Part II

PHYSICAL PROPERTIES

EVALUATION OF COMPOUNDS AND MATERIALS

Properties of Green River Oil Shale

Determined from Nitrogen Adsorption and Desorption Isotherms

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OIL SHALE, a major potential source of liquid fuels, consists of a complex mixture of organic and inorganic constituents in variable proportions. Data have been reported (*9*) on particle size, particle-size distribution, and particle-size classification of the inorganic constituents.

The present study indicates that oil shale is a highly consolidated organic-inorganic system with no significant micropore structure, pore volume, or internal surface. The mineral constituents have an appreciable surface area, about 3 to 5 square meters per gram, which appears to be limited mainly to external surface. They contain some micropore structure which has random pore-size distribution, pore radii ranging from 10 to 100 A.

The distribution of the organic matter within the inorganic matrix is essentially inter- and not intraparticle. That within the micropore volume of the inorganic constituents is less than 4%.

Estimates made from surface area data suggests that perhaps only a small amount of the organic matter is bonded either physically or chemically to the mineral constituents.

EXPERIMENTAL

Preparation of Oil-Shale Samples. The oil shale used in this study was from the Bureau of Mines experimental mine near Rifle, Colo. Because the formation is not homogeneous, shale was taken from two different levels which differed widely in organic content. Two samples, approximately 200 pounds each, were prepared by compositing random samples from 1-foot sections of B and EF shale beds in the Mahogany Zone (*8*). The two samples, assaying 28.6 and 75 gallons of oil per ton respectively, were crushed to pass a ⅜-inch screen. The samples used for studying both the raw shale and its inorganic constituents were selected from each of the crushed shales.

The samples selected for studying the inorganic constituents did not contain the fines but included only pieces of shale ranging in size from ¼ to ⅜ inch. These pieces were large enough to permit the inorganic particles, except possibly those exposed at the surfaces, to retain their original size.

The samples selected for studying surface area and pore structure of the raw shale were further reduced to pass a 200-mesh sieve (74μ) and the particles smaller than 44μ were removed using a screening and washing technique which left a particle-size range of 44 to 74μ. This size range permitted adequate representation of the initial shale in a 4 to 5 gram sample (limited by the size of the adsorption bulb used in measuring surface area), facilitated exposure of any naturally existing noncontinuous micropore structure, and eliminated the fine particles which were not desired for some of the analyses. Because the organic matter was more resistant to crushing than the mineral constituents, the raw shale did not crush uniformly with respect to composition. The distribution of the organic carbon, approximately 80 weight % of the total organic matter, is shown in Table I which also presents the distribution of the crushed shales with respect to particle size. The fractionation of the organic matter as evidenced by the organic carbon data was not considered excessive for studying the raw shales.

Preparation of Inorganic Constituents. Previous work (*9*) indicated that a high percentage of the inorganic particles were smaller than 44μ. To retain their original size and to maintain representation of the initial shales, a composite sample consisting of 200 to 300 pieces (¼ to ⅜ inch) were selected from each of the two shales crushed to pass a ⅜-inch screen. The organic matter was removed from these samples by controlled oxidation over a period of about 40 hours at a temperature not exceeding 750° F. (*9*). The resulting shale residues contained less than 0.1 weight % of the initial organic carbon.

Although the raw shales contained only trace amounts of calcium sulfate and ferric oxide, the inorganic residue from the leaner shale contained 1.7% calcium sulfate and 2.8% ferric oxide and the respective values for the residue from the rich shale were 5.1 and 4.5%. The probable manner in which these compounds were formed was discussed previously (*9*). Because the calcium sulfate could exist as extremely fine particles and hence have an appreciable surface area it was leached from a portion of each of the shale residues. Attempts to remove the ferric oxide by flotation techniques using blends of bromoform and acetone were unsuccessful.

