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PLASTIC PROPERTIES OF COAL

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ABSTRACT

Two coals of similar chemical analyses and plastic temperature characteristics but of different maximum fluidities (Gieseler) were investigated to determine what components of coal are responsible for its plastic properties. An Illinois high-volatile B bituminous coal and an Eastern high-volatile A bituminous coal were investigated. A portion of the Illinois coal that had been oxidized in air until its plastic properties were destroyed also was studied.

The three samples were subjected to an extraction procedure. The coals were extracted with pyridine, the pyridine extract was then extracted with chloroform, and finally the chloroform extract was extracted with n-hexane. The coals and their extracts and residues were analyzed and the atomic H/C and O/Cratios were calculated. They were investigated further by x-ray scattering and infrared spectroscopy. Their plastic characteristics were determined by the Gieseler plastometer and the hot-stage microscope, and the relative thermal decomposition ranges were ascertained by differential thermal analysis. Molecular weight determinations were made on all materials except the original coals and the residues from the pyridine extractions.

Pyridine extraction of the coals rendered the residues nonplastic. The yield of extract for each solvent appears to be proportional to the fluidity. Chemical, x-ray, and infrared data showed a relative increase in aliphaticity with each progressive extraction. In each series, as the progressive scheme of extraction is carried out, each extract possesses a lower melting point, a lower molecular weight, and a similar thermal decomposition temperature range. In each series, the pyridine, chloroform, and n-hexane extracts are similar to the corresponding extracts of the other coals studied.

INTRODUCTION

Knowledge of the plastic properties of coal is necessary to a fundamental understanding of coal behavior and has practical application to the carbonization of coal.

Within a limited range of rank, coals soften on heating and resolidify as the temperature increases. Concurrent with this phenomenon, thermal decomposition occurs and gas evolves. The addition of a gaseous phase to the solid and liquid phases complicates measurement of coal properties, and the methods of measuring plasticity are consequently empirical. Numerous laboratory tests have been designed. In the United States, especially in the laboratories of the Illinois State Geological Survey, the Gieseler plastometer yields results that permit useful evaluation of coals for certain applications (Reed et al., 1952). The Gieseler plasticity data allow the comparison and grouping of coals and coal blends on a qualitative or semiquantitative basis.

This study was made to determine, by means of solvent extraction, the fundamental components of coal that are responsible for its plastic characteristics, as determined by the Gieseler plastometer. Knowledge of the physical properties and chemical nature of such components may lead to more dependable methods of classifying and comparing coals.

Acknowledgments

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HISTORY

Several hypotheses have been advanced to explain the plastic behavior of coal.

Jones and Wheeler (1915, 1916), Fischer and Gluud (1916), Bone et al. (1924), and several others, postulated that the plastic characteristics of coal were induced by the "bitumen" fraction. This fraction, sometimes referred to as the "coking principle", is found in certain coal extracts.

Audibert (1926) originally suggested a homogeneous melting of all the coal within its plastic range. However, this phenomenon might occur only in the case of high concentration of such a maceral component as pure vitrinite. In general, as exinite, inertinite, and mineral matter are present to a certain degree in all coals, this hypothesis may be misleading.

Blayden et al. (1944) and Hirsch (1954) offered a turbostratic lamellar model based on x-ray studies, which assumes that coal may be represented as flat poly-condensed aromatic "lamellae" whose average dimensions and degree of ordering increase with rank. This theory explains the softening of coal by assuming that the small lamellae become mobile at higher temperatures and act as a lubricant for the bigger lamellae.

Bangham et al. (1949), inferred the existence of units called "micelles" with diameters of about 200 Å. The arrangement of the micelles becomes more compact as the rank of the coal increases. Bangham explains plasticity phenomena by assuming that these colloidal particles are covered by surface films that become fluid when heated. Such a concept may be considered as being halfway between the "bitumen" and the "lamellae" theories.

More recently Fitzgerald (1956) and Chermin and van Krevelen (1957) proposed a mathematical model for the carbonization process. The first reaction considered is a depolymerization in which an unstable intermediate product, "metaplast," is formed. The metaplast is responsible for the plastic behavior of coal. The second reaction involves both a cracking process in which nonaromatic groups are split off, and a recondensation of the metaplast units to form semi-coke. The third reaction is a secondary degasification in which the semi-coke units polymerize as methane evolves and, at higher temperatures, as coke is formed hydrogen evolves. It is not surprising to find so many concepts of the plastic behavior of coal considering its complex, heterogeneous nature. In spite of this complexity, plasticity has been determined empirically for a number of years, especially for coals used in making metallurgical coke.

Of the numerous types of equipment for measuring plastic properties of coal, at least three instruments have been tried in the United States - the Agde-Damm, Davis, and Gieseler plastometers. The Agde-Damm apparatus gives reproducible results, but the data are not readily interpreted in terms of practical application. The Davis plastometer has not given useful results with coals of low plasticity. Rees and Pierron (1955) evaluated the Gieseler plastometer. They found that it was useful in obtaining qualitative or semiquantitative data on plastic properties but not satisfactory for quantitative interpretation. In the case of highly swelling coals, addition of diluents to improve results was found unsatisfactory because their effect is not linear and is not the same for different coals. The addition of increasing amounts of diluents progressively decreases, by an unpredictable amount, the fluidity of the coals to which they are added.

EXPERIMENTAL PROCEDURES

Solvent Extraction

Preliminary Investigations

Considerable work has been done on coal by means of solvent extraction. Approximately 160 different solvents and solvent mixtures have been used. In addition, extractions have been made in different types of apparatus, at different temperatures, pressures, and lengths of time.

Several theoretical objections have been raised as to whether the coal extracts represent original entities of the coal itself, degradation products of the coal, or perhaps in part the products of chemical interactions between coal and solvent. Another objection to the use of solvent extraction has been the difficulty of obtaining solvent-free extracts and residues. Traces of solvent induce errors in structure studies based on analytical data.

As this study deals with the extractable constituents that render the coal plastic and not with the actual molecular structure as such found in coal, the above objections are not considered pertinent.

Preliminary studies were undertaken to select solvents and to establish the type and technique of extraction to be used. The factors governing the choice of solvents were ability of the solvent to extract components responsible for the plastic characteristics of the coal, the amount of extract the solvent yields, and the ease with which the solvent can be separated from the extract. Pyridine, ethylenediamine, and dimethylformamide were chosen.

In previous studies on solvent extraction of coal, pyridine and ethylenediamine have been used more extensively than other solvents. Jones and Wheeler (1915), Fischer and Gluud (1916), and several later workers indicated that pyridine removes substances that are responsible for a coal's coking ability.

More recently the work of Dryden (1949, 1950, 1951) demonstrated the possibility of using ethylenediamine as a solvent and its advantages over a fairly large number of other solvents.

The use of dimethylformamide as a solvent has been reported by the British Coal Utilisation Research Association Laboratories in 1954. MacKensie (1909), Bone and Sarjant (1920) and Malanowicz (1932) have shown the importance of using dry pyridine in order to obtain maximum yield. Berkowitz (1948) and Dryden (1948, 1949) reported an increase in yield of extract when anhydrous ethylenediamine was used.

To obtain a maximum yield of extract, the solvents were dried as described below.

