies of the nature just described would be to eliminate oxygen from the oily distillate by causing it to form water and carbon dioxide with the hydrogen and carbon of gaseous hydrocarbons. This idea was strengthened by the fact that in his experiments to produce petroleum-like substances and paraffine from linseed oil Sadtler* noticed the odor of acrolein and referred to it as follows: "At first the odor of acrolein was very pronounced and powerful, showing that the glycerine of the glycerides composing the oil was being decomposed; later the odor was more that of a cracked petroleum oil, showing that the linoleic and other acids of the oil were undergoing decomposition." On another page the same writer says: "Of course the fractions must be obtained on a sufficiently large scale to admit of thorough purifying before the character of the hydrocarbons can be studied. At present they contain impurities, such as aldehyde-like and possibly ketone products. They reduce ammoniacal silver solutions and indicate thus the presence of these impurities."

The following facts, based upon a consideration of the

* "Proc. Amer. Philos. Soc.," **36**, 93.

character of the distillates obtained from the mixed animal and vegetable matter, the fish alone and the wood alone, tend to show the correctness of the writer's position in an attempt to produce an asphalt low in oxygen. The table of ultimate analyses given below shows that there is less than half as much oxygen in the asphalt from wood and fish mixed as in that from fish alone.

ULTIMATE ANALYSES.

	Ash.	Carbon.	Hydrogen.	Sulphur.	Nitrogen.	Oxygen.
Utah gilsonite . . .	0.10	85.83	10.59	0.26	2.59	0.63
Utah elaterite . . .	—	73.49	9.46	undtm.	undtm.	17.05
Artificial gilsonite from						
wood and fish . . .	—	86.56	7.06	0.08	1.91	4.39
Asphalt from wood . .	—	86.20	8.28	trace	0.29	5.23
Asphalt from fish . .	—	76.93	9.10	0.19	4.23	9.55

The following table, giving the yields of water and oil in the various distillations, is also of interest, as showing the effect of water forming reactions between hydrocarbons and oxygen compounds, which, doubtless, took place in the hot tube through which the vapors were passed before condensation.

Material Used,		Oil Produced,	Water Produced,
Grams.		Cubic Centimeters.	Cubic Centimeters.
Wood.	Fish.		
9,882	8,170	3,010	8,240
—	4,585	700	2,830
4,588	—	1,150	890

If the wood and fish, when distilled together, had yielded oil and water in the same proportion as when each was distilled by itself, then there should have been a yield of 3,724 cubic centimeters of oil from the mixture, instead of the 3,010 cubic centimeters actually produced, and, instead of 8,240 cubic centimeters of water, there should have been only 7,321 cubic centimeters.

The question of the origin of asphalts is one that cannot be intelligently discussed apart from that of the origin of petroleum, or, more broadly still, apart from the origin of the bitumens in general, which include natural hydrocarbons in all states of matter, solid, liquid and gaseous. Of these three states, liquid petroleum has, for a variety of

obvious reasons, received the most attention scientifically and technologically.

The connection quite generally believed at present to exist between petroleum and the asphalts is expressed in Dana's "Mineralogy," p. 751, as follows: "The more solid kinds graduate into the pit asphalts, or mineral tar, and through these there is a gradation to petroleum. The fluid kinds change into the solid by the loss of a vaporizable portion on exposure, and also by a process of oxidation, which consists, first, in a loss of hydrogen, and finally in the oxygenation of a portion of the mass."

If it be accepted as true that petroleum and the asphalts are related, as the quotation just made would indicate, then it follows, of course, that any view as to the origin of petroleum also applies to the asphalts. A study of the literature concerning theories as to the origin of petroleum reveals a number which differ fundamentally from each other, and which are based largely upon geological evidence. It does not seem necessary here to give detailed consideration to these hypotheses in view of the thorough manner in which they have been recently summed up and reviewed by Messrs. Sadtler, Peckham, Mabery, Phillips and D. T. Day in a series of papers* read before the American Philosophical Society, February 5, 1897. The comprehensive *résumé* given by Boverton Redwood in his work on petroleum also contributes to make further detailed review superfluous at this time. It seems, however, that the propriety of attempting to make any one of these theories cover the entire question of the origin of petroleum is very questionable in view of the fundamental differences in character and properties between petroleums of different sources, which, by the work of Schorlemmer, Warren, Mabery, Beilstein and Kurbatow, Markownikoff, Schutzenberger and Jonine, Zaloziecky and others, have been shown to exist. The following quotation from Boverton Redwood's work is of interest in this connection.

