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A study of fossil resins in Huntington Canyon coal

Ross D. Gardner
Brigham Young University - Provo

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A STUDY OF FOSSIL RESINS IN
HUNTINGTON CANYON COAL

A Thesis
Presented to
The Faculty of The Department of Chemistry
Brigham Young University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

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by
Ross D. Gardner
June, 1948

This thesis by Ross D. Gardner is accepted in its present form by the Department of Chemistry as satisfying the thesis requirements for the degree of Master of Science.

PREFACE

This study of the resins in coal was undertaken at the suggestion of Mr. Adriaan Nagelvoort of Huntington, Utah. The author had long considered coal to be one of Utah's greatest natural resources and, therefore, welcomed the opportunity to contribute something to the fund of knowledge concerning it. Besides his helpful suggestions Mr. Nagelvoort furnished a sample of resin for the investigation directly from his resin recovery plant in Huntington Canyon. By taking the sample from the large-scale recovery operations the author obtained a more representative sample than would have been possible had he taken the resin from the coal himself. The author takes this opportunity to express his gratitude to Mr. Nagelvoort for his assistance.

Acknowledgements are also due Dr. Loren C. Bryner, under whose direction the work was done, and the others of the staff of the Chemistry Department of the Brigham Young University for their cooperation and help given in the experimental work and in the writing of this thesis.

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INTRODUCTION

According to Webster[1], the natural resins are a group of solid or semisolid organic substances of high molecular weight, chiefly of vegetable origin, having an amorphous structure and being, usually, yellowish to brown in color. They are transparent to translucent, soluble in most organic solvents but insoluble in water, soften and melt on heating and burn with a smoky flame. They are nonconductors of electricity and very poor conductors of heat.

Natural resins are associated with, and sometimes confused with gums[2,3] and waxes[4]. Bennett[5] says that in the varnish industry natural resins are commonly called gums but that, correctly, the gums are soluble in water whereas the resins are insoluble. Chemically, the gums are largely carbohydrates[6]; the waxes are fatty acid esters of higher monohydroxy alcohols or hydrocarbons with physical properties similar to such esters[7]; and the resins are mixtures of resin

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[1] "Resins", Webster's New International Dictionary.

[2] Lange, N. A., Handbook of Chemistry, 6th. Ed., Handbook Publishers, Inc., Ohio, 1946, pp. 700-709.

[3] Bennett, H., Concise Chemical and Technical Dictionary, Chemical Publishing Co., Brooklyn, N. Y., 1947, p. 447.

[4] Nagelvoort, Adriaan, "An American Source of Natural Resins for the Paint and Varnish Industry", Chem. and Met. Eng., Vol. 49, Oct. '42, p. 80.

[5] Bennett, op. cit., p. 447.

[6] Dull, Charles E., Modern Chemistry, Holt, 1942, p. 584.

[7] Bennett, op. cit., p. 982.

acids, esters of resin acids, and resenes[8].

Value

Lange[9] calls the resins a waste product of the plants which produce them; but Nagelvoort[10] suggests that, especially in the case of coniferous trees, they have the function of protecting the plant from decay. According to Moore[11] the dominant portion of most, if not all, of our Paleozoic and Mesozoic coals have been formed chiefly from coniferous plants. Selvig[12] says that there are resins in practically all bituminous coals including those of the Paleozoic Age, and that they have changed very little since they were first formed by the plants. The age of these coals is placed at about 250 million years by Schuchert[13], indicating that the resins are very stable material.

It is in this stability that the fossil resins are finding, at present, their chief commercial value. They are used

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[8] "Resins", Webster's New International Dictionary.

[9] Lange, op. cit., p. 1646.

[10] Nagelvoort, op. cit., p. 80.

[11] Moore, Elwood S., Coal, John Wiley and Sons Inc., New York, 1940, p. 30.

[12] Selvig, W. A., Resins in Coal, U. S. Bureau of Mines Technical Paper 680, 1945, p. 3.

[13] Schuchert, Charles, Outlines of Historical Geology, Wiley, New York, 1946, p. 14.

in protective coatings such as varnishes, paints and lacquers.[14] Synthetic resins produced from rosin are cutting deeply into this market. Conant and Blatt[15] say that in 1944 146 million pounds of glyptal (glycerol ester) resins were produced from abietic and maleic acids for use in protective coatings. Still, the demand for fossil resins is shown by Nagelvoort[16] who quotes the United States Department of Commerce in the following importation of resins, before the war, by the paint and varnish industries : dammar (19 million pounds annually) from the East Indies; manila copal (20 million pounds annually) from the Phillipines; kauri from New Zealand; sandarac and accroides from Australia; and sandarac, mastic and congo copal from Africa.

The idea of replacing these foreign imports with a local product has lead to considerable interest in the last few years in the vast supplies of fossil coal resins within our own country[17].

Chemical Nature

The exact chemical nature of the fossil resins has not been described in the literature. The coal resins, especially,

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[14] Selvig, op. cit., p. 1.

[15] Conant and Blatt, The Chemistry of Organic Compounds, Macmillan, 1947, p. 513.

[16] Nagelvoort, op. cit., p. 80.

[17] Selvig, op. cit., p. 1.

have received little attention. However, since the coal resins bear some similarity in physical properties to the rosin of the modern pine trees[18], and since, according to Moore[19], the coal resins were produced by trees probably similar to modern pines, let us look briefly into the chemical nature of rosin[20].