The pyridine, reagent grade, obtained from Fisher Scientific Company, was first dried over NaOH pellets for 48 hours with occasional shaking, then filtered into a liter distillation flask and boiled with metallic sodium for three hours. Fresh sodium was added, and the pyridine distilled into a storage bottle containing freshly ignited BaO. The first 150 ml of distillate was discarded.

The ethylenediamine, 95 to 100 percent pure, obtained from Eastman Organic Chemical Company was dried by the same procedure used for pyridine.

The dimethylformamide, technical grade, obtained from du Pont de Nemours and Company, Inc., was dried with KOH following a procedure described by Sears et al. (1955).

The coal used in the course of the preliminary investigation was prepared as follows. A fresh sample of approximately 20 kilograms of Illinois high-volatile B bituminous No. 5 Coal from Saline County, size 2 by 3 inches, was collected at the mine and sealed in an airtight container. In the laboratory about four to five hours later approximately 4 kilograms of the sample were reduced to less than one-fourth inch by means of a jaw crusher, and air-dried overnight at 34°C. The air-dried sample was then stage-ground, producing a minimum amount of fines, to pass a 40-mesh sieve. A sieve analysis indicated that only 5 percent of the minus 40-mesh sample was less than 60-mesh size. The minus 40-mesh sample was stored under an O_2 -free nitrogen atmosphere in a bottle.* Approximately 100 grams of the sample were introduced in a steel roll mill, under an O_2 -free nitrogen atmosphere, and ground to pass a 200-mesh sieve.

Three soxhlet extraction units, extraction tube 40 mm I. D. and flask capacity 250 ml, were set up. Exactly 15 grams of minus 200-mesh coal were weighed into the three 33 by 80 mm double-thickness extraction thimbles. Cotton plugs were packed lightly on the surface of the coals, and the thimbles placed in the soxhlet on top of 1/4-inch porcelain Berl saddles in such a way that the tops of the thimbles were higher than the maximum height of the solvent in the extraction tube. Three boiling flasks, one containing 150 ml of pyridine, one 150 ml of ethylenediamine, and the third 150 ml dimethlyformamide, were attached to the apparatus, and the extractions carried out for 48 hours.

Thermocouples, inserted through the condensers with the hot junctions at the base of the thimbles, indicated the temperature for pyridine was 60° C, for ethylenediamine 61° C, and dimethylformamide 87° C.

Upon completion of the extraction, it was noted that samples subjected to pyridine and ethylenediamine swelled to about twice their original volume. In contrast, the sample submitted to dimethylformamide did not swell; instead, the volume of the sample seemed to decrease to about 85 or 90 percent of its original value.

^{*} It was found that commercially available nitrogen contained a small amount of oxygen and that coal stored under such nitrogen will oxidize. To minimize the effect of oxidation, all samples of coals, extracts, and residues prior to further use were first submitted to vacuum, 1 or 2 mm of Hg, and then stored under an O_2 -free nitrogen atmosphere.

Washing the residues with water to remove the last traces of solvents and drying the residue both proved unsatisfactory. Washing the residues with dilute hydrochloric acid produced only slight improvement for extracts prepared with pyridine and ethylenediamine. Examination by microscope showed the residue particles were somewhat coated with a brown material similar to the extract. It may be postulated that each particle of residue was surrounded by a layer of solvent that still contained traces of extract in solution; when water was added during washing, the extract was precipitated on to the surfaces of the particles.

Because of the difficulties encountered during the washing and our inability to remove the last trace of solvent from the minus 200-mesh residue, it was decided to carry out extraction on minus 40- to plus 60-mesh coal in the hope that by decreasing the area of contact between sample and solvent, adsorption of the solvent would be considerably reduced. Another factor in favor of the choice of the larger particle size was that Gieseler plasticity data were based on a minus 40-mesh sample and a better comparison between coal and residue could be made where both determinations were made on substances of comparable size.

Unfortunately, as the particle size increases the solvent action decreases. To compensate for this effect the temperatures of extraction with pyridine (60° C), ethylenediamine (61° C), and dimethylformamide (87° C) were increased to the boiling points of the solvents, 114°, 115°, and 153°C, respectively.

The digestion apparatus is shown on plate 1A. To keep the coal from bumping and splashing on the side of the liter digestion flask, a stirrer rotating at the rate of 150 rpm was provided. The distance of the teflon stirrer from the bottom of the flask was gauged to allow, insofar as possible, only the solvent to be agitated, so that the possibility of reducing the particle size of the sample during digestion would be minimized.

The coal studied had an air-dry moisture of 4 percent. To eliminate any further drying that might influence plastic characteristics by oxidation, the digestion was made on an air-dried sample. An air-cooled condenser was used so that an anhydrous extraction could be made by removing the water at the top of the condenser.

The separation of solvent and extract from residue was made by means of the filtration apparatus shown on plate 1B. It consists of a 160 ml capacity funnel with a fritted glass plate of fine porosity, Pyrex brand. The nominal maximum pore size is 5 microns. The apparatus permits filtration under vacuum in a dry nitrogen atmosphere.

The difficulties encountered in separating the residue particles from their coating of solvent and extract were overcome by first washing the minus 40- to plus 60-mesh material with 50 ml of fresh solvent, then with 50 ml of anhydrous ether. Microscopic examination of the particles after such treatment indicated the absence of the brown coating material previously described.

As it is imperative to obtain solvent-free extracts, several techniques of separating solvent from extract were investigated. The most common type of separation, precipitation of the extract by addition of a large volume of water, proved unsatisfactory because 1) a gelatinous precipitate was formed that prevented quantitative filtration and absolute drying of the precipitate, and 2) with a dilution ratio of water to solvent-plus-extract originally set at 10 to 1, the filtrate had a yellowish hue, indicating a nonquantitative precipitation of extract. When the ratio was increased to 100 to 1, the filtrate remained clear, but a gelatinous precipitate appeared in it after 48 hours.

To increase the rate of precipitation and improve the precipitate, flocculating agents including sodium chloride, ferric chloride, thorium nitrate, methanol, and ethanol were tried. Concentrations of the flocculating agents from .01 to 1 percent showed little increase in the quality of the precipitate. Change of pH by addition of hydrochloric acid improved the precipitate only when the dilution ratio was more than 90 to 1. In this case, when the precipitate was washed with distilled water to remove the acid, peptization occurred.

Kirkby et al. (1954) found that in certain coals a large proportion of the extract produced at room temperature could be precipitated by centrifuging. In our study, centrifuging for four hours at 1200 rpm allowed approximately 50 percent of the estimated extract to be recovered. The remaining extract in solution proved to be nonquantitatively precipitated by addition of water.

A rotating vacuum evaporator (pl. 1C) was built in our laboratories for separation of heat-sensitive compounds from solvents and it gave very satisfactory results. The evaporating flask was about one-third immersed in water maintained at a constant temperature $(\pm .1^{\circ}C)$ in a range from 26° to 85°C. The condensing flask was immersed in water at 0° to 2°C. Through a 3-way stopcock the pressure of the system could be reduced to 1 mm of Hg or a nitrogen atmosphere established.

To permit a rapid distillation of the solvents without danger of distilling the extracts, control of the temperatures and pressures to which the flask was subjected was investigated. The indexes of refraction of the solvents were used as checks.

	Distillation flask				
Solvent	Temperature °C	Pressure mm/Hg			
Pyridine	65	80			
Ethylenediamine	66	80			
Dimethylformamide	82	80			

To distill 250 ml of solvent in approximately 20 minutes, the following settings were necessary:

Table 1 indicates some physical properties of the solvents used during the course of the preliminary study.

