Constitution, Properties, and Analytical Methods

Extractable Waxes in United States Lignites

Solvent extraction of certain German brown coals with either benzene or a mixture of benzene and alcohol yields an extract that is termed montan wax. The montan-wax industry prior to the war had been developed extensively in Germany, as the wax finds use in many industrial applications. In 1939, over 7,000,000 pounds of montan wax was imported into the United States, nearly all of which was shipped from Germany. As little information on the potential use of American low-rank coals as a source of wax is available, an investigation is in progress to determine the nature and amount of material extractable from such coals.

Preliminary extractions of dry lignite with benzene as solvent have been made on samples from deposits in Arkansas, California, North Dakota, Texas, and Washington. The results show that a considerably greater quantity of extract was obtained from the samples examined from Ouachita County, Ark., and Amador County, Calif., than from the other sources. The Arkansas and California lignites gave 6 to 7 percent of extract on a dry-coal basis, whereas the North Dakota, Texas, and Washington samples usually yielded less than 1 percent of extract. Slightly higher yields were obtained from air-dried samples than from samples dried at 105°C. If an azeotropic mixture of benzene and alcohol is used as solvent, considerably higher yields of extract are obtained from air-dried samples than if benzene is used alone. Yields of extract from the Arkansas and California lignites are as high as 11 to 13 percent on a dry-coal basis using the benzene-alcohol mixture as solvent. The properties of the wax extracted from a sample of California lignite is dependent somewhat on the solvent used in the extraction. The acid number and saponification number both increase with increase in the amount of extract obtained. The melting point, ester number, and so-called "resin" content show only small differences.

Although a number of tests have been used for evaluating montan wax, those most quoted in the literature are the melting point, acid number, saponification number, ester number, and "resin" content. The term "resin" is usually applied to those constituents that are more soluble in solvents as ethyl ether, ethyl acetate, ethyl alcohol, and benzene-alcohol mixtures at or below room temperature than is the true ester wax. The results that have been completed indicate that the waxes from the Arkansas and California lignites examined have properties similar in many respects to crude montan wax from German brown coal. One difference so far detected is that the waxes examined may have a higher "resin" content than crude commercial montan wax.

Analyses of Miscellaneous Materials

A total of 195 samples of miscellaneous materials was analyzed and reported during the year. The samples represented a wide variety of materials for which chemical analyses or tests were requested in connection with investigations of coal utilization or of problems concerned with health and safety.

Forty samples, including 25 catalysts, were analyzed in connection with the Synthetic Liquid Fuels Program. Twenty-four of the catalysts were collected from German synthetic liquid fuel plants and were analyzed to identify the active constituents. Molybdenum was determined in a molybdenum catalyst and in three catalyst residues from a converter. Tin was determined in a residue from coal hydrogenation where tin sulfide was used as a catalyst. Water from a gas holder was tested for sulfur, and seven samples of kieselguhr, distilled water, water conditioner, and magnesium oxide used in preparing catalysts for Fischer-Tropsch synthesis were examined for impurities.

Seventeen samples of coal were analyzed for water-soluble chloride as a part of a study of the preparation of coal adaptable for use in coal hydrogenation. On an air-dried coal basis, the amount of chloride calculated as Cl ranged from 0 percent each for a Montana and a North Dakota coal to 0.36 percent for an Indiana coal. Samples of ash from another series of 23 samples of coal were analyzed for SiO_2, Fe_2O_3, CaO, and Mn_3O_4. Fifteen of the ash samples represented 1-1/2-inch by 14-mesh coal mines in Illinois, Indiana, Kentucky, Montana, North Dakota, Ohio, Pennsylvania, Utah, West Virginia, and Wyoming. Eight samples represented float on 1.60 specific gravity of 3/8-inch by 14-mesh coal from eight of the same mines. Fusain in two samples of coal was determined by a chemical oxidation method. A sample of minus 5/8-inch raw screenings from Illinois No. 6 bed coal contained 5.0 percent fusain, and a channel sample of Pittsburgh-bed coal from the Experimental Mine contained 4.2 percent. In comparison, relatively inert organic material determined petrographically by the powdered-coal method in the same samples was 4.4 and 5.0 percent, respectively.