Low-Temperature Adsorption Apparatus. The low-temperature adsorption apparatus and technique used in this study were similar to those described by Emmett (*4*), Joyner (*1*), and Reis (*7*). The all-glass adsorption apparatus, fabricated in this laboratory, consisted of an adsorption bulb, calibrated gas burets, mercury manometer, McLeod gage, nitrogen-vapor-pressure thermometer, high vacuum system, purification trains for nitrogen and helium, and reservoirs for the purified gases. The purity of the nitrogen and helium exceeded 99.9 mole % as determined by mass spectrometer.

Procedure for Oil Shale. A 4- to 5-gram sample of the 44- to 74-micron shale was tightly packed in an adsorption bulb and degassed at 220° F. under high vacuum, 10^{-6} mm. of mercury, to clean the shale's surfaces without significantly changing its chemical and physical structure. After degassing, the dead-space volume was measured using helium at the temperature of liquid nitrogen. Subsequently, the helium was pumped from the adsorption bulb and the sample again degassed at 220° F. and 10^{-6} mm. of mercury for 30 minutes.

A complete low-temperature adsorption isotherm was obtained by measuring, at the temperature of liquid nitrogen, the quantity of nitrogen adsorbed on the shale at pressures from a few millimeters of mercury to the saturation pressure of the nitrogen. Adsorption equilibrium was reached rapidly below a relative pressure of 0.35. However, 15 minutes were allowed for equilibrium before the subsequent known volume of nitrogen was admitted into the adsorption bulb. Above 0.35, 2 hours were allowed for the sample to equilibrate. This appeared to be ample time for the heat of adsorption to dissipate and for equilibrium to be established, as no significant pressure differences were noted when periodically the time intervals were extended to 6 hours in the higher relative pressure region, above 0.75.

After the adsorption data were completed, desorption data were obtained down to a relative pressure of 0.2 by removing known volumes of nitrogen and permitting the sample to equilibrate each time nitrogen was removed. Time allowed for desorption to occur at each relative pressure was the same as for adsorption equilibrium at approximately corresponding relative pressures.

Several adsorption-desorption runs were made for each of the two shales using different samples for each run and degassing periods up to 96 hours. The loss in weight of the samples, probably due to decarboxylation and loss of volatile organic matter, ranged from 0.20 to 0.34 weight %.

Procedure for Inorganic Constituents. A 5- to 6-gram sample of shale residue was tightly packed in an adsorption bulb and degassed at 600° F. under high vacuum for 16 hours. The dead-space volume was measured as previously described and then the sample again degassed at 600° F. under high vacuum for 30 minutes before determining its adsorption data. The time allowed for equilibrium to be attained was 15 to 30 minutes for relative pressures below 0.35 and 2 to 3 hours for those between 0.35 and the saturation pressure of the adsorbate. Equal time intervals were allowed for the sample to equilibrate at corresponding relative pressures during the desorption stage. In a number of instances, the time interval between addition or removal of the adsorbate was increased to 10 hours in the relative pressure region above 0.75. Comparison of these data with the shorter periods, 2 to 3 hours, indicated that ample time was allowed for either adsorption or desorption equilibrium to occur.

Complete adsorption-desorption runs were made for the initial residues from both shales and the residue from the rich shale free of water-soluble material, (essentially calcium sulfate). Because the residue from the leaner shale did not contain much calcium sulfate, the adsorption data for the residue free of water-soluble material was terminated at a relative pressure of 0.6.

INTERPRETATION OF RESULTS

The experimental data can be expressed in graphic form as adsorption and desorption isotherms. These relate the volume of nitrogen adsorbed or desorbed per gram of sample as a function of the relative pressure, P/P_o, where P is the measured pressure within the adsorption bulb and P_o is the liquefaction pressure of the adsorbate. The adsorption-desorption isotherms of the two raw shales, their respective inorganic constituents, and the inorganic constituents from the rich-shale residue free of water-soluble material are presented in Figure 1, *A* through *E*. Interpretation of these adsorption and desorption isotherms yields information about surface area, pore volume, and pore structure.