To compare the three solvents, extractions on representative samples of the Illinois high-volatile B bituminous coal, minus 40-to plus 60-mesh size, were made by the procedure described in detail below.

Ten-gram portions of coal were digested with 150 ml of each of the anhydrous solvents for exactly six hours, after which time the residues were separated from solvents-plus-extracts by filtration. The extracts were in turn separated from the solvents. The yields of extracts were calculated on a moisture- and ash-free basis.

To obtain an indication of the relative degree to which the caking properties of coal are affected by solvent extraction, volatile-matter determinations (single run)

EXPLANATION OF PLATE 1

A - Digestion apparatus used in experiment.

B - Filtration apparatus used to separate the residues from the solvents plus extracts.

C - Rotating vacuum evaporator used to separate the extracts from their solvents.



were made on the coal, on each of the three dry extracts, on each of the three solvent-wet residues, and on each of the three dry residues. The relative degrees of agglomeration were established by the resistance to breaking exhibited by the volatile-matter buttons under manual pressure.

Physical	Solvents						
properties	Pyridine	Ethylenediamine	Dimethylformamide				
Boiling point, 760 mm	114°C	115°C	153°C				
Viscosity, cen- tipoise at 25°C	0.931	1.725	0.802				
Dipole moment, μ debye units	2.2	1.95	3.82				
Dielectric con- stant. ϵ	12.5 (20°C)	12.9(25°C)	26.6(25°C)				
μ^2/ϵ	0.39	0.29	0.55				
Surface tension dynes/cm	38.0(20°C)	32 (?)(20°C)	35.2(25°C)				

Table 1. - Physical Properties of Solvents

Table 2. - Yields of Extraction, Agglomeration Characteristics of Extracts and Residues, and Physical Properties of Solvents

	Yield of extract*	Agglomeratio	on chara	cteristics	Physical properties of solvent			
		Residues	Extracts			Surface tension: ε	Boiling point	
Solvent e		Solvent-wet	Dry	Dry	μ ² /ε	(dynes/cm)	760 mm	
Dimethyl- formamid	19.4 e	Low	None	Strong	0.55	35.2	153°C	
Pyridine	17.9	Medium	None	Medium	0.39	38.0	114°C	
Ethylene- diamine	16.8	Strong	Low	Medium	0.29	32.0	115°C	

* Moisture- and ash-free basis.

Table 2 shows the respective yields of extracts, the agglomerating characteristics of wet and dry residues and of dry extracts from each solvent. Some physical properties of the solvents are repeated in the table for correlation. For the three solvents investigated, the agglomerating characteristics of the dry residues were lower than those for solvent-wet residues.

Agde and Hubertus (1937) attempted to correlate the amount of solvent retained by coal as a function of μ^2/ϵ , where μ is the dipole moment and ϵ the dielectric constant of the solvent. Ostwald (1939) correlated swelling and solution action of solvent on high polymers as a function of μ^2/ϵ and of surface tension. The work of Dryden (1951), in which he classified solvents by means of four simple experimental tests, indicated that in some cases it was possible to correlate the physical properties of the solvents with their solvent action on coal; in other cases such correlation was not possible.

When pyridine is compared to ethylenediamine of similar boiling point (table 2), the yield of extract increases as μ^2/ϵ , and surface tension increases. Compared to dimethylformamide, pyridine gave a lower yield with a lower μ^2/ϵ and boiling point but with a higher surface tension. It appears that the relative extraction power of pyridine-class solvents, as defined by Dryden (1950), may be more closely related to the boiling points of the solvents, and to a lesser degree to the dipole moments, than to any other physical properties.

Ultimate analysis with atomic H/C and O/C ratios, infrared data, and x-ray scattering data, indicated that the dimethylformamide, pyridine, and ethylenediamine extracts were similar. Gieseler plasticity study shows that in each case extractions render the coal nonfluid.

Extraction Procedure

On the basis of the factors governing the choice of solvent and the considerable amount of work published by Jones and Wheeler (1915, 1916) in which they claimed that the coking properties of coal depend on the presence of a pyridinesoluble constituent, it was decided to choose pyridine as a solvent and to study the pryidine extracts and residues.

The pyridine extracts were subsequently extracted with reagent grade chloroform, conforming to A. C. S. specifications, obtained from Merck and Company, Inc. The chloroform extracts in turn were extracted with freshly redistilled pure grade normal-hexane obtained from Phillips Petroleum Company.

To obtain a better basis for comparing yield of extraction, physical properties, and chemical nature of the extracts and residues, two coals of similar chemical composition and plastic temperature characteristics but of different maximum fluidities were chosen.

The two samples were an Illinois high-volatile B bituminous No. 5 Coal from Saline County, and an Eastern high-volatile A bituminous Hernshaw Coal from West Virginia. The Illinois coal, size 2 by 3 inches, was taken fresh from the mine. The Eastern coal, size minus one-fourth inch, was obtained from a fresh shipment at a plant in St. Louis, Missouri. Both coals were prepared in the same manner described previously.

In addition, the minus 40-mesh portions were screened to obtain minus 40- to plus 60-mesh stock samples. Such samples were not representative of the coals but were prepared specimens that permitted a better basis for comparison. Half of the fresh Illinois coal minus 40- to plus 60-mesh stock sample was spread in a pan to a uniform depth not exceeding one-fourth inch and left in the air at 36°C until oxidation completely destroyed the plastic characteristics. A period of 45 days sufficed for this.

Each of the three samples, the two from fresh coals plus the oxidized sample, was extracted in exactly the same manner, according to the scheme shown in the flow diagram on page 10.

In order to obtain a sufficient amount of the n-hexane extract, it was necessary to treat 100 grams of coal. The pyridine extraction was carried out on ten 10-gram portions of coal, two each day. The following procedure was used. The



digestion apparatus (pl. 1) was flushed with nitrogen for 15 minutes. Exactly 10 grams, weighed to the nearest 0.2 mg, of minus 40- to plus 60-mesh stock sample were transferred to the digestion flask, 150 ml of anhydrous pyridine added, and the stirring and heating started. After 30 minutes of boiling, the water that had condensed at about half the height of the air condenser was driven out by gently heating the condenser tube. Boiling was then maintained for exactly six hours.

Meanwhile, a clean evaporation flask was filled with nitrogen, weighed, and connected to the filtration apparatus (pl. 1). Fifteen minutes after the digestion was stopped the apparatus was cold enough to be disassembled, and the contents of the flask were transferred into the funnel of the filtration apparatus. The digestion flask was washed with 50 ml of fresh anhydrous pyridine in small amounts. Care was taken to transfer the residue quantitatively into the filter.

The filtration was aided by applying vacuum to the evaporating flask. A nitrogen atmosphere and the vacuum were maintained on the residue for an additional 15 minutes, after which the evaporator flask was transferred to the rotating vacuum evaporator (pl. 1). The pyridine was removed at 85°C under 80 mm of Hg pressure.

Meanwhile the residue in the suction filter was washed with 50 ml of anhydrous ether. The residue was sucked dry under a nitrogen atmosphere for an additional 15 minutes, then transferred into a stainless steel tray fitted in an Abderhalden type of vacuum drying apparatus. It was dried for two hours at 116°C at 5 mm pressure, after which the drying chamber was flushed out by introducing nitrogen and evacuating six times. The residue was left overnight at room temperature under vacuum and weighed in a nitrogen atmosphere.