A total of 50 analyses was made in connection with fuel engineering service of the Bureau of Mines to other Government agencies. These samples included 11 boiler-water compounds, 2 samples of tannin used in boiler-water treatment, 16 boiler scales and deposits, and 2 boiler waters analyzed in connection with work on boiler feed-water conditioning in Federal power plants. Also, 3 external deposits on boiler tubes, 5 fly ashes, and 11 deposits on air-preheater plates of steam plants were analyzed as part of investigations of corrosive deposits on boiler surfaces.

Nineteen samples of slag, residue, coke ash, and limestone were analyzed in connection with tests of a slagging-gas producer using Rhode Island anthracite for the direct production of mineral wool.

Nine samples of petroleum coke contained 0.02 to 0.05 percent silicon and 0.05 to 0.09 percent iron. Three samples of foundry coke contained 0.008 to 0.023 percent phosphorus, which is considerably under the maximum of 0.09 percent permitted in the specifications. A face sample of coal from Pierce County, Wash., contained 0.08 percent phosphorus. A sublimation product collected from the surface of a smoldering refuse dump at the Cadogan mine, Armstrong County, Pa., contained mainly free sulfur and ammonium chloride. Iron was determined in the ash of lignite, char, blow-over dust, and sludge from a test run at the Bureau of Mines lignite-gasification plant at Grand Forks, N. Dak., to assist in making a materials balance.

Five samples of limestone and four samples of fly ash were examined to determine their suitability for rock-dusting coal mines to prevent the propagation of coal-dust explosions. The fly-ash samples, representing fine ash from furnaces burning powdered coal, were considered unsuitable for rock dusting because they were highly siliceous and contained 6.3 to 8.4 percent combustible matter, which is more than the maximum of 5 percent allowed in Mine Safety Board Decision 32. Four of the five limestones examined were of sufficient purity to be suitable for rock dusting. Flash and fire points were estimated for a sample of gilsonite submitted by the Michigan Department of Health for tests of explosibility of the dust. A sample of resin removed from an Army Ordnance canister containing steel balls imbedded in resin was tested to determine its softening point, flash point, and fire point as part of a study of the feasibility of using surplus canisters as steel scrap. Phosphine was determined in acetylene produced from two samples of calcium carbide in connection with investigations of explosions of acetylene generators. The remaining 13 samples examined included anthracite ash, mine water, and clay.

Electron Microscope Studies of Coal and of Fischer-Tropsch Catalysts

Although used for other purposes, the electron microscope was applied mainly during the year to studies of coal petrography and catalysis of synthetic liquid-fuel processes. Electron micrographs of aluminum powders revealed particle size and shape differences that accounted for their varying susceptibilities to rapid ignition and explosion. Electron micrographs of carbon blacks resulting from the ignition of acetylene and other gases showed that the particles were spherical and of a range of size similar to commercial carbon blacks.

A large number of electron micrographs has been made in a study of various types of kieselguhrs used as carriers in Fischer-Tropsch cobalt catalysts. Preliminary tests have shown that the type of kieselguhr has some effect upon the catalytic activity. Varieties from Portugal and Germany, presumably used in successful Fischer-Tropsch catalysts (the former in England), and American commercial types have been tested to determine bulk density, pore volume, surface area, chemical analysis, and X-ray diffraction characteristics, and the results have been combined with the electron microscope study in a publication.[7] Figure 1 illustrates the particle size and shape characteristics of some of these kieselguhrs. The magnification of the micrographs, 2,000X, is rather low for the electron microscope, but diatoms are comparatively large specimens for which greater enlargement is not required. The Portugese kieselguhr is characterized by small, compact particles, many of which do not show the porous structure predominating in other types. Disk-shaped structures averaging 5 microns in diameter are the most common regular forms. In the German varieties, such disk-like skeletons are numerous, and nearly all of the particles are of porous regular design. These foreign varieties presumably are from