Fieser[21] describes the material which exudes from the bark of the American pine tree as a viscous solution of about four parts nonvolatile acid material in one part of terpene hydrocarbons, largely pinene. He states that the nonvolatile acids, or resin acids, consist of several isomers of abietic acid ($C_{19}H_{29}COOH$) which change to abietic acid when heated with an inorganic acid or with acetic acid. Fieser states, further, that these resin acids are derived polymers of the terpenes ($C_{10}H_{16}$) which are in turn composed of two units of isoprene (C_5H_8). This is in agreement with the "Isoprene Rule" which is quoted from Conant and Blatt[22].

> The occurrence in natural products of structures which can be considered to be built up of isoprene units is so frequent that chemists making preliminary decisions between alternative formulas for a naturally occurring compound will choose the structure that is composed of isoprene units.

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[18] Tropsch, <u>Brennstoff Chem.</u>, Vol. 8, p. 369, 1927 (Chem.Abs.)

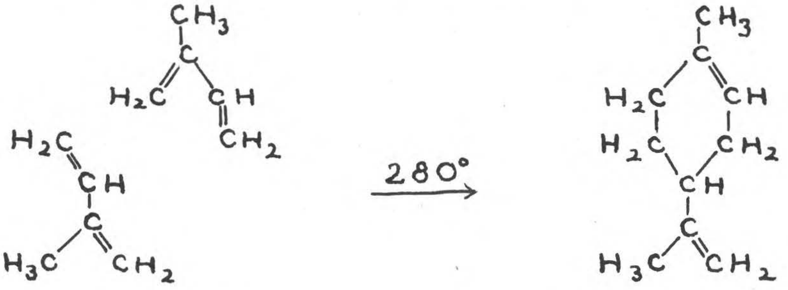
[19] Moore, <u>op. cit.</u>, p. 30.

[20] Palkin, S., "The Acids of Pine Oleoresin and Rosin", <u>J. Chem. Ed.</u>, 12, 1, p. 35.

[21] Fieser and Fieser, <u>Organic Chemistry</u>, Heath, 1944, p. 991.

[22] Conant and Blatt, <u>The Chemistry of Organic Compounds</u>, Macmillan, 1947, p. 584.

Fieser[23] classifies a large number of plant products as "isoprenoids". He says that isoprene seems to be the fundamental building unit and offers the following equation to illustrate the formation of a terpene from isoprene:



Isoprene Dipentene (a terpene)

This reaction, Fieser says, will take place in the laboratory at 280°C. and involves simply the 1,4 addition of one molecule of isoprene to the 1,2 position of another.

The absence of isoprene, itself, in plants leads Richter[24] and others[25,26,27] to consider that terpenes are the fundamental units. They call isoprene a hemiterpene; compounds with the impirical formula $C_{10}H_{16}$ and their close derivatives are called terpenes. Compounds with fifteen carbon atoms per molecule are sesquiterpenes; those with twenty carbon atoms per molecule are diterpenes; etc.

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[23] Fieser and Fieser, op. cit., p. 992.

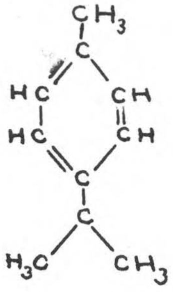
[24] Richter, George H., Textbook of Organic Chemistry, John Wiley and Sons, 1943, p. 647.

[25] Lucas, H. J., Organic Chemistry, Am. Bk. Co., 1935, p. 589.

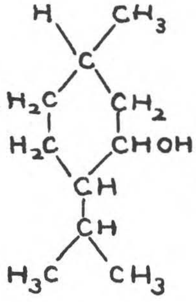
[26] Porter, The Carbon Compounds, Ginn and Co., 1931, p. 335.

[27] Degering, F., An Outline of Organic Chemistry, 1941, p. 263.

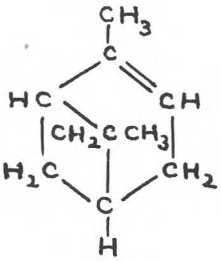
Degering[28] lists many terpenes which he says occur in rubber, citrus fruits, lemon grass oil, and in the products of cone bearing trees. Typical examples are:



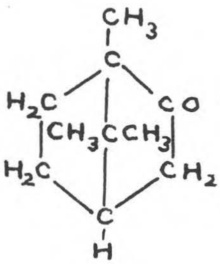
Cymene



Menthol

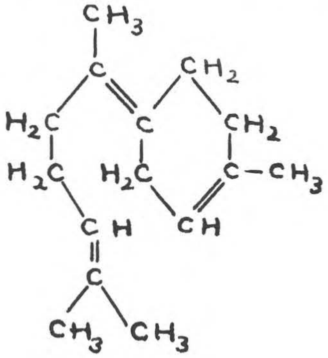


Pinene

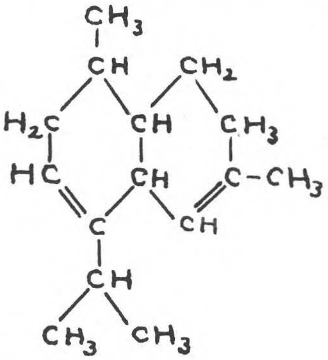


Camphor

Typical sesquiterpenes are taken from Richter[29]. He describes each as occuring in a great many essential oils.



Bisabolene



Cadinene

Richter says that bisabolene is especially abundant in Bisabol Myrrh and Oil of Bergamot, and cadinene is the main constituent of Oil of Cubebs.

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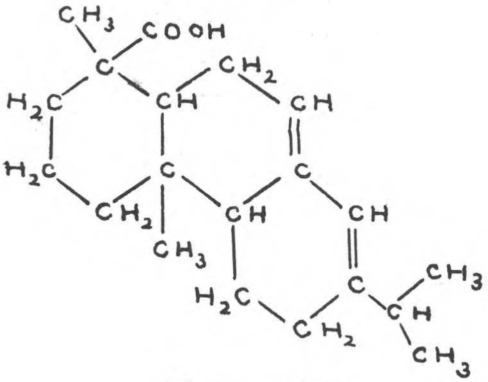
[28] *Ibid.*

[29] Richter, op. cit. p. 669.