EXPLANATION OF PLATE 2

- A Gieseler plastometer used to determine the plastic characteristics of the coals investigated.
- B Leitz Panphot microscope used to determine melting and solidification temperatures.



When the evaporator flask appeared dry, a nitrogen atmosphere was reestablished, and the flask was disconnected and attached to the filtration apparatus for receiving the extract from a duplicate run. After the solvent had been removed from the extract of the second daily run and the evaporator flask appeared dry, the flask was flushed by introducing nitrogen and evacuating to about 5 to 7 mm pressure. This was done six times, and then the flask was disconnected from the apparatus, flushed with nitrogen at atmospheric pressure while it cooled to room temperature, and weighed. The extract was then chipped out of the flask and transferred into a previously weighed weighing bottle filled with nitrogen. A negligible amount of extract remained in the flask.

The extract was further dried for two hours at 100° C and 5 mm pressure, cooled to room temperature, and weighed in a nitrogen atmosphere.

The yield of the extract was calculated by means of the following formula:

Yield in % =
$$\frac{A \frac{100 - B}{100}}{S} \times 100 = \frac{A(100 - B)}{S}$$

where:

A = weight of extract in the evaporator flask

B = a correction factor comprising the percentage loss in weight during drying of the portion of extract removed from the flask

S = coal sample weight

For the fresh Illinois coal, determinations of the yield of extract and plasticity were made daily over the five-day period required to complete the extraction of 100 grams. For the oxidized Illinois coal and the Eastern coal, final drying of the extracts and calculation of the yields were made only at the end of the fiveday pyridine extraction period.

The chloroform extraction was carried out in the same manner as the pyridine extraction, except that 10 grams of pyridine extract were used with 150 ml of chloroform. After six hours of digestion, the contents of the flask were transferred quantitatively into the filter apparatus, which was fitted now to a 250 ml Erlenmeyer flask instead of to the evaporator flask. Digestion flask and residue were washed with an additional 50 ml of chloroform. The chloroform residue was dried for three hours at room temperature under vacuum. The extract was separated from the solvent by evaporating the chloroform on a steam bath at atmospheric pressure, and was then dried for three hours at room temperature under vacuum.

A weighed amount of the chloroform extract (1 to 2 grams) was digested with 150 ml of n-hexane in a 250 ml round bottom digestion flask for six hours. The extract and residue were obtained and dried following the procedure described for the chloroform extraction.

Chemical Analysis

Because the amounts of extracts obtained were so small, micro techniques were used for the ultimate analyses of extracts and residues. All oxygen values were determined on an ash-free basis by subtracting from 100 the sum of carbon, hydrogen, nitrogen, and sulfur.

To prevent oxidation, all samples were kept under an oxygen-free, dry nitrogen atmosphere in an air-tight sample container. The Dumas method for nitrogen determination yielded high results. It was found that drying the sample, prior to analysis, for one hour at room temperature under 2 to 5 mm of Hg gave nitrogen results lower by .2 to .6 percent, and the lower values checked with the expected values based on a nitrogen balance. This may be explained by the fact that the Dumas method will determine the nitrogen gas adsorbed on the coal, whereas the Kjeldahl method will not.

In general, in microchemical analyses, the acceptable tolerance for values of each major element is 0.3 percent, assuming the determination is made correctly. For substances containing only C, H, N, and S, the sum of the elements should be 100 ± 0.5 percent. This applies in most cases, because it is probable that the errors in the various determinations are more or less compensating. It may be expected that the oxygen values obtained by difference could be in error by ± 0.5 percent.

Table 3 compares macro and micro ultimate analysis data for coal, pyridine extract, and pyridine residue. For the most part, values obtained by the two procedures appear to be in reasonable agreement, thus assuring the validity of the micro values for this study.

Item	Coal		Pyridine extract		Pyridine residue	
determined	Macro	Micro	Macro	Micro	Macro	Micro
Atomic H/C **	.784	.743	.851	.853	.786	.787
Atomic O/C **	.078	.083	.050	.049	.077	.077
H	5.44	5.16	6.10	6.12	5.40	5.46
C	82.80	82.76	85.50	85.57	82.60	82,62
N	1.94	1.80	2.00	2.01	2.04	2.03
0	8.68	9.18	5.70	5.66	8.46	8.43
S	1.14	1.10	.70	.64	1.50	1.46

Table 3. - Ultimate Analysis by Macro* and Micro† Techniques (Moisture- and ash-free basis)

Made in accordance with ASTM methods for coal and coke D271-48.

† The improvements of these methods and a description of the combustion tube packing for the carbon-hydrogen and the nitrogen determination were published by Clark and Rees (1954).

**Calculated.

÷.

Plasticity Measurements

Plasticity measurements of coal, extracts, and residues were made by a Gieseler plastometer (Soth and Russell, 1943). The instrument, as modified by Rees and Pierron (1954) and shown on plate 2, includes a fixed position for the thrust bearings in the head of the plastometer and provision for removal of the decomposition gases by suction.

In contrast to coal, the residues from the extraction have no fluidity. After a determination, during which a temperature of 500°C had been attained, the barrel was removed from the heating bath, cooled to room temperature, and disassembled. The residues could then be poured out of the crucible, indicating that no agglomeration had occurred. To check the possibility that return of extracts to residues might restore agglomerating or fluid properties, a blend of pyridine extract and residue and a second blend of dimethylformamide extract and residue were made in such a way that the original percentage composition of the coal was reestablished.

Table 4 gives Gieseler plasticity data of the original coal, pyridine and dimethylformamide extracts, and blends 1 and 2. The indicated maximum fluidities of blends 1 and 2 were much higher than the maximum fluidity of the original coal. However, these values will require further investigation.

	Charac				
Sample	Softening (.5 dial div /min)	Fusion (5.0 dial div /min)	Maximum fluidity	Solidifi- cation	Maximum fluidity (dial div /min)
Coal	392	414	433	469	61
Pyridine extract	350	390	420	450	15,000
Dimethylformamide extract	347	388	421	453	15,000
Blend 1	355	396	427	460	12,000
Blend 2	356	397	425	461	12,500

Table 4. - Gieseler Plasticity Data for Coal and Extracts

X-ray Investigation

Mahadevan (1929) was one of the first to study coal structure by the diffraction method. On the basis of similarity between data obtained from coal and data from graphite, he concluded that coal contains compounds having a hexagonal ring structure similar to that of graphite.

Blayden et al. (1944) made detailed investigations of the x-ray patterns of coals, and compared the coal carbonization products with those of cellulose, lignin, and glycine. They also postulated a graphite-like structure for coal based on the fact that data indicated the presence of interplanar spacing d(002) of the same order, 3.5Å, as that between successive layers in a graphite crystal. In addition, they suggested other lamellar structures that could also stack with a distance of 4.5Å between layers.

Nelson (1954), by using improved techniques, was able to calculate the statistical distribution of atoms around any arbitrary center in coal. Hirsch (1954) derived the average number of aromatic rings from the average diameter of the lamellae. Whitaker (1955), in his review of the ultimate structure of coal, stated that although the x-ray methods allow deductions somewhat indirectly related to the structure, they allow no direct interpretations. This was probably because of the very diffuse nature of the halos produced by essentially noncrystalline solids, in comparison with sharply resolved peaks in diffraction patterns of crystalline solids. Nevertheless, if x-ray study shows the same trend or indication as do other techniques, its use may be justified. We therefore decided to obtain x-ray scattering data for each sample investigated by means of a General Electric Unit XRD-3, copper anode tube, Ni filter, 50KV-15 ma, equipped with a 1° slit and a .2° screen.