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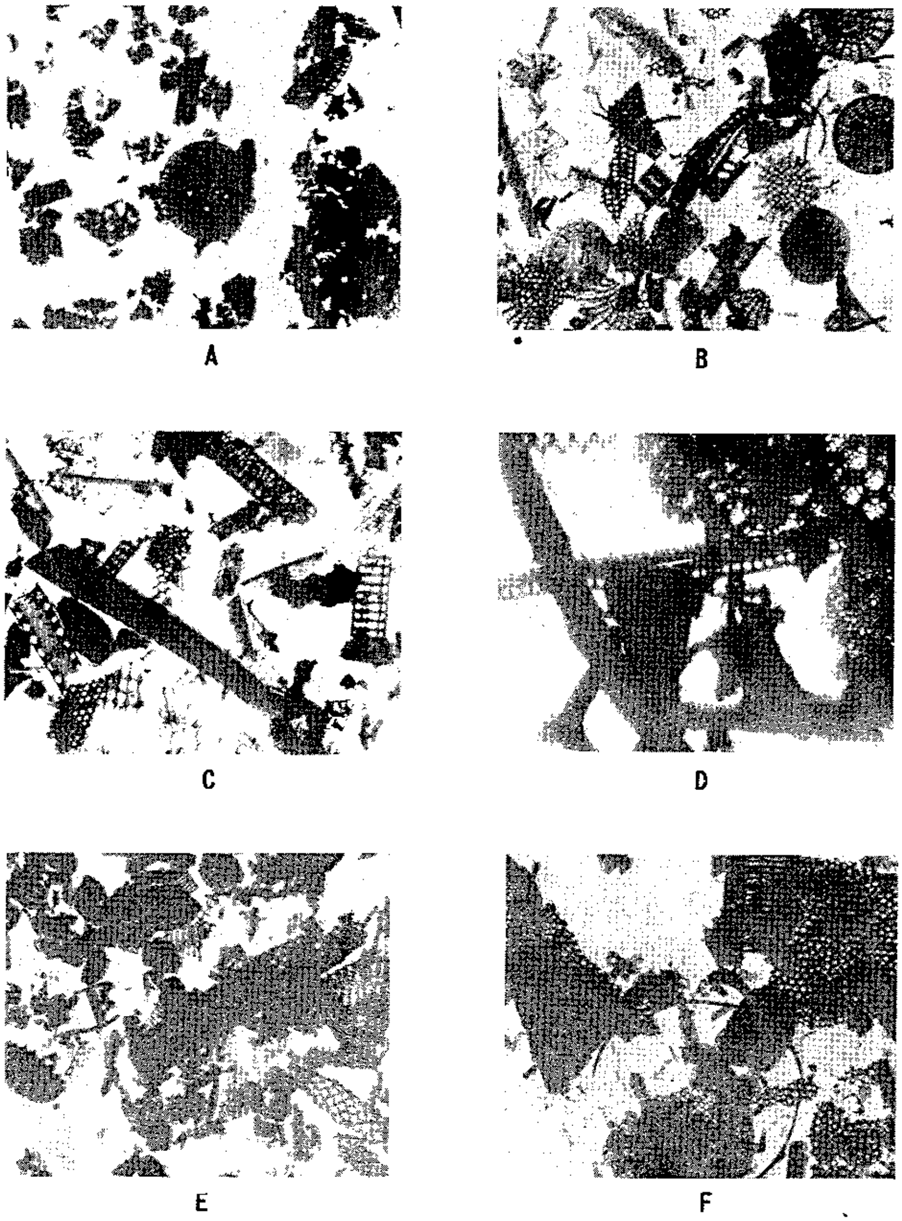
7/ Anderson, R. B., McCartney, J. T., Hall, W. K., and Hofer, L. J. E., Properties of Kieselguhrs Which may Determine Their Suitability as Carriers in Catalysts: Ind. and Eng. Chem. (In press.)