As classified by Brunauer (*2*), all of the adsorption isotherms are Type II isotherms with an asymptotic approach to the P_o line. These were further interpreted according to the method of Brunauer, Emmett, and Teller (*3*) who showed that Type II isotherms can be plotted according to the equation:

$$\frac{P}{V(P_o - P)} = \frac{1}{VmC} + \frac{(C-1)P}{VmCP_o} \qquad (1)$$

where

P = measured pressure
P_o = liquefaction pressure of the adsorbate
V = volume of gas adsorbed at pressure P
Vm = volume of gas required to form a monolayer
C = constant relating to heat of adsorption

In Type II adsorption isotherms, a plot of $P/V\ (P_o - P)$ as a function of P/P_o is linear within the relative pressure range of 0.05 to about 0.35. Deviations from linearity occur which are negative up to 0.05 and positive above 0.35. The experimental data, plotted according to Equation 1 for the two oil shales and the initial and water-soluble-free inorganic constituents of the respective shales presented in Figure 2, *A* through *C*, yield plots that are in excellent agreement with the BET theory. The volume of nitrogen, Vm, required to form a monomolecular layer was calculated from the slope and intercept of these isotherms and then it was translated into area units, square meters per gram, using 16.2 square A. (*6*) as the area of the adsorbed nitrogen molecule.

Oil Shale. The surface areas of the two raw shales are presented in Table II. That of the rich shale remained essentially constant with different degassing times while that from the leaner shale differed by 0.15 square meter per gram. Because it did not appear that degassing was completed before 96 hours, the values selected to represent the areas of the crushed shale particles were 0.75 and 0.58 square meter per gram for the 75 and 28.6 gallons per ton shales respectively. In terms of the unit volumes, the areas of the respective shales are about equal, 1.22 and 1.24 square meters per cubic centimeter. These values indicate no significant internal surface even though they are considerably greater, approximately 20 times, than the surface area of an equivalent volume of nonporous spheres with diameters midway between 44 and 74μ.

Much of the measured surface area of the shale particles probably was contributed by surface roughness and by fractures introduced in both the inorganic constituents exposed at the surfaces of these particles and in the organic matter when the shale samples were prepared. Some of the surface area may be attributed to naturally occurring pores or capillaries with diameters less than 10 A. If such exist, their surfaces could not be determined directly from the adsorption-desorption isotherms nor their presence detected, because within the relative pressure region, 0.05 to 0.35, capillary condensation presumably does not occur and hysteresis therefore would not be evident. The coverage of nitrogen on the adsorbent within this region varies from less than a monolayer to about 1.5 monolayers (*5*). The surface areas presented in Table II indicate that surfaces attributed to capillaries or pores accessible through openings less than 10 A., if they occur, are not very large.

Information pertaining to pore size, pore-size distribution, and pore volume of the adsorbent can be obtained