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A brief preliminary study of the effect of particle size on scattering data from 5° to 45° scattering angle was made. Three particle sizes (minus 60- minus 100- and minus 200-mesh) for the coal, for the pyridine and dimethylformamide extracts, and for the residues were prepared. Each sample was mounted by pressing the powder in a 1 by $\frac{1}{2}$ -inch sample holder. To permit a quantitative comparison between sizes, care was taken to pack the samples as uniformly as possible. It was found that when a minus 100-mesh sample was used, a better resolution of the scattering curve was obtained. In general, there was an indication that the extracts possessed a higher degree of oriented arrangement than the original coal.

The period of 3.5 Å (25.4° scattering angle) is related to stacking of aromatic compounds. In coal this distance represents the space between two condensed aromatic clusters (one on top of the other, for example). Similarly, the period of 4.5 Å (19.7° scattering angle) represents the space between two aliphatic chains parallel to each other. It is possible that this 4.5 Å spacing may be related to the special lamellar structures reported by Blayden et al. (1944).

The scattering curve of a high-volatile-matter bituminous coal shows a maximum in the region from 17.5° to 27° scattering angle. The measurement of the relative intensities at 25.4° and 19.7° may be assumed to indicate the relative amounts of aromatic and aliphatic materials present in the substance analyzed. Following accepted procedure, the base lines from which relative intensities were measured were determined by a straight line intercepting the scattering curves at 10° and 35°. Table 5 gives the ratios calculated on the basis of these assumptions.

Intensity	at	19.7°		Aliphatic
Intensity	at	25.4°	Ŧ	Aromatic

		Pyri	dine	Dimethy	lformamide
	Coal	Extract	Residue	Extract	Residue
<u>Aliphatic</u> Aromatic	1.24	2.06	1.73	2.32	1.73

fable 5.	-	X-Ray	Scattering	Ratios
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Because the preliminary study indicated a relative increase in the aliphaticity of the extracts, scattering data were obtained for each coal and for the extracts and residues of the three series investigated.

The samples were prepared to minus 100-mesh, packed uniformly into the holder, and subjected to analysis. The n-hexane extract, which is a viscous liquid at room temperature, was heated to about 60°C, and smeared uniformly to a thickness of 2 mm on a glass slide. The slide was placed on dry ice for a few minutes to make the liquid so viscous that no difficulties were encountered during the determination. It was found that subjecting the n-hexane extract to x-ray study at different temperatures had no detectable effect on the resulting scattering curves.

Infrared Investigation

Use of infrared methods to study coal originated in England with the work of Sutherland et al. (1944). Since that time most laboratories studying coal constitution or related subjects have published much data. Cannon and Sutherland (1945) assigned some of the absorption bands to specific chemical bonds. Cannon (1953) later made further assignments such as oxygen-containing groups, CH_2 and CH_3 groups, and both single-ring and condensed aromatic structures. Vucht et al. (1955) summarized their conclusions, together with the findings of other investigators, in the form of a table that assigns wave lengths of the absorption bands to specific molecular vibrations.

Several techniques have been developed for the infrared examination of coal. Cannon and Sutherland (1945), and later Orchin et al. (1951), used successfully the "thin section technique." Gordon et al. (1952) and Cannon (1953) adopted the Nujol mull method in which coal is ground with Nujol. This method has two serious disadvantages. First, to keep the effect of light scattering as small as possible, the coal particle size must be reduced to a minimum; and second, the resultant spectrum curve contains absorption bands characteristic of the Nujol, thus limiting the interpretation to certain regions of the coal spectra.

The latest technique was developed by Schiedt (1953) and used most advantageously by Vucht et al. (1955) and Friedel (1956). For this method the coal is ground with dry potassium bromide and subsequently compressed under high pressure and vacuum to form translucent pellets.

Preliminary studies using the Nujol technique indicated that, as the length of time for which the coal is ground with Nujol increases (that is, particle size decreases), the spectrum background decreases, especially in the frequency region 4000 to 2000 cm⁻¹.

Early in the preliminary work it became apparent that the relative aliphaticity might be investigated, and therefore the potassium bromide pellet technique was used. It was found that grinding a minus 60-mesh sample with KBr for 45 minutes was sufficient to obtain satisfactory resolution of the bands. By studying the ratio between extinction coefficients of the bands of aromatic and aliphatic CH groups, Brown (1955) estimated within limits the relative proportions of the two forms of hydrogen in coals. He selected the 3.30μ or 3030 cm^{-1} band for the aromatic CH stretching vibration, and the 3.43μ or 2910 cm^{-1} band for the aliphatic CH stretching vibration.

In our study the sample considered had a very small band in the 3030 cm^{-1} region, and in some instances this band was absent, probably because of the relatively small amount of aromatic CH stretching, or the interference of the hydrogen bonding. We decided, therefore, to choose another band as representative of aromatic structure. The band at 1600 cm^{-1} , common to all coals, was chosen. This band was assigned to single and condensed aromatic ring structures by Brown (1955). It may, however, be influenced by conjugated carbonyl groups that probably are hydrogen-bonded, and by phenoxy structures. The width rather than the height of the band, especially toward the higher wave number region, probably would be most affected by such interferences. We decided to measure the height of the bands at 2910 and 1600 cm⁻¹ as an indication of the relative amounts of aliphatic and aromatic materials present in the samples analyzed.

A Perkin-Elmer, Model 21, double beam, recording infrared spectrophotometer was used. The operating conditions of the instrument were: prism, NaCl; resolution, 927; response, 1; gain, 5.5; speed, 7; and suppression, 2. The samples were prepared for analysis in the following manner: 0.0025 grams, weighed to the nearest 0.1 mg, of the minus 100-mesh sample, were transferred into a mortar containing exactly 1 gram of dried potassium bromide. The mixture was ground by hand for ten minutes, and approximately 200 mg of the mixture was transferred to the pelleting machine. A pressure of 14,000 lb. per square inch for five minutes, and a vacuum of 2 to 3 mm of Hg were necessary to obtain circular pellets 13 mm in diameter and .5 mm thick. For the n-hexane extracts, a 0.5 percent solution of the sample in carbon tetrachloride was used. This concentration of extract gave a 1600 cm⁻¹ band of approximately the same height as the one obtained when hexane residue in potassium bromide was used.

Adduct Investigation

To determine whether the increase in aliphaticity was due to selective extraction of long-chain aliphatic materials, such as waxes, or short chains attached to condensed structures, the urea and thiourea complex technique was used.

Bengen (1940) in Germany discovered the urea adduct formation. He found that urea forms adducts with a variety of straight-chain compounds such as aliphatic hydrocarbons, acids, alcohols, aldehydes, ketones, and esters. The adducts so formed could be decomposed into their components by heating, or by dissolving the urea. Zimmerschied et al. (1950) confirmed and extended the work of Bengen. Smith (1952) made a complete structure determination on single crystals of urea adduct. Angla (1949) investigated the thiourea complex formation. Truter (1953) gave a brief survey of the literature on the subject, in which eight references are given.