A B C D E F

Figure I. - Electron micrographs of varieties of kieselguhr proposed as carriers in cobalt catalysts for the Fischer-Tropsch synthetic liquid-fuel process. A, Portuguese; B, German; C, Johns-Manville Filter Cel; D, Johns-Manville Hyflo Super Cel; E, Dicalite 911; F, Dicalite 637T. 2,000X.

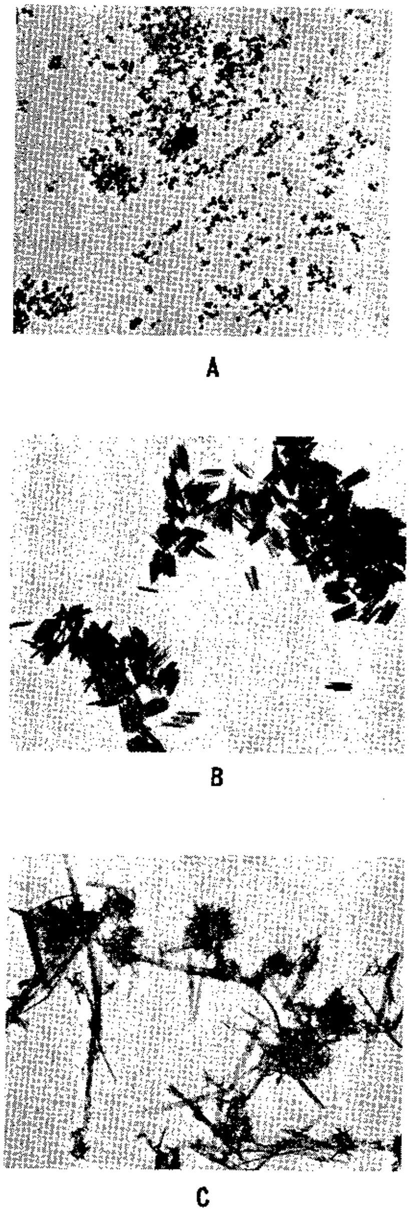


Figure 2. - Electron micrographs of phases of hydrated iron oxide occurring in catalysts for the Fischer-Tropsch synthetic liquid-fuel process. A, α-FeOOH; B, β-FeOOH; C, γ-FeOOH. 5,400X.

fresh-water deposits. All the American types examined were derived from extensive beds in the Lompoc district of California and are known to be of marine origin. Of a number of grades tested and micrographed, the two shown represent the extremes in particle size. The Filter Cel is a natural material, whereas the Hyflo Super Cel has been flux-calcined. Most of the particles are very porous, with rod and plate forms apparently exceeding the disk type in number. The Dicalite samples come from various American beds, some of fresh-water origin. The two illustrated are from such deposits in Oregon and Nevada. They apparently contain more circular and fan-shaped forms and fewer rodlike particles than the Johns-Manville marine types. Correlation of the physical properties of these kieselguhr carriers with catalytic activity will be attempted in later publications after further testing. This summary of the physical features of various available types is presented for general interest to the users of such materials in industrial applications.