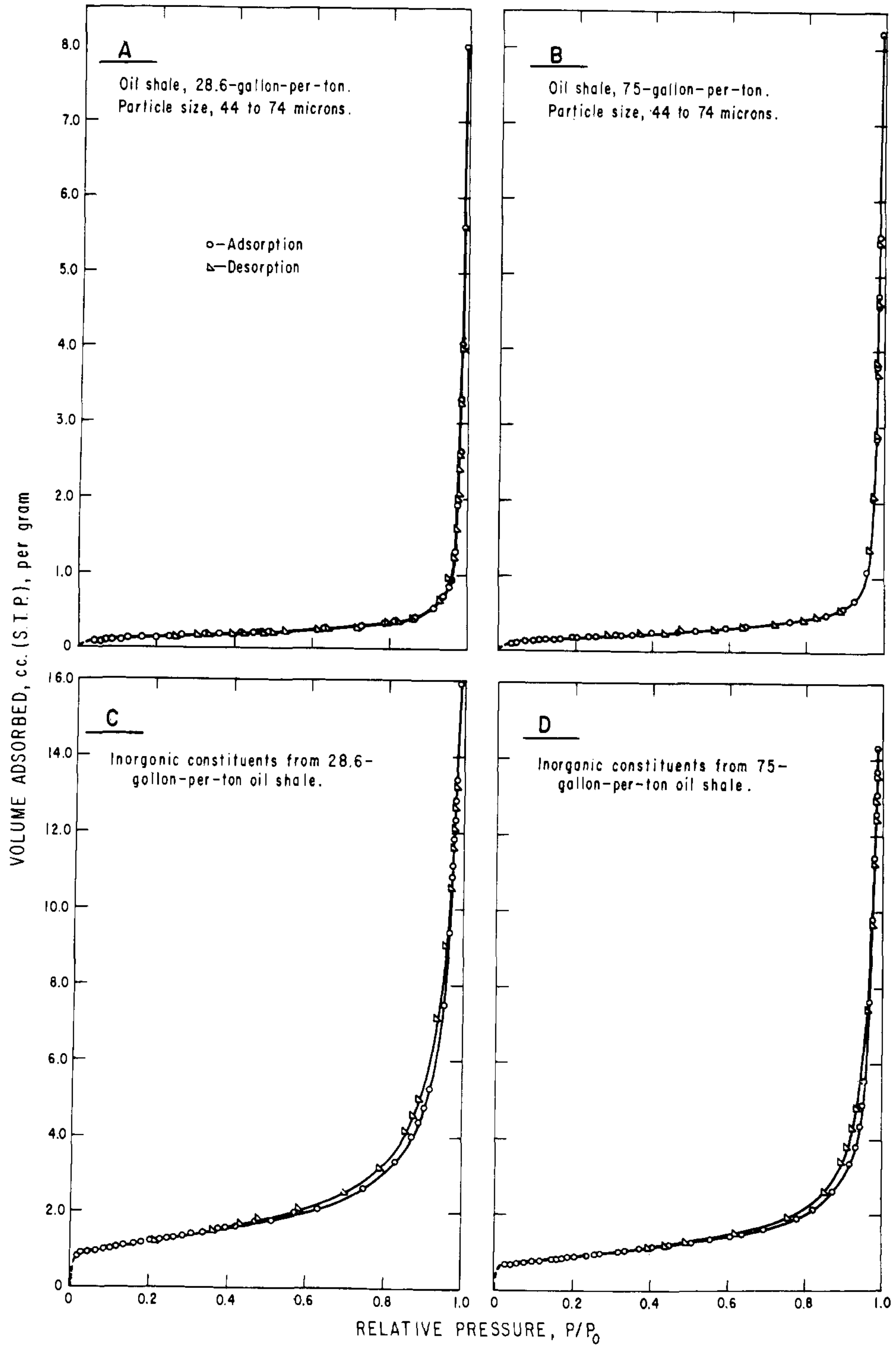

Figure 1. Nitrogen adsorption-desorption isotherms

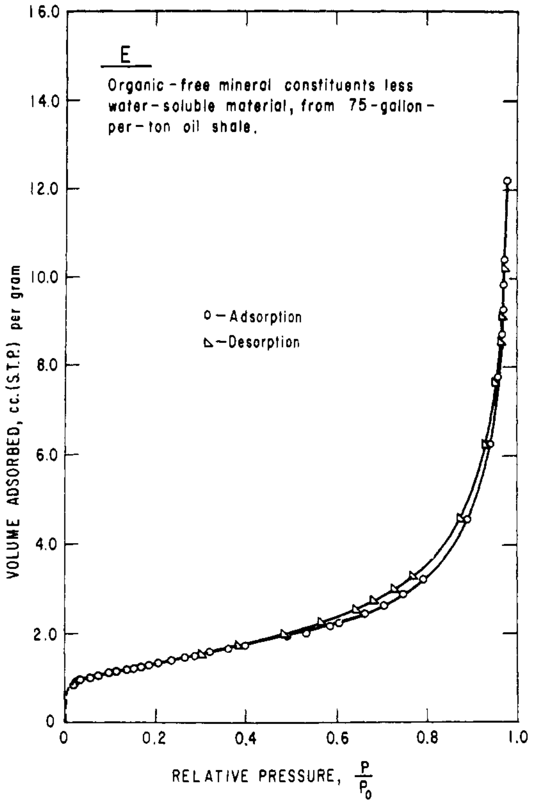

Figure 1. Nitrogen adsorption-desorption isotherms (*continued*)