Fieser[30] uses abietic acid as a representative of the diterpenes. This, as quoted above, Fieser says is the principal constituent of rosin.



Abietic Acid

Fieser also gives examples of triterpenes and tetraterpenes, the latter including the carotenes.

Source of Resins

Cady[31] says that bituminous coal is made up of bands of the following types: Fusain, which is carbonized wood or mineral charcoal, having a fibrous appearance and being very friable--breaking down to a soiling black powder; Vitrain, or anthraxylon, forming thin bands of bright, glassy, jetlike coal having conchoidal fracture; Durain, a dull coal having an earthy appearance and black to gray color, consisting of cuticles, spores, resins, and other of the more resistant plant bodies; and Clairain, having a bright color and being translucent but not having the conchoidal fracture nor the friability of Vitrain.

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[30] Fieser and Fieser, op. cit., p. 991.

[31] Cady, G. H., "Coal Petrography", Chemistry of Coal Utilization, 1945, Vol. I, pp. 86-102.

According to Bateman[32] the various bands in the coal are all made up of partly decomposed and macerated vegetable matter, mostly land plants, of which the following parts have been recognized:

cellulose	(2)	protoplasm	(1)	resins	(10)	pigments	(3)
pentosans	(2)	starches	(2)	gums	(6)	oils	(5)
lignin	(7)	cutin	(8)	waxes	(9)	fats	(5)

The number in parenthesis after each part, he says, represents the order of susceptability of that part to bacterial action and shows why resins are a prominent constituent of coal.

Selvig[33] recognizes two types of resins in coal, microscopic and macroscopic resins. He says that the microscopic form consists of small particles existing about as they did in the original cells of the plants except that they are now more concentrated due to the decomposition of the less resistant parts of the cells. They form a prominent part of the vitrain and durain of practically all bituminous coals, including the older Paleozoic coal. The amount of microscopic resins present depends both upon the kind of tree from which the coal came and the degree of concentration due to decomposition of the less resistant materials. Selvig estimates that they average five percent of the total coal. These resins, he says, are usually ovoid and light yellow to brown in color.

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[32] Bateman, *Economic Mineral Deposits*, Wiley, 1942, p. 630.

[33] Selvig, *op. cit.*, p. 3.

The macroscopic or lump type resins, Selvig says, are found only in the coals from the Cretaceous and Tertiary periods (formed in the last 200 million years). He describes them as occurring in relatively large irregular, golden yellow to dark red lumps readily visible to the naked eye. He states they are probably about the same as the microscopic resins except for the particle size, having been exuded from the bark of the trees in large lumps instead of remaining inside the cells or resin ducts. He calls his classification one of convenience only.

Many of the western Cretaceous and Tertiary coals evidently contain some visible lump resin. White[34] describes lump resins in the lignites of the Fort Union Tertiary of North Dakota and Montana, the Cretaceous lignites of Arkansas and Texas, the sub-bituminous coals of the Cretaceous in the Denver Basin and in the Gallup district of New Mexico, the Eocene coals of the Cascade region of Washington, and the Cretaceous coals of the Hanna district of Wyoming. According to Nagelvoort[35], however, there is probably no better source anywhere in the United States than a certain vein in Utah running from Castle Gate on the north to Salina Canyon on the south. Nagelvoort estimates that it runs about five percent lump type resin.

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[34] White, David, Resins in the Paleozoic Plants and in Coals of High Rank, Geol. Survey Prof. Paper 85, 1914, pp. 65-96.

[35] Nagelvoort, Adriaan, Personal Interview at the Nagelvoort Resin Recovery Plant in Huntington Canyon, Emery Co., Utah, June 8, 1947.

SURVEY OF LITERATURE

Methods of Recovery

A commonly used method of recovery of the resins is one based upon the difference between the density of coal and that of the resin particles. This is known as the float-and-sink method. It was described in connection with resin recovery from coal by Carnochan[36] in 1924. He used a sodium chloride solution with a density between that of the resin and that of the rest of the coal. Coal has a density of about 1.28 and the resin of about 1.03; so a salt solution with a density of 1.10 caused the coal to sink and the resin to float. Carnochan's work was done on a shipment of resinous coal from Coalmont, British Columbia. His conclusions are as follows:

> 1. It is possible to recover the resin from the coal obtaining a high grade concentrate and clean tailings.
> 2. Sodium chloride is the best salt to use. It gives as good results as calcium chloride and is cheaper to use.
> 3. The coal should be ground to pass a 20-mesh sieve before separating.
> 4. A cone is the best apparatus to use for the separation.
> 5. In mixing the coal and resin with the solution some vigorous agitator is necessary as the coal wets with difficulty and when dry floats on the surface of the solution.

Nagelvoort[37] applied the float-and-sink-process to Huntington Canyon coal after considerable research of his own.

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[36] Carnochan, R. K., Separation of Fossil Resins from Coal, Canada Dept. of Mines, No. 605, 1924, pp. 114-120, quoted in Selvig, op. cit., pp. 7-9.

[37] Nagelvoort, op. cit., pp. 80-82.

He found that by crushing the coal to pass a one inch screen, then passing it over a 10-mesh screen, eighty-five percent of the resins would be in the finer screenings. This, he says, is because the resin is much more friable than coal; therefore, the lumps break along the resin seams. By using this process much handling of the coal was eliminated and the coal remained in a more marketable condition.