Tests were made on iron catalysts for the Fischer-Tropsch process, prepared in different ways in the search for the basic reasons for their varying degrees of catalytic activity. Electron micrographs have been made of a number of these catalysts and of different forms of iron oxides that occur in them. Some of the latter are illustrated in figure 2, which shows the α, β, and γ forms of the hydrated iron oxide FeOOH. Marked differences in size, shape, and crystal form can be seen. The particles of α-FeOOH are smallest, of fairly uniform size (about 0.1 micron in diameter), and approach spherical shape. The rod-shaped particles of β-FeOOH, about 0.7 micron long and 0.1 micron in diameter, are suprisingly uniform in size. γ-FeOOH also consists of particles of fibrous nature but varying considerably in size. Another common oxide found, α-Fe_2O_3, is similar to α-FeOOH in appearance. These micrographs can be used as standards, in conjunction with X-ray diffraction data, to identify the various phases present in iron oxide catalysts.

A Method of Petrologic Analysis

A new petrologic method has been devised for obtaining comparative information from standard samples of commercial coal. The new procedure combines the high level of optical resolution of components inherent in thin-section preparations with a method of sampling that can be expanded to serve any practical accuracy expectation. A new area of petrologic study is opened for investigation by this method to include such diverse materials as deduster dusts, carbonization blends, and fractions of coal from various stages of preparation schedules. The crux of coal sampling has always been to obtain enough coal particles so that all variations in the coal are presented proportionately. Single pieces of coal were needed for individual sections in all previous studies that utilized the property of light transmission. A prohibitive number of sections was therefore required to obtain adequate sampling of a commercial lot of coal, even if the pieces too tiny to section formed a small enough proportion of the whole to be disregarded. Actually, the fines of a commercial sample should never be disregarded, because this fraction, though it may be a small percentage of the whole, represents an extreme of component segregation, and a small percentage of fines influences the petrologic composition of the whole sample to a disproportionate extent.

Lithology of the coal - that is, the occurrence and distribution of components - is important in conditioning segregation of the various petrologic entities. Thus, some coals have an even and consistent enough distribution of diverse elements, so that very little segregation can occur in the sizes produced by normal breakage or crushing. Other coals show important tendencies of component segregation in the same range of sizes because of more irregular distribution of the various constituent materials. In order to determine the effects of lithology upon segregation, it is necessary to use petrologic concepts that have compositional and not lithologic connotation. Both vitrain and anthraxylon have certain lithologic as well as compositional connotations in quantitative petrology, inasmuch as fragments of similar optical character, but which occur in fragments smaller than critical and arbitrary sizes, are excluded from them. In recent work at the Bureau of Mines, vitrain is interpreted as a megascopic ingredient, including bands thicker than one-half millimeter. Anthraxylon in a microdetermined constituent that includes all bands thicker than 14 microns. These bands correspond to vitrain, so far as composition is concerned. The complete amount of material in a coal sample that is preserved in the same way as anthraxylon or as vitrain is referred to as vitrinized. This constitutes a larger fraction of coal and one that is not defined by reference to any thickness of occurrence. It is regarded, therefore, as a primary component, and it can be measured at high magnification by the pulverized-coal method to establish the influence of lithology upon petrologic composition.

Coal prepared for commercial utilization is frequently crushed, so that composition rather than lithology is a dominant consideration. Pulverized-coal analyses can be used comparatively to establish what influence petrologic composition has upon utilization properties. Because of limitation in sampling, this phase of petrologic study could not be undertaken systematically previously. It now seems feasible, as a routine method, to determine the petrologic composition of prepared fractions and of other commercial-type samples with a comparative accuracy of about one-half of one percent.

The method involves careful hand crushing of the sample for analysis to pass an 80-mesh screen. The minus 80-mesh sample is then separated into a fine and coarse fraction by means of a 325-mesh screen. The two resultant fractions are compressed into 1-inch-diameter briquettes by using a small amount of water-glass binder and approximately 60,000 p.s.i. pressure. The briquettes are dried and further hardened by impregnating with carnauba wax (m.p. ca 85°C.). Resultant briquettes are hard and can be sawed, smoothed, and polished by the same methods used in sectioning integral coal specimens. Skillful preparation results in sections that show excellent resolution of the components of randomly oriented particles.