Referring to his *résumé* of theories, he says: "From the

* "Proc. Amer. Philos. Soc.," 36, 93.

account given in this section, it will be seen that there has been an abundance of speculation as to the origin of bitumen, and that, in regard to some of the theories, a considerable amount of experimental proof has been forthcoming. Probably, on the whole, the Höfer-Engler views at present have the largest number of adherents, and in respect, at any rate, to certain descriptions of petroleum, are the most worthy of acceptance. At the same time, a careful study of the subject leads to the conclusion that some petroleum is of vegetable origin, and it therefore follows that no theory is applicable in all cases."

When we consider, for example, the striking differences in character between California petroleum and Pennsylvania petroleum, to which Peckham, in a number of different papers, has earnestly called attention, the force of the last sentence quoted from Redwood will undoubtedly be keenly appreciated. Commenting upon the Höfer-Engler theory, Professor Peckham* says: "Dr. Engler, therefore, considers that some change in the animal remains must have taken place in the earth, whereby all nitrogenous and other matters, save fats, were removed, the petroleum being formed from this fat alone by the combined action of pressure and heat, or by pressure only.

"In summing up the evidence as to origin, Höfer expresses the belief that petroleum is of animal origin, and has been formed without the action of excessive heat, and observes that it is found in all strata in which animal remains have been discovered.

"Combining these two statements, we arrive at this conclusion as the Höfer-Engler theory, that bitumens are of animal origin, formed at low temperatures from fats alone by the combined action of pressure and heat.

"Steam is left out of this formula, and it is, therefore, inadequate. There is no evidence whatever that any portion of the crust of the earth has ever been subjected to the combined action of heat and pressure without the presence of steam or hot water, and in my judgment the steam has

*" Proc. Amer. Philos. Soc.," **36**, 106.

been a very potent factor in determining not only the formation, but the transference of bitumens."

The writer, from his experience in the production of asphalts, as already described in this paper, feels like endorsing most heartily the views of Peckham in regard to the necessity of steam as a factor in the production of such asphalts, at least, as have been made the subject of experimental study.

The following is a quotation from Professor Peckham's paper on "The Genesis of Bitumens as Related to Chemical Geology,"* which sums up the most important features of his views as to the genesis of bitumens. The laboratory results which I have so far obtained seem to be quite fully in accordance with the conclusions which Professor Peckham has reached.

"Upon this hypothesis, that bitumens are distillates, all of the variations observed in bitumens of different geological ages are easily explained. The earliest forms of animal and vegetable life are admitted to have been nearly destitute of nitrogen; hence, when these forms accumulated in sediments which, borne down by deposits above them, invaded an isothermal that admitted of their distillation, they must have been distilled, in the presence of steam, at the lowest possible temperature; they must have been distilled under a gradually increasing pressure, the extent of which depended upon the porosity of sediments above them up to the surface. They must also have been distilled under a gradually increasing temperature, which would have been largely controlled by the pressure. While the temperature and pressure would have, in every instance, been the least possible, with steam always present, these physical conditions would, on account of the varying porosity and consequent varying resistance of the overlying mass, have produced very great effects in some instances, and very slight effects in others. As a consequence, we have in natural bitumens, as in artificial distillates, materials varying in density from natural gas to solid asphaltum.

**Loc. cit.*

"If these distillates proceeded from materials that would yield paraffine, these permanent and stable compounds from marsh gas to solid paraffine remained in the receptacles that nature had provided for them until they were released by the drill. If, however, the distillates proceeded from sediments of a different geological age, containing animal and vegetable remains more highly organized, that would yield different series of hydrocarbons, with compounds of nitrogen, then a very different bitumen would be stored in these receptacles. Secondary reactions would convert these primary distillates into a great variety of substances.