Nagelvoort also found that one part per million of tannic acid in the salt solution made it much easier to wet the coal and thus easier to get a complete separation. He found, too, that certain admixed waxes could be removed from the resins by further flotation in water, sp. gr. 1.0, using 10 parts per million tannic acid as a wetting agent. The waxes, having a density of less than one, floated and the resins sank. The floated waxes constituted about one percent of the resins and are described as being soft as talc and having a melting point of 100°C. He concluded that both this wax and a dark, asphalt-like substance dissolved in the resins must be removed in order to make the resins acceptable to the varnish industry.

Nagelvoort found that removal of the asphalt could be accomplished by use of solvents. A mixture of 60 percent naptha and 40 percent alcohol gave the best separation. It dissolved the resins completely and precipitated the asphaltic material as a black, sticky mass that settled out rapidly. This material constituted about twenty percent of the original resin. Boiling the solution concentrated the alcohol and precipitated one type of resin which melted at 250°C. Further evaporation left another type which melted at 120°C. He found that both types were suitable for the preparation of light-colored varnishes.

Nagelvoort obtained several U. S. patents on his processes[38,39].

In 1930 Combined Metals Reduction Company obtained British and American patents[40] on a froth flotation process as a result of the work of W. D. Green, Concentration Engineer for the company. The process is described as follows:

> "The finely powdered coal is mixed with water to form a paste. A frothing agent is added (such as ammonium hydroxide, turpentine, pine oil, or cresol) and the mixture is subjected to froth flotation. The resin froth is separated and may be freed from coal particles by refloating in the presence of potassium alum and additional ammonium hydroxide".

Klepetko[41] who is present metallurgical manager for the same company made further contributions. He says the best preparation of the coal is a graded crushing to not finer than minus 3/8 inch and floating only the minus 6-mesh product therefrom. This, he says, involves the flotation of about 66 percent of the original coal. It gives a slightly lower yield, but an improved product which can be refined without undue difficulty. Klepetko also describes a new refining process involving the extraction of the resins with hexane, separation of residue by direct filtration, and evaporation of the solvent. He found that only about 65 percent of the hexane could be

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[38] U. S. 2,310,492 Feb. 9, 1943 (Chemical Abstracts)

[39] U. S. 2,364,090 and 2,364,091 Dec. 5, 1944 (Chem. Abs.)

[40] Brit. 357,733 Aug. 22, 1930; U. S. 1,773,977 Aug. 26 1930 (Chemical Abstracts)

[41] Klepetko, Ernest, "Recovery of Resins from Utah Coal", Inst. Min. and Met. Eng., Tech. Pub. No. 2166, May 1947.

evaporated directly. Then the solution frothed and insulated the heating coils. This difficulty he overcame by passing the last 35 percent of the solution across a steam jet to evaporate the last of the solvent. He says the refined product can be made less bulky for shipment by melting it.

According to Catteral[42], the United States Fuel Company is currently extracting resins from coal screenings at its mine at Hiawatha, Utah for the Combined Metals Reduction Company using a froth flotation process. He says the resins are shipped to the Combined Metals Refinery at Bauer, Utah for refining.

In 1943 Higgens[43] obtained a patent on a process for extracting resins from coal by use of solvents. The coal is treated with turpentine to dissolve the resins then with kerosene to recover the turpentine. The resin is then obtained by distillation of the solvents.

Other Studies

Elworthy[44] did some work on the shipment of coal from Coalmont, B. C., that was used by Carnochan as mentioned above. He used the float-and-sink method of recovery with sodium chloride solution. He described the resin as occurring in thin seams about ½ inch thick or in isolated fragments seldom more than ¼

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[42] Catteral, James, Personnel Manager of U. S. Fuel Co., Personal Interview at Carbon College, April 13, 1948.

[43] U. S. 2,330,887 Oct. 5, 1943 (Chemical Abstracts)

[44] Elworthy, R. T., Some Canadian Fossil Resins, Can. Dept. Mines, No. 605 (1924) pp. 45-57, quoted in Selvig, op. cit. pp. 9-12.

inch in diameter. The pieces were irregular in shape, brittle, and broke with a conchoidal fracture. The color ranged from a light yellow through all the shades of brown to black. Most pieces were transparent to translucent but the darker pieces were opaque.

Elworthy notices a considerable variation in the specific gravity. He attributed this to the occurrence of varying quantities of occluded gas bubbles in the different fragments. He separated a sample according to specific gravity using salt solutions of various densities from 1.00 to 1.20 with the results given in table I. He also observed that the lower-specific-gravity fractions were lighter in color than the heavier fractions and proposed that this system of separation be used for commercial grading of the resins as to quality.

TABLE I.

FLOAT-AND-SINK ANALYSIS OF RESINS FROM COALMONT, B. C.
ACCORDING TO ELWORTHY

Density		Percent
0.00 — 1.00		.19
1.00 — 1.03		3.93
1.03 — 1.05		35.65
1.05 — 1.08		19.68
1.08 — 1.10		10.60
1.10 — 1.15		15.10
1.15 — 1.20		4.16
Above 1.20		3.92
	Loss	6.77
	Total	100.00

Elworthy made a chemical analysis of the resin obtaining the following results: Carbon 76.40%, Hydrogen 10.19%, Oxygen 10.66%, and ash 2.75%. He compared this to Prussian Amber which, according to Lange[45] is a fossil resin from coniferous trees. Elworthy's results for the Prussian Amber were: Carbon 78.82%, Hydrogen 10.23%, and Oxygen 10.15%.

After preparing a batch of varnish, Elworthy concluded that it would be difficult to find a satisfactory industrial use for the resins investigated unless they could be obtained in considerable quantities and cheaply enough to compete with the darker varnish resins.