Table I. Distribution of Organic Carbon in Raw and Crushed Oil Shale

Oil Shale	Raw Shale, Wt. %	Organic Carbon, Wt. %
28.6 Gal./Ton	100.0	12.6
Fraction 1, 44 to 74μ	32.6	13.7
Fraction 2, less than 44μ	67.4	12.2
75 Gal./Ton	100.0	30.8
Fraction 1, 44 to 74μ	53.4	33.9
Fraction 2, less than 44μ	46.6	26.2

from adsorption-desorption isotherms and Kelvin's equation (7) which relates the radius of a capillary to the relative pressure at which condensation takes place. Kelvin's equation is expressed

$$\ln \frac{P}{P_o} = \frac{-2\sigma V \cos\theta}{rRT} \qquad (2)$$

where

P/P_o = relative pressure
r = capillary radius
σ = surface tension of adsorbate
V = molar volume of liquid adsorbate
θ = angle of contact
R = gas constant
T = absolute temperature

When capillary condensation occurs, the desorption isotherm usually lies well above the adsorption isotherm down to a relative pressure of about 0.4, which corresponds to the thickness of two monolayers of adsorbate. The nature of the pore structure determines the contour of the hysteresis loop in the desorption isotherm. Hysteresis loops with plateaus followed by steep portions indicate a narrow pore-size distribution, whereas those free of inflection points indicate a broad pore-size distribution. The desorption isotherms in Figures 1 *A* and 1 *B* show the absence of a distinct hysteresis loop; therefore, little, if any, capillary condensation and evaporation occurred. Deposition and removal of nitrogen apparently involved similar physical forces. This phenomenon indicates that the shale particles contained no appreciable amount of pore openings with radii ranging from 10 to 235 A. as determined by Kelvin's equation.

The pore volume accessible through micro- and macropores can ordinarily be calculated from the quantity of adsorbate adsorbed in the relative pressure range of 0.4 to 1.0, (micropore refers to pore openings with radii smaller than 100 A.). In Type II isotherms, however, which approach P_o asymptotically, the relative pressure at which capillary condensation is complete and interparticle condensation occurs is not readily discernible. In Figures 1 *A* and 1 *B* the pore volumes were calculated from two reference points. One was the intersection of the extrapolated near-linear portions of each isotherm which occurred at a relative pressure of 0.96 in both isotherms and the second reference point selected was 0.90. Reis (7) points out that there is reason to believe that

Table II. Surface Area of Oil-Shale Particles, 44 to 74μ

Oil Shale	Sample Wt., G.	Degassing Temp., ° F.	Degassing Time, Hr.	*Vm*, Cc./G.	Surface Area, Sq. M./G.	Surface Area, Sq. M./Cc.
28.6 Gal./ton	5.056	220	8	0.850	0.73	1.57
	5.271	220	24	0.838	0.70	1.50
	5.080	220	96	0.690	0.59	1.27
	4.885	220	96	0.646	0.58	1.24
75 Gal./ton	3.609	220	8	0.616	0.75	1.22
	3.609	220	60	0.594	0.72	1.17
	3.930	220	96	0.616	0.75	1.22

Table III. Pore Volume of Oil-Shale Particles, 44 to 74μ

		Pore Volume			
		$P/P_o = 0.96$		$P/P_o = 0.90$	
Oil Shale	Sample Wt., G.	Ml./G.	Porosity, %	Ml./G.	Porosity, %
28.6 Gal./ton	4.885	0.0013	0.28	0.0005	0.11
75 Gal./ton	3.930	0.0013	0.21	0.0005	0.10

in Type II isotherms, adsorption above a relative pressure of 0.90 may be principally interparticle condensation. According to Kelvin's equation, the respective pore radii at these relative pressures are 235 and 90 A., respectively. The pore volume and per cent porosity of the two shales are given in Table III.