"The contents of the original reservoirs, borne down and invaded by heat, might become involved in a second distillation at an increased pressure and temperature. Fractures of these reservoirs from excessive pressure might lead their contents to the surface along lines of contact of strata or with water containing sulphates, by which an originally pure hydrocarbon would be converted into a sulphur bitumen. A nitro-hydrocarbon, reaching the surface under these conditions, might, by the combined action of evaporation and reaction with sulphates, pass through all the varying degrees of density from petroleum to maltha, and become finally solid asphaltum, and this, through the lapse of time and abundance of material, on a scale of vast magnitude."

While it is true that most of the theories that have been advanced to explain the origin of bitumens have been directly concerned with the liquid variety ordinarily known as petroleum, and seem at least to have been based upon study, whether geological or chemical, of this variety to the exclusion of the solid form generally known as asphalt, still it is true that some theories have been advanced to explain directly the formation of asphalts, aside from and independently of their possible relation to liquid petroleum.

Thus the Trinidad asphalt was looked upon by Wall* as having resulted from the gradual decomposition of vegetable matter found imbedded in it. This view is, however,

* "Q. J. G. Soc.," 16, 460.

no more tenable than the idea that the material originated from animal remains which have been found clearly indicated from a study of the composition of the asphalt.

When we consider the amount and the character of the strictly chemical work that has been done upon the asphalts or solid bitumens, it must be admitted that they have been decidedly neglected as compared with the liquid form. Even elementary analyses are, in many cases, unreliable, and there is much need of painstaking and persistent study in this field.

When we contemplate the marked differences between bitumens from different sources, it hardly seems reasonable to believe that any one theory as to the origin of these bodies can cover all the actual occurrences. It would seem that heat and pressure, singly and combined, and of various intensities, acting with water, both as liquid and as steam, upon the same fundamental material, whether animal or vegetable, should produce a variety of carbonaceous substances differing from each other quite profoundly in physical and chemical properties. Again, similar or identical conditions prevailing with different kinds of material, whether animal or vegetable, or mixtures of the two, should also yield products of various kinds. When, therefore, we consider the great possibilities of variation in combinations of natural forces, and also equally great possibilities of variation in the nature of the organic material upon which these forces may act, it is not surprising that we find, as we do, in various parts of the earth, complicated and intimate carbonaceous mixtures, gaseous, liquid and solid, which are usually summed up under the general heading, bitumens.

The facts and figures given in this communication speak for themselves. Summed up, they show that three asphaltic substances have been obtained by operations of distillation, primarily in presence of steam from natural animal and vegetable material, both separately and combined. The material obtained from the mixture of fish and wood, and called artificial gilsonite, so closely resembles the gilsonite from Utah that it is impossible by inspection to tell the two materials apart. The material obtained from fish alone also

resembles what has been called (with questionable propriety elaterite from Utah. While these two pairs of substance differ from each other to a greater or less extent in respect to the various parallel treatments to which they have been subjected, and while they also differ somewhat in chemical composition, as well as in physical solubility, specific gravity, streak, etc., these differences are all *in degree* and not in any single case *in kind*.

I am now engaged in the study of an asphalt known as nigrite, which occurs near the gilsonite of Utah. The differences between these two bitumens are throughout more striking than any that I have observed between the natural and the artificial substances considered in this paper.

In conclusion, I take pleasure in acknowledging the benefit and the satisfaction I have derived from a study of the papers published by Professor Peckham, particularly the two entitled "The Genesis of Bitumens as Related to Chemical Geology"* and "On the Nature and Origin of Petroleum."†

I am indebted to my assistant, Mr. Eugene Leamy, for able assistance throughout the entire work, and to one of my former pupils, Miss Georgia Porter, for the nitrogen determinations.

SWARTHMORE COLLEGE, PA.. February 18, 1899.

* "Proc. Amer. Philos. Soc.," **37**, 108.

† *Ibid*, **36**, 103.