Benson[46] studied resins from the Newcastle coal mines in Washington and from the Clear Creek mine in Utah. The Newcastle sample was hand-picked and raw while the Clear Creek sample, which could not be conveniently hand-picked was extracted directly from the crushed coal with petroleum ether. His results are given in table 2.

From the close agreement between the acid and the saponification values of the Washington resin, and from the lowness of both, Benson concluded that Washington resin was composed almost entirely of resenes rather than acids or esters. The two values were close also for the Utah resin, but in this case both were high, indicating a high content of resin acids and little of esters or resenes. The Washington resin showed a greater degree of unsaturation according to the iodine numbers.

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[45] Lange, N. A., Handbook of Chemistry, 1939, p. 526.

[46] Benson, H. K., "A Study of the Resins in Western Coal", Ind. Eng. Chem. 17, 1925, pp. 21-23.

TABLE 2

ANALYTICAL CONSTANTS OF RESINS ACCORDING TO BENSON

Property	Utah Resin	Washington Resin
Color	Light brown	Light yellow
Light Transmission	Transparent	Transparent to translucent
Specific gravity at 22°C.	0.9887	1.03
Hardness (Mohr)	Powders easily	Scratched by copper sulfate crystal
Ash	-----	1.05%
Moisture	-----	.15%
Melting point	98--101°C.	395--402°C.
Acid number	156--160	5.3
Saponification no.	163--173	8.3
Iodine number	60	281--312
Analysis		
Carbon	80.4%	79.6%
Hydrogen	9.4%	10.63%
Oxygen	10.2%	8.94%

Benson also studied the extraction of resins from Utah coal by solvents. The coal was crushed to pass a 10-mesh sieve and 10 gram portions were extracted in a Soxhlet apparatus with the results shown in table 3. The cymene gave the greatest quantity of resin but it was of poor quality. After considering both quantity and quality Benson decided that petroleum ether was the best solvent.

Cochram[47] studied the effect of resins upon the properties of coal. He obtained resins from Hamstead vitrain by the removal of the surrounding material with sodium hydroxide and hydrogen peroxide. The resin appeared in yellow rods

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[47] Cochram and Wheeler, "Resins in Coal and Their Effect on its Properties", Fuel in Science and Practice, 6 (1927) p. 425, Chemical Abstracts (1928).

varying up to .02 inches in length. Photomicrographs of the vitrain indicated that the resin rods existed in the vitrain in the same position that they originally occupied in the woody tissue. He found that the principal effect of a high percentage of resin in the coal was to reduce swelling on carbonization.

TABLE 3

SOLUBILITY TEST WITH RESIN FROM UTAH COAL
ACCORDING TO BENSON

Solvent	Percent of Coal Extracted
Benzene	3.25
Ether	3.17
Ethyl alcohol	.34
Carbon Disulfide	Coal substance also dissolved
Petroleum ether	7.72
Carbon tetrachloride	3.26
Cymene	10.86
Acetone	8.42

A similar study was made by Davis and Reynolds[48] on coal from Deercreek mine in Huntington Canyon, Utah. They carbonized samples of the original coal and samples from which the resins had been removed by the float-and-sink process developed by Nagelvoort[49]. They evaluated the cokes produced on the basis of the size of their pieces and their resistance to breakage and abrasion as determined by a tumbler test.

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[48] Davis and Reynolds, "Influence of Resins in a Utah Coal on its Coking Properties", Fuel, 23 (1944) pp. 37-40, quoted by Selvig, op. cit., p. 18.

[49] Nagelvoort, op. cit., p. 81

They found that removal of the resins did not increase the quality of the coke but perhaps even decreased it. The yield of coke was increased, accompanied by a decrease in the yield of coal tar.

Fieldner, Storch and Hirst[50] found that resins, along with any spores and oil algae present in the coal liquify very readily under mild conditions of hydrogenation.

Povarnin[51] emulsified a resin with aqueous alkali, exposed it to the air for oxidation, then treated it with a dilute acid. The resulting product was found suitable for light surface coatings, He obtained U. S. S. R. patent 66, 876 on August 31, 1946.

Gardner[52] reports that at least some of the resin in Horse Canyon coal will volatilize in the coking ovens without decomposing. He exhibited a sample of light-colored resin separated from the coal tar at the by-products recovery plant laboratory of the Geneva Steel Company at Provo, Utah. No determination had been made of the properties of the resin.

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[50] Fieldner, Storch, and Hirst, "Hydrogenation and Liquifaction of Coal Resins", Bureau of Mines Technical Paper 666, 1944, p. 69. (Chemical Abstracts)

[51] Povarnin, I. G., "Oxidation of Conifer Resins", Chemical Abstracts, July 1947.

[52] Gardner, W. J., Personal Interview at his home in Provo, Utah, Dec. 28, 1947.

STATEMENT OF PROBLEM

The object of this investigation was to determine whether or not a certain sample of raw resin, collected by Mr. Adriaan Nagelvoort from coal from Huntington Canyon, Emery County, Utah, could be separated into more than one fraction with each fraction having distinctly different properties. Three methods of separation were attempted: (1) Separation of specific gravity fractions, (2) separation by use of solvents, and (3) chromatographic separation. Properties determined as a means of establishing any differences in the resins were: solubility, softening points, acid numbers, and iodine numbers.

EXPERIMENTAL METHODS

Separation Into Specific Gravity Fractions

The separation on the basis of specific gravity fractions was first suggested to the author by Nagelvoort[53] at the time the sample of resin was obtained at his recovery plant. He said (in agreement with Elworthy[54]) that the different particles of resin had different specific gravities ranging from 1.00 to 1.10 and that the color of the resin was more intense in the denser particles. Mr. Nagelvoort suggested the following means of separation.