The main difference between the urea and thiourea adducts is that the channel in the thiourea complex is larger than the one in the urea. Thiourea forms complexes with branched-chain or some cyclic types of compounds. The straight-chain molecules have too small a cross section to form complexes spontaneously (that is, they slip out of the channels too easily), but do so when anchored by a branchedchain or cyclic group.

Nearly saturated solutions of urea and thiourea in methyl alcohol were added slowly in small amounts to a solution of pyridine extract in pyridine and a solution of chloroform extract in chloroform. Precipitation occurred immediately. After addition of approximately 50 grams of urea or thiourea to each gram of extract, the precipitates were allowed to settle out for one hour, and were then filtered and dissolved in water. The water solution was inspected for traces of oily material and then filtered. It was found that thiourea did not form an adduct, but with urea approximately .5 percent of the pyridine extract formed an adduct. Data from infrared studies indicated that the material so obtained was aliphatic. Owing to the very low yield of extraction of this material, the adduct approach was considered not worth further study.

Microscopic Examination

The quantities of extracts and residues produced during the experiment were so small that plasticity data could not be obtained by the Gieseler plastometer. Hot-stage microscopic examinations were used to determine melting and relative plastic range temperatures.

The Leitz Panphot microscope, equipped with a Leitz high-temperature heating stage (pl.2), was used. The temperature was measured by a calibrated platinumplatinum 10 percent rhodium thermocouple, with the hot junction in contact with the quartz window on which the sample was placed. The rate of heating was maintained at 3°C per minute. It was found that oxygen-free dry nitrogen must flow through the hot stage to prevent oxidation of the material. In general, the melting points of the substances studied were 10° to 20°C higher in an air atmosphere than in an inert atmosphere. The choice of a 30X hot-stage objective and a 4X eyepiece proved satisfactory. Visual inspection was made through the viewer at the top of the microscope; photographs were taken at specific intervals.

Differential Thermal Analysis

Differential thermal analysis was used only to estimate the relative temperature ranges in which coal, extracts, and residues underwent thermal decomposition. Clegg (1955) made a careful study of the shifting of peak and shape of curve when amounts of inert diluents in the sample, particle size, rate of heating, packing, and other variables were changed.

In the present study it was found that, as the extracts possess such high percentages of volatile matter, dilution with alundum was necessary. Mixtures of 25 percent sample with 75 percent diluent, loosely packed, proved best for comparative purposes. The samples were covered to minimize oxidation, and duplicate determinations were made to ascertain that results could be duplicated when a uniform technique was used.

Molecular Weight Determination

The boiling point elevation (ebullioscopic) method was used to determine molecular weight. The apparatus developed and improved by Rieche was used but was further improved by providing the boiling chamber with electric instead of gas heating.

The solvents used were pyridine, chloroform, and n-hexane for their respective extracts. The ebullioscopic factor for a known volume (4.5 ml) of each solvent was determined by measuring the increase of boiling point when a known amount of azobenzene (mol.wt 182.22) was added. The following formula was used to calculate the factor:

$$K_{solv.} = \frac{182.22 \times \Delta T}{S}$$

where

 ΔT is the increase of the boiling point of the 4.5 ml of solvent in degrees C S is the weight of azobenzene

The samples were pressed into small pellets of 25 to 30 mg each, weighed accurately on a microbalance, and introduced into the boiling chamber after a constant boiling temperature of the solvent had been established. The increase in boiling point, ΔT , was then noted. Each determination was made in triplicate, and the average reported. The solvents used were as follows: pyridine for pyridine extracts and chloroform residues; chloroform for chloroform extracts and n-hexane residues; and n-hexane for hexane extracts.

RESULTS

Table 6 gives the chemical analyses made on a moisture- and ash-free basis, the free swelling indexes, and the Gieseler plasticity data for the samples investigated — Illinois high-volatile B bituminous, oxidized Illinois high-volatile B bituminous, and Eastern high-volatile A bituminous coals.



PYRIDINE

CHLOROFORM

N-HEXANE

÷

HOT-STAGE PHOTOMICROGRAPHS OF EXTRACTS Illinois high-volatile B bituminous coal series: temperatures, in degrees C, are those of extracts when the photographs were taken. (100X)

ILLINOIS STATE GEOLOGICAL SURVEY

	Illinois	HVBB	Eastern HVAB
	Nonoxidized	Oxidized	
Gieseler			
(dial div /min)	80	Ο	37 500
	00	v	37,300
Free swelling index	6	1	5 1 /2
Yield in percent			
(1)* Pyridine extract	20.7	13.6	23.8
Chloroform extract	5.8	5.1	9.0
n-hexane extract	2.4	.7	3.4
(2)* Chloroform extract	.9	.8	1.3
n-hexane extract	none	none	none

Table 8. - Yields of Extract, Free Swelling Index and Maximum Fluidity of the Three Coals

(1) Following the previously described extraction scheme.

(2) Submitting coal directly to chloroform and n-hexane extractions.

* Moisture- and ash-free basis

Table 8 gives for each of the coals considered the Gieseler maximum fluidity, the free swelling index, and the yields of extract in percent obtained by the pyridine scheme of extraction previously described and by chloroform and n-hexane extractions applied directly to the coal.

Tables 9, 10, and 11 summarize the ultimate analysis data obtained by micro technique on a moisture- and ash-free basis for the three coals considered, and for the respective extracts and residues.

(Moisture- and ash-free basis)											
		Pyric	line	Chlor	oform	n-hexane					
	Coal	Extract	Residue	Extract	Residue	Extract	Residue				
н	5.85	5,99	5.53	7.12	5.37	7,85	7.92				
С	83.18	84.02	81.91	84.76	79.45	87.27	86.32				
N	2.02	2.10	2.13	2.25	2.25	,56	2.42				
0	7.25	7.17	9.04	4.80	11.70	3.32	2.67				
S	1.70	.72	1.39	1.07	1.23	1.00	.67				
Atomic											
н/С	.837	.849	.805	1.000	.805	1.072	1.093				
Atomic											
0/C	.065	.064	.083	.042	.110	.029	.024				

Table 9. - Illinois HVBB Nonoxidized Series Ultimate Analysis Data Obtained by Micro Technique

			_		-	-	
		Pyric	line Chlorofo		oform	orm n-hexane	
	Coal	Extract	Residue	Extract	Residue	Extract	Residue
Н	5.95	5,95	5.42	7.11	5.32	8.30	7,28
С	82.49	83.91	81,66	84.85	80.72	87.08	84.82
N	1.56	1.61	1,45	1.63	1.65	1.54	3.69
0	8.50	7.70	10.30	5.61	11.74	2.29	3.59
S	1.50	.83	1.17	.80	.57	.79	.62
Atomic							
н/с	,859	.844	.791	.999	.786	1.135	1.023
Atomic						-	
0/C	.077	.069	.094	.050	.100	.019	.031

Table 10. - Illinois HVBB Oxidized Series Ultimate Analysis Data Obtained by Micro Technique (Moisture- and ash-free basis)

Table 11. - Eastern HVAB Series Ultimate Analysis Data Obtained by Micro Technique (Moisture- and ash-free basis)

	Pyridine			Chlore	oform	n-hexane	
	Coal	Extract	Residue	Extract	Residue	Extract	Residue
Н	5,93	6,42	5.43	6.70	5.95	8.58	6.88
С	86.66	86.75	85,67	87.64	82.76	87.99	88.45
N	1.34	1.96	1.49	1.32	1.86	1.32	2.00
0	5.13	4.14	6.33	3.29	8.60	1.59	1.90
S	.90	.73	1.08	1.05	.83	.52	.77
Atomic							
H/C	.814	.882	.756	.911	.856	1.161	.928
Atomic							
0/C	.044	.036	.056	.029	.078	.014	.016

Figure 1 shows x-ray scattering curves of the three series of samples studied. The relative intensities at 3.5 and 4.5Å periods are indicated by arrows.