Quantitative determinations of constituents are made at 450X occular magnification. At this magnification, even the most dispersed components are clearly resolved; the largest individual particles in the 80 x 325-mesh briquette are smaller than the single field of view, and so no small group of particles can fortuitously monopolize the quantitative determination.

The primary entities determined include (1) vitrinized matter; (2) yellow, waxy matter (spore coats, cuticles, and other similar optical material); (3) various forms of opaque matter, including fusain; (4) translucent mineral matter; (5) pyritic mineral matter, and (6) open interstitial space. Determinations are prepared on a visually pure basis by arithmetic rejection of items (4), (5), and (6). In other words, significant values are determined as nearly as possible by visual methods on the organic coal substance alone.

In preliminary work, areas equivalent to 100 solid micro fields of visually pure coal substance have been determined for each sample. Areas determined are selected on an arbitrary 1/2-millimeter spacing grid on each section to avoid any possibility of bias due to selection of areas. Each of the pulverized-coal sections is studied proportionately to the percentage of sample represented by their respective briquettes. Thus, if the 80- by 325-mesh briquette equals 80 percent of the sample, determinations equivalent to 80 solid micro fields of visually pure coal are established from it.

Subsequent to proportional study of slides prepared from both coarse and fine fractions of a sample, the results are combined arithmetically to give the final compositional values for the whole of the original sample. Precautions are taken against any form of segregation or differential loss or inequitable determination of compositional constituents throughout the sequence of operations, with the exception of the one sizing operation using the 325-mesh screen. This division of the sample has seemed necessary in order to make the briquettes hard enough to withstand preparation of excellent-quality sections. It is hoped that modification of briquetting procedure may serve later to obviate the need for dividing the samples into two size fractions. The method as now developed is practical in application and has provided information of relative precision on samples not amenable to detailed high-resolution microscopy by any previous method. It further has the distinct advantage of utilizing the same light transmission properties of the coal that have been extensively reported previously in analysis of column specimens of American coal beds. No question, therefore, enters regarding the essential compatibility of the petrologic entities reported by the two methods of analysis.

The following tabulation of analyses (table 1) indicates the nature of samples and results that are being obtained by this pulverized-coal method of analysis.

TABLE 1. - Petrologic analyses of pulverized coal samples.
(All results expressed on a visually-pure basis.)

	Reactive components		Organic inert components
	Vitrinized matter, percent	Yellow (waxy) matter, percent	Opaque plus fusinized matter, percent
Pittsburgh coal bed - whole experimental sample	92.9	0.6	6.5
Pittsburgh coal bed - air-separated dust fraction (approximately minus 100-mesh)	87.2	.5	13.3
Pittsburgh coal bed - concentrate fraction following elestrostatic preparation of minus 10-mesh coal	96.2	.6	3.2
Herrin (Illinois No. 6) coal bed - crushed raw screenings	94.5	.4	5.1
Herrin (Illinois No. 6) coal bed - air-separated dust fraction (approximately minus 100-mesh) .	71.0	.3	28.7
Herrin (Illinois No. 6) coal bed - concentrate fraction following electrostatic preparation of minus 10-mesh coal	97.6	.6	1.8
Pittsburgh coal bed - 70 percent fraction of 1/4- x 10-mesh coal from experimental head sample ..	93.7	.9	5.4
Pittsburgh coal bed - 30 percent fraction of minus 10-mesh coal from experimental head sample ..	92.0	1.0	7.0
Pittsburgh coal bed - 64 percent float fraction at 1.50 sp.gr. from 1/4- x 10-mesh experimental sample	94.0	1.2	4.8
Pittsburgh coal bed - 17 percent concentrate fraction obtained by experimental electrostatic preparation of 10 x 100-mesh coal ..	96.1	.7	3.2
Herrin (Illinois No. 6) coal bed - 21 percent fraction of tipple sample obtained by experimental electrostatic preparation of 10 x 100-mesh coal	95.0	1.5	3.5