Sodium chloride solutions were prepared having the following specific gravities: 1.08, 1.06, 1.05, 1.04, 1.03, 1.02, and 1.00. Specific gravities were checked by means of a hydrometer. Tannic acid was placed in the 1.08 solution to act as a wetting agent. One hundred grams of air-dried resin sample was weighed out and triturated in a mortar with the 1.08 salt solution until thoroughly wet. More of the solution was then added until a thin suspension of the resin was obtained. The suspension was then centrifuged and the material which packed at the bottom of the centrifuge tubes was taken as having a specific gravity greater than 1.08. The remaining suspension was filtered and the residue re-suspended in the salt solution of specific gravity 1.06. This process was repeated with each solution in turn down to water, thus dividing the one hundred gram sample into eight portions.

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[53] Nagelvoort, Adriaan, Personal Interview, June 8, 1947.

[54] Elworthy, op. cit., p. 57.

Determination of Solubility in Various Solvents

The refining procedure of the commercial producers of resins from Utah coals indicates that the coloring material in resins is not an essential part of the resins, but constitutes an impurity. Nagelvoort[55] and the Combined Metals Reduction Company[56] (as already described in this paper) both clarify their products by extraction with solvents. The residue of such extraction is a black, sticky, asphalt-like substance not resinous in character. Since the object of this investigation was to establish differences in the resin and not degrees of contamination, it became necessary to refine each fraction before going further. In order to choose the best solvent for this purpose, the following procedure was adopted.

One gram samples of the whole crude resin were weighed out and dissolved in ten milliliter portions of a few common organic solvents. After maximum dissolution had taken place the solutions were centrifuged and decanted. The residues were dried and weighed. The solutions were then transferred to watch glasses and the solvents allowed to evaporate.

Determination of Softening Points

Melting point determinations were attempted, using the capillary tube method but were unsatisfactory. Attempts were made therefore to determine softening points by observing the

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[55] Nagelvoort, op. cit., p. 82.

[56] Klepetko, op. cit., pp. 1 ff.

temperature at which the resin would yield to a definite pressure.

Rangaswami[57] describes a method for determining the melting points of resins, Two-tenths grams of resin is melted in a crucible. After cooling, 25 grams of mercury is added and the temperature raised gradually. At the melting point, the resin appears at the surface of the mercury.

This procedure was tried, but inconsistant results were obtained by it. The resin, instead of breaking free at a certain temperature and rising quickly to the surface, would cling to the crucible and creep slowly up the side.

Better results were obtained by using the modification of Krauz and Majrich[58] which is as follows: A plug of resin is placed in the end of a fine glass tube; two parallel copper wires are slipped into the tube so that their ends touch the resin; and the plugged end of the tube is immersed in a mercury bath so that the ends of the wire are below the level of the mercury. The temperature is raised gradually. When the resin melts, the mercury pushes it up and establishes contact between the wires, lighting a bulb.

By using this apparatus it was possible to duplicate results more closely. Tubes were prepared having uniform openings of approximately three mm. diameter. The resin was pack-

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[57] Rangasami, "Melting Point Apparatus", J. Oil and Chem. Colour Assoc. 13, 287, 1930, (Chemical Abstracts)

[58] Krauz and Majrich, "Apparatus for Determining Melting Points of Resins", Chem. Obzor. 15, 1-2, 1940, (Chem. Abs.)

ed into the end of the tube to a depth of two mm. by means of a small glass rod. The tube was immersed in the mercury to a depth of approximately four cm. each time. The mercury was allowed to cool to about 20 degrees below the melting point each time before the next tube was inserted, and the temperature was raised at a uniform rate of about two degrees per minute.

Determination of Acid Numbers

The acid number is a measure of the free acid in a material. It is defined as the number of milligrams of potassium hydroxide required to neutralize the free acids in one gram of material.

The procedure for the determination of acid numbers of the resin fractions was taken from Coburn[59]. He recommends doing the titrating in a two-phase medium composed of an organic solvent layer and an aqueous layer. He says that saturation of the aqueous layer with sodium chloride adds sharpness to the endpoint by salting out the soaps formed by the neutralization of the acids.

A 1.0 gram sample of the resin was weighed out and dissolved in 25 ml. of a mixture of two parts benzene to one part ethyl alcohol. After the resin was completely dissolved, 25 ml. of saturated, neutral salt solution and several grams of solid sodium chloride were added. Phenolphthalien indicator was used and 0.5 N. sodium hydroxide

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[59] Coburn, "Acid Numbers of Dark Resins", Ind. Eng. Chem. Anal. Ed., 2, 181 (1930)

solution was added until the aqueous layer remained red after vigorous shaking. The excess of standard alkali was then titrated with a standard acid. In this last titration it was not necessary to shake the mixture so vigorously as to break the two layers.

Determination of Saponification Numbers

According to Mathews[60] the saponification number is obtained in the same way as the acid number, except that in the determination of the saponification number the sample is refluxed for an hour with a fairly concentrated alkali before being titrated, in order to hydrolyze the esters present. The saponification number is the number of milligrams of potassium hydroxide required to completely saponify one gram of a substance. It includes the acid number and when used with the acid number is a measure of the amount of material present as esters.

Mathews' procedure was modified to correspond to Coburns' procedure for acid numbers. One-half gram samples were dissolved in 25 ml. of a mixture of two parts benzene and one part ethyl alcohol, and refluxed for one hour with 1.0 N. potassium hydroxide solution. Saturated salt water was then added as in the acid number determination and the excess alkali was titrated to phenolphthalein with standard acid.

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[60] Mathews, A.P., Physiological Chemistry, Wm. Wood and Co. New York, 1925, p. 937.