Figures 2, 3, and 4 show the infrared spectra of the three series investigated. The measure of the relative intensities at 2910 and 1600 cm^{-1} is indicated by the height of the bands.

Microscopic examination revealed that identical behavior occurred in each series of coals. Table 12, therefore, summarizes the visual observations for the three series in regard to melting temperatures, relative degree of fluidity, color, and presence or absence of residues above temperatures of 600°C.

Plates 3 and 4 show photomicrographs at four different temperatures for the three extracts and residues of the nonoxidized Illinois coal. This series is representative of all coals studied because changes occur at similar temperatures.

Differential thermal analysis data indicate that the three series of coal investigated are similar to each other. No interpretable differences are evident. Because of this, only the Eastern coal series is shown in figure 5.

Table 12. - Hot-Stage Microscope Examinations Inert atmosphere, rate of heating: 3° C per minute

	•	100°	200°	300	400°	500°	600
Temperature °C	20°	•06	170°				
Coal		•	•	Parti	al plastic		Residue
Pyridine				w	tate		
Extract		·		N	lelting	Shrink	Residue
Residue	ţ		Solid ph	ase			Residue
			only			k	
Chloroform							
Extract		Melting	I	Jecreasing fl	uldity	i	No residue
		Brown	Ye.	llow	Blac	×	
Residue				Parti	al plastic	Partial	No residue
on eved - n				<u>.</u> 0	ate	.mlduz	
atiovali_li							
Extract	Viscous	s Fluid		,		No residu	le
	Yellow		Brown	Black		Ŧ	
Residue			Melting	Decreasing	fluidity		. No residue
			Yellow	Brown	Black	ł	

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PLASTIC PROPERTIES OF COAL



Fig. 1. - X-ray scattering data of the three series of coal investigated.

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Fig. 2. - Infrared spectra of the Illinois high volatile B bituminous coal series.





Fig. 4. - Infrared spectra of the Eastern high volatile A bituminous coal series.



Fig. 5. - Differential thermal analysis of the Eastern high volatile A bituminous coal series.

	Pyridine	Chlor	oform	n-hexane	
Coal	Extract	Extract	Residue	Extract	Residue
Illinois HVBB nonoxidized	1500	475	600	362	520
Illinois HVBB oxidized	1600	490	700	380	550
Eastern HVAB	1740	565	895	447	710

Table 13. - Ebullioscopic Molecular Weights

Table 13 lists the average of triplicate ebullioscopic molecular weight determinations of pyridine extracts, chloroform extracts and residues, and n-hexane extracts and residues. Tables 14, 15, and 16 summarize for each series the atomic H/C and O/C ratios, x-ray and infrared aliphaticity, characteristic temperatures, and molecular weights.

Table 14. - Illinois HVBB Nonoxidized Series . H/C and O/C Ratios, X-ray and Infrared Aliphaticity, Characteristic Temperatures, and Molecular Weights

	Pyridine			Chloroform		n-hexane	
	Coal	Extract	Residue	Extract	Residue	Extract	Residue
H/C	.837	.849	.805	1.000	.805	1.072	1.093
o/c	.065	.064	.083	.042	.110	.029	.024
X-ray Al/Ar	.75	.84	.84	1,99	.86	2.22	1.61
IR Al/Ar	.31	.45	.33	1.00	.48	2.96	.96
Softening T°C	384*	300	None*†	90 †	350†	20†	170†
Decomp. T°C (DTA) Mol.wt.	400-500	3 75- 525 1500	350-400 425-500	400-525 475	450-500 600	375-550 362	350-400 450-550 520

* Obtained by Gieseler plastometer.

† Obtained by microscopic examination.

		Pyridine		Chloroform		n-hexane		
	Coal	Extract	Residue	Extract	Residue	Extract	Residue	
H/C	.859	.844	.791	.999	.786	1.135	1.023	
0/C	.077	.069	.094	.050	.100	.019	.031	
X-ray Al/Ar	.80	.89	. 89	1.19	.71	1.27	1.13	
IR Al/Ar	.50	.64	. 27	1.17	.50	2.16	.96	
Softening T°C	None*	300	None*†	90†	350†	20 †	170†	
Decomp. T°C (DTA)	400-500	375-525	350-400 425-500	400-525	450-500	375-550	350-400 450-550	
Mol. wt		1600		490	700	380	550	

Table 15. - Illinois HVBB Oxidized Series H/C and O/C Ratios, X-ray and Infrared Aliphaticity, Characteristic Temperatures, and Molecular Weights

* Obtained by Gieseler plastometer.

† Obtained by microscopic examination.

Table 16 Eastern HVAB Series
H/C and O/C Ratios, X-ray and Infrared Aliphaticity,
Characteristic Temperatures, and Molecular Weights

			ridine	Chloroform		n-hexane	
	Coal	Extract	Residue	Extract	Residue	Extract	Residue
H/C	.814	.882	.756	.911	.856	1,161	.928
0/C	.044	.036	.056	.029	.078	.014	.016
X-ray Al/A	r.74	.91	.78	1.19	.72	1.41	1.08
IR Al/Ar	.58	.86	.44	1.79	. 62	2.53	1,26
Softening	2544	200	NT	00++	250+	60±	1704
T°C	3041	300	None **	90 † *	350T	20Ŧ	1707
Decomp. T°C (DTA)	400-500	375-525	350-400 425-500	400-525	450-500	375-550	350-400 450-550
Mol.wt		1740		565	895	447	710

* Obtained by Gieseler plastometer.

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† Obtained by microscopic examination.

DISCUSSION

The following discussion is limited to the three specially prepared samples of coal investigated by the described techniques and procedures. No effort is made to project similar conclusions to other coals of similar rank lest such conclusions be misleading.

Whitaker (1955) stated that dimethylformamide has a greater dispersive power for coal than has ethylenediamine. Table 2 confirms this statement, and in addition shows that the residue, after the dimethylformamide extraction, possesses no agglomeration characteristics. In contrast, the residue after ethylenediamine extraction still retains such characteristics. Similar extractions made on a series of duplicate samples demonstrate that the values of yields reported are within \pm .1 percent. Therefore, the yields of extracts reported in table 2 show a definite increase from ethylenediamine to dimethylformamide.

Table 3 demonstrates the duplicability of results obtained by the macro and micro analytical techniques. Such comparison was necessary to determine the degree of accuracy of the latter technique compared to the ultimate analysis of coal



Fig. 6. - Yields of pyridine extract versus maximum Gieseler fluidity for the Illinois high volatile B bituminous coal series.

made by ASTM methods D 271-48. In all cases, values reported by the two methods check reasonably well, the greatest difference appearing in the hydrogen values of coal. The results obtained by the different techniques check within the expected tolerance for micro determinations, 0.3 percent.