The relative pressure selected to represent completion of capillary condensation significantly influenced the calculated pore volume (Table III). The measured pore volume, although small, may still be higher than the true pore volumes of the two shales because of interparticle condensation and induced fractures in the shale particles.

Inorganic Constituents. The surface area of the inorganic particles free of organic matter and those free of both organic matter and water-soluble material, calculated from their respective BET plots (Figure 2 *B* and 2 *C*), are presented in Table IV. The particles free of water-soluble material had the higher values even though the calcium sulfate was removed. The increase in surface area over the initial inorganic particles may be attributed to separation of the platelet structure of some of the clay minerals, to etching on the surface of minerals slightly soluble in water, or to a combination of these factors.

The desorption isotherms in Figures 1 *C* through 1 *E* exhibit characteristics of porous materials yielding Type II adsorption isotherms. The hysteresis loops begin at about 0.96 relative pressure and end near 0.4, indicating that the pore radii range from about 10 to 235 A. However, if condensation above a relative pressure of 0.90 were principally interparticle (7), the upper limit of the pore radii would be about 90 to 100 A. The smooth contour of the desorption isotherms indicates that the pore openings have random size distribution.

The pore volumes of the inorganic particles calculated from their respective isotherms, Figures 1 *C* through 1 *E*, are presented in Table V. Included are per cent porosities and amounts of organic matter from each shale that could exist within these pore volumes. The volume occupied by the organic matter in the 28.6 and 75 gallons per ton shales is 0.151 and 0.417 ml. per gram, respectively. The pore volumes given in Table V show that the inorganic particles do not contain a great amount of micropore

Table IV. Surface Area of Inorganic Particles

Degassing temp., F. = 600
Degassing time, hr. = 16

Source[a]	Sample Wt., G.	*Vm*, Cc./G.	Surface Area, Sq. M./G.
28.6[b]	6.261	0.969	4.24
28.6[c]	6.915	1.081	4.73
75[b]	5.711	0.713	3.12
75[c]	6.323	1.029	4.51

[a] Gal. per ton of shale. [b] Initial. [c] Free of water-soluble material.

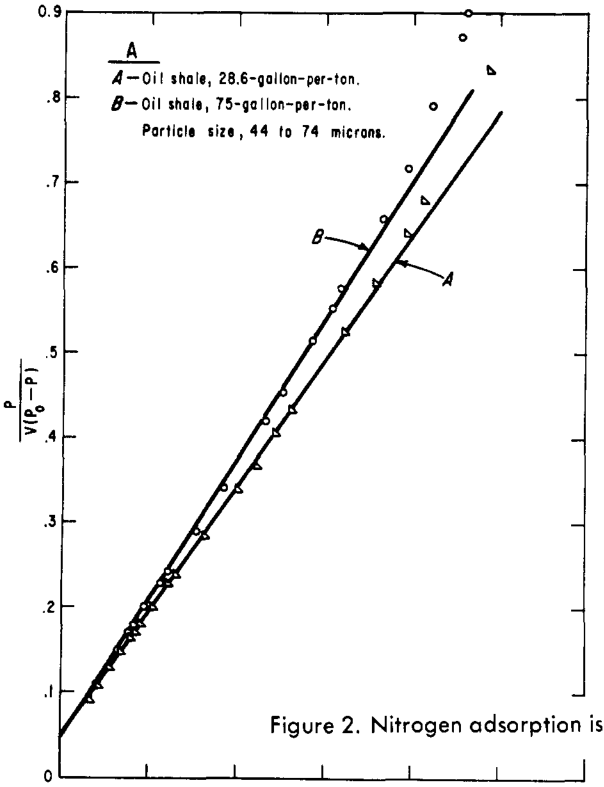

Figure 2. Nitrogen adsorption isotherms according to the BET equation