Determination of Iodine Numbers

The iodine number is defined as the number of grams of iodine which can be absorbed by 100 grams of the material being tested. It is a measure of the proportion of unsaturated linkages present. The method used here was the Hanus method as described by Winton[61].

A sample of about .5 gram was weighed accurately into a glass-stoppered erlenmeyer flask and dissolved in 15 ml. of chloroform. Exactly 20 ml. of Hanus solution (prepared by adding free bromine to iodine dissolved in glacial acetic acid)[62] was then added using a volumetric pipette. The flask was then swirled gently to mix the liquids thoroughly and then allowed to stand in the dark for one hour. After standing, 15 ml. of 15 percent potassium iodide was added and the unabsorbed free iodine titrated with sodium thiosulfate solution which had been standardized with potassium bichromate. A blank was run at the same time. The difference between the volume of sodium thiosulfate required for the blank and that required for the determination represented the amount of iodine absorbed by the sample.

Chromatographic Methods

Standard procedures were not available for chromatographic separations. Ideas on the subject were obtained from Strain[63]

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[61] Winton, A. L., The Analysis of Foods, Wiley, New York, 1945 pp. 498-99.

[62] Ibid.

[63] Strain, H. H., Chromatographic Adsorption Analysis, Interscience Publishers, N. Y. (1945)

and from Beck[64]. According to Strain the theory of chromatographic separation is that the attractive forces between the particles of a substance and the surface area of an adsorbent are specific for that substance under given conditions concerning the nature of the adsorbent and the solvent from which the substance is to be adsorbed. Since two substances in the same solution traveling through a column of adsorbent will have different adsorptive forces, they will travel at different speeds, the one with greater attraction moving the more slowly. In this way they become separated.

Strain[65] lists common adsorbents in the order of their activity and common solvents in the order of the ease with which solutes may be adsorbed from them. There was no way of determining what combination would work best on this problem except trial and error. Several combinations of fullers earth, activated alumina, and charcoal as adsorbents with benzene, petroleum ether, and chloroform as solvents for the resin were tried. Variations were also introduced in the size of the adsorption column and in the application of positive and negative pressure to force the solution through the column.

The following procedure was finally adopted. Activated alumina was made into a slurry with petroleum ether and poured into a 50 ml. burette to form a tightly packed column about

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[64] Beck, S. Marion, Personal conferences during summer of 1947 at Brigham Young University, Provo, Utah.

[65] Strain, <u>op. cit</u>., p. 5 ff.

ten inches long with cotton pads at the top and bottom. A solution of resin in petroleum ether of sufficient volume to cover all the alumina was poured in at the top and forced down into the column by air pressure from the top. This solution was then replaced by pure petroleum ether in a similar manner and the solution containing the portion of the resin not adsorbed by the alumina was placed in a watch glass and allowed to evaporate. The part of the resin which was adsorbed was then washed out of the column with chloroform, which being more polar than petroleum ether has a greater attraction for solutes.

Separation by Solvents

Nagelvoort[66] reported that he used a method of refining his resin which gave two different products. He dissolved the raw resin in a mixture of 40 parts ethyl alcohol to 60 parts petroleum ether. After separating the residue the solution was evaporated and since the petroleum ether was more volatile it evaporated faster and changed the proportions of the mixture. This caused one resin to precipitate which had a melting point of 250°C. The remainder of the solution was then evaporated, which yielded another resin with a melting point of 120°C.

This procedure for the separation was used but the softening temperatures were taken instead of the melting points. Other physical constants were also determined on the fractions obtained.

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[66] Nagelvoort, <u>op. cit</u>., p. 82.

RESULTS

TABLE 4

FLOAT-AND-SINK ANALYSIS OF RESIN FROM HUNTINGTON CANYON COAL

Density		Percent
1.08 — up		4.55
1.06 — 1.08		4.24
1.05 — 1.06		9.70
1.04 — 1.05		20.62
1.03 — 1.04		44.24
1.02 — 1.03		5.67
1.00 — 1.02		1.74
Below — 1.00		6.45
	Loss	2.79
	Total	100.00

TABLE 5

SOFTENING POINTS OF RAW SPECIFIC GRAVITY FRACTIONS

Density	Softening Point
1.08 — up	Above 260°C
1.06 — 1.08	219
1.05 — 1.06	205
1.04 — 1.05	198
1.03 — 1.04	193
1.02 — 1.03	190
1.00 — 1.02	186
Below — 1.00	190

With the decrease in density of the specific gravity fractions the color became steadily lighter, changing from black for the heaviest fraction to pale yellow for the lightest fraction.

TABLE 6

SOLUBILITY OF WHOLE RESIN IN VARIOUS SOLVENTS

Solvent	Percent Soluble	Softening pt. Degrees cent.	Appearance of resin
Petroleum ether	74.0	162	Yellow
40-60 mixture of alcohol and pet. ether	38.8	117	Lt. Yellow
Ether	75.8	171	Lt. Brown
Carbon Tetrachloride	89.9		Dk. Brown
Toluene	81.6	173	Brown
Benzene	87.3		Brown
Chloroform	94.7		Very dark
Acetone	3.8		Very light

TABLE 7

SOLUBILITY OF SPECIFIC GRAVITY FRACTIONS IN PETROLEUM ETHER

Density of Resin	Percent of Resin Soluble
Greater than 1.08	23.2
1.06 — 1.08	45.3
1.05 — 1.06	54.0
1.04 — 1.05	72.1
1.03 — 1.04	85.5
1.02 — 1.03	87.6
1.00 — 1.02	87.0
Less than — 1.00	57.5