Figure 6, plotted on a linear scale, demonstrates the relationship between yields of pyridine extract for the Illinois high-volatile B bituminous coal compared with the Gieseler maximum fluidity. The curve was derived by combining the yield of pyridine extract from the oxidized Illinois coal with data presented in table 7. This curve confirms the findings of Rees, Pierron, and Bursack (1955) in which it was shown that as coal oxidized the Gieseler maximum fluidities decreased. In this study, as oxidization increased, fluidity decreased. and the yield of pyridine extracts also decreased.

It is noteworthy that the oxidized Illinois coal, with no fluidity detectable by the Gieseler method, still gives 13.6 percent of pyridine extract. The amount of fusible material necessary to achieve a given amount of plasticizing of the mixture may depend on the volume of the porous structure. Therefore, if this amount is decreased below a certain level by oxidation, plasticity characteristics may disappear, even though fusible material still remains in the structure. Dryden (1957), in his study of coal fluidity versus rank by means of internal surface, suggested a similar explanation for low-rank coals.

Figure 6 also indicates that the effects of oxidation progressively decrease as the elapsed time increases.

Figure 7 shows the yields of pyridine, chloroform, and n-hexane extracts as a function of the Gieseler maximum fluidities for the three series of coals investigated. The yields of extracts are plotted on a linear scale and the fluidities on a logarithmic scale. Here again, as the fluidity increases the yield of extracts increases. In considering these curves, especially for the Eastern high-volatile A bituminous coal, two sources of error must be considered in determining maximum fluidity:

1) At such high rates of turning of the instrument pointer, an error of 0.1 second will increase or decrease the value obtained by approximately 4200 dial divisions per minute.

2) This coal has such high fluidity and swelling properties that it expands while in the plastic stage, greatly reducing the amount remaining in the cup in contact with the stirrer. This behavior might account in part for the very high fluidities observed and might be considered the most probable source of error.

Because of these two factors, the fluidity of such coal probably may be considered only as greater than 15,000 dial divisions per minute.

Table 8 indicates that, for the series studied, direct extraction of coals by chloroform gives much lower yields than those obtained by the described extraction scheme. It also shows no yield when the direct n-hexane extraction is carried out.

Ultimate analyses presented in tables 9, 10, and 11 indicate a definite increase in atomic H/C and a decrease in atomic O/C ratio from coal to pyridine extract and its subsequent extracts. In all cases, the chloroform extractions of the pyridine extract produced greater chemical differences between the resulting chloroform extracts and residues than between the original pyridine extracts and residues. Possibly the interaction of pyridine with coal causes solution and dispersion of certain colloidal-size particles of the coal structure, whereas in comparison the chloroform extraction may limit itself to a higher degree of solubility. Also, in all cases, pyridine residues possess a lower H/C ratio and higher O/C ratio than their parent coals. In each series investigated, the H/C ratios of the n-hexane extract and residue are higher than the corresponding chloroform extract from which they were obtained. This seems to indicate that solvent (n-hexane) still remains in either extract or residue or in both.

Following the scheme of extraction, the nitrogen values appear to remain constant in each extract and residue, except in the n-hexane residues, in which they are the highest. The sulfur remains more or less constant for the Eastern coal, but in the case of the Illinois coal it is selectively more concentrated in the pyridine residue than in the pyridine extract.

The aliphatic/aromatic ratios obtained from x-ray scattering data (fig. 1, tables 14, 15, and 16) increase progressively in the extraction series from coal to n-hexane extract. These values for the pyridine and chloroform residues are simi-



Fig. 7. - Yields of extracts versus maximum Gieseler fluidity of the three series of coal investigated.

lar to those of the parent coals, but in this respect the n-hexane residues resemble the chloroform extracts from which they were derived.

The progressive increase in alighaticity of each subsequent extract also is indicated by the slight shift of the band maximum toward the 4.5 Å period. In general, the extracts show an increasingly higher degree of orientation, as measured by the relative height of the band maximum.

The peaks at 37.4° and 43.6° scattering angle, as shown, for example, in the pyridine extracts and more especially in n-hexane residues of the oxidized Illinois coal and the Eastern coal, are not from the coal substance but from the aluminum sample holder.

The aliphatic/aromatic ratios obtained from infrared data (figs. 2, 3, 4; tables 14, 15, 16) increase progressively in the extraction series from coal to n-hexane extract. The effect of the choice of the base lines in the calculation of the ratios is demonstrated for the n-hexane extract in figure 4, infrared spectra, Eastern coal. In this case, the difference in the height of the 1600 cm⁻¹ band caused by using a different base line produces a difference of 0.13 in the calculated ratios. Such error is much smaller than the differences found between ratios of the three subsequent extracts in this series, and so is assumed to be negligible.

The spectra of the residues are similar to those of the parent coals. In the case of the Illinois coal and Eastern coal the shoulder on the 1600 cm⁻¹ band, located at approximately 1700 cm⁻¹ and related to a carbonyl bond, becomes more pronounced in the spectra of the n-hexane extracts. It appears also that this carbonyl band is greater in the oxidized Illinois coal than in the nonoxidized Illinois coal. This confirms the finding of Vucht et al. (1955) that oxidation develops a relatively stronger C = O band.

The strong OH bands at 3400 cm⁻¹ in all spectra made by the potassium bromide pellet method may be ascribed largely to water absorbed by the salt.

It may be added that in spite of differences in the chemical composition and in the physical properties, as described later, infrared spectroscopy and x-ray scattering data of extracts and residues are similar to those of coal in general. Therefore, the data presented in tables 14, 15, and 16 in regard to aliphatic/aromatic ratios are interpreted only on a qualitative basis. They represent a trend and not an actual degree of aliphaticity. Nevertheless, both the x-ray and infrared ratios show the same trend indicated by the atomic H/C ratios derived from chemical analyses.

It is thought that the pyridine extracts may have contained dispersed coal particles. This is suggested by the information obtained by microscopic examination (table 14, plates 3,4), and by the fact that residues remained after heating these extracts to $600^{\circ}C$.

Noteworthy is the relatively long plastic range of the chloroform extract (90 to 500 °C) and of the n-hexane extract (room temperature to 400 °C) in comparison with the pyridine extract or with the coal itself. The thermal decomposition temperatures indicated by the base of the major endothermic peaks shown in figure 5 remain constant.

The ebullioscopic molecular weights of the extracts (table 14) decrease from pyridine extracts (1500-1740) to chloroform extracts (475-565) to n-hexane extracts (362-447). The molecular weight of the pyridine extract may be too high if it is assumed that this material contains insoluble dispersed colloidal particles from the parent coal. In general, the molecular weights are highest for the Eastern coal and lowest for the nonoxidized Illinois coal.

CONCLUSIONS

The following conclusions have been drawn from the studies of the three series of coal by the described procedures and techniques:

- The plastic behavior of a fluid coal, as measured by the Gieseler plastometer, is destroyed by pyridine extraction.
- 2) The yield of extract for each solvent appears to be proportional to the fluidity as measured by the Gieseler plastometer.
- In each series, as the progressive scheme of extraction was carried out, each extract showed a higher relative degree of aliphaticity, a lower melting point, a lower molecular weight, and a relatively constant thermal decomposition temperature range.
- 4) For each coal the pyridine, chloroform, and n-hexane extracts are similar to the corresponding extracts of the other coals studied.
- 5) The oxidized Illinois coal, in spite of showing no Gieseler fluidity, still yielded 13.6 percent of pyridine extract. The significance of this phenomenon is not yet known, but it may be tentatively interpreted as the possible inability of the Gieseler plastometer to detect very low fluidity.

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