TABLE 8

SOFTENING POINTS OF REFINED SPECIFIC GRAVITY FRACTIONS

Density	Ave. Softening Temperature °C.	Maximum Deviation °C.
Above — 1.08	165	3
1.06 — 1.08	169	3
1.05 — 1.06	167	2
1.04 — 1.05	165	3
1.03 — 1.04	159	5
1.02 — 1.03	160	4
1.00 — 1.02	156	3
Below — 1.00	155	1
Whole refined resin	163	1

TABLE 9

ACID AND SAPONIFICATION NUMBERS OF THE RESIN FRACTIONS

Density	Acid Number	Saponification Number
Above — 1.08	7.4	15
1.06 — 1.08	7.0	16
1.05 — 1.06	6.2	14
1.04 — 1.05	7.6	15
1.03 — 1.04	9.0	16
1.02 — 1.03	9.0	14
1.00 — 1.02		
Below — 1.00	9.1	12
Whole refined resin	7.2	16
Whole unrefined resin		24
Asphalt-like residue	4.0	88

TABLE 10

IODINE NUMBERS OF THE RESIN FRACTIONS

Density	Iodine Number
Above — 1.08	32.8
1.06 — 1.08	32.3
1.05 — 1.06	32.0
1.04 — 1.05	33.2
1.03 — 1.04	33.0
1.02 — 1.03	34.2
1.00 — 1.02	
Below — 1.00	37.0
Whole refined resin	34.6
Whole unrefined resin	33.4

TABLE 11

SOFTENING POINTS OF THE CHROMATOGRAPHIC FRACTIONS

Fraction	Softening Point Degrees Centigrade
Adsorbed by alumina	95
Not adsorbed by alumina	184

TABLE 12

ANALYTICAL CONSTANTS OF THE SOLUBILITY FRACTIONS

Resin Type	Softening Temperature	Acid Number	Iodine Number
A*	105°C	11.2	35
B**	185	2.2	33

*Soluble in alcohol-petroleum ether mixture.
**Insoluble in alcohol-petroleum ether mixture.

DISCUSSION OF RESULTS

Separation into Specific Gravity Fractions

Table 4. shows the majority of the resin sample in the specific gravity range 1.03 to 1.05 with decreasing amounts above and below. The lighter-than-water fraction was rather large and perhaps subject to some doubt. During the centrifuging process there was a tendency for particles of resin on the surface to dry out and when they did it was very difficult to wet them again. Any particle remaining dry would float on through the various solutions and end up in the lighter-than-water group. Though the fractionation was repeated several times this difficulty was not entirely overcome; therefore the results on that particular fraction might be questionable.

To the naked eye there was a distinct positive correlation between the specific gravity and the intensity of the color of the resin particles. However, examination with a microscope revealed that there were some dark-colored particles in the lighter fractions and some light-colored particles in the heavier fractions. It is assumed that this would indicate either that the density was influenced by something other than the concentration of dissolved coloring matter or that the separation of the fractions was imperfect.

Table 5. shows a positive correlation between the softening points of the raw resins and their densities.

Solubility in Various Solvents

Table 6. shows that different solvents give different degrees of refinement. The greater the dissolving power of the solvent the darker was the resulting resin. Petroleum ether was chosen as the best solvent tried. It gave a lighter colored product than any of the other effective solvents.

The results of extracting the specific gravity fractions with petroleum ether (table 7) show a negative correlation between the solubility in petroleum ether and the density. The heavier and darker resins were the least soluble. Upon evaporation of the solvent the refined resins of the various fractions were quite similar in appearance. The residues of these extractions also appeared similar except in quantity. They were black and sticky in contact with the solvent but dried into a very friable mass having a fibrous structure which broke down easily to a soiling black powder.

Softening Points

The softening points of the specific gravity fraction after refining (table 8) do not indicate any differences in the refined fractions. Variations between fractions were no greater than variations between different determinations of the same fraction. In table eight the values given are averages of four determinations on each fraction. Deviations shown are maximum deviation from that average.

Acid and Saponification Numbers

Acid and saponification numbers are given in table 9. Again there is not sufficient variation in values to indicate any differences in the resin fractions. The values given do indicate approximately equal concentration of free acid and esters in the resin; but both are low, indicating a high proportion of resenes. The higher value for the saponification number of the asphalt-like residue of the petroleum ether extraction indicates that it contains considerably more saponifiable material than the resins themselves.

Chromatographic Separation

Chromatographic separation of the resin into fractions was extremely slow and at best was but qualitative in nature. The process was designed, as the name implies, for the separation of colored materials which can be seen while adsorbed on the column. In the separation of the resin no colors were involved; so it was necessary to evaporate the solution to see if any results had been obtained. Table 11. shows that the resin is made up of more than one component which have different properties and which travel through the column at different rates. Softening point determinations showed that this method gave about the same separation of the resin as was obtained by the solvent method. The chromatographic separation was therefore discontinued, after a limited number of trial separations, in favor of the easier solvent method.

Separation by Solvents

Table 12 gives some analytical constants for the solubility fractions. The wide difference in softening temperature proves the two fractions have some difference in composition. The similarity in iodine numbers would indicate about the same degree of unsaturation for each, but the acid numbers show some difference in concentration of free acid. In the latter case it must be recognized that while one fraction has an acid value several times that of the other, both are so low that the difference is not very important.

CONCLUSIONS

In view of the results of the determinations of softening points, acid numbers, saponification numbers and iodine numbers of the specific gravity fractions after refinement, it was concluded that separation into specific gravity fractions does not produce different kinds of resin, but merely the same resin with different concentrations of impurities, and that these impurities produce the observed differences in specific gravity and in the color of the particles.

It was further concluded on the basis of observed softening points that the resin studied can be separated into fractions with distinctly different properties by use of a combination of alcohol and petroleum ether or by preferential adsorption on a column of activated alumina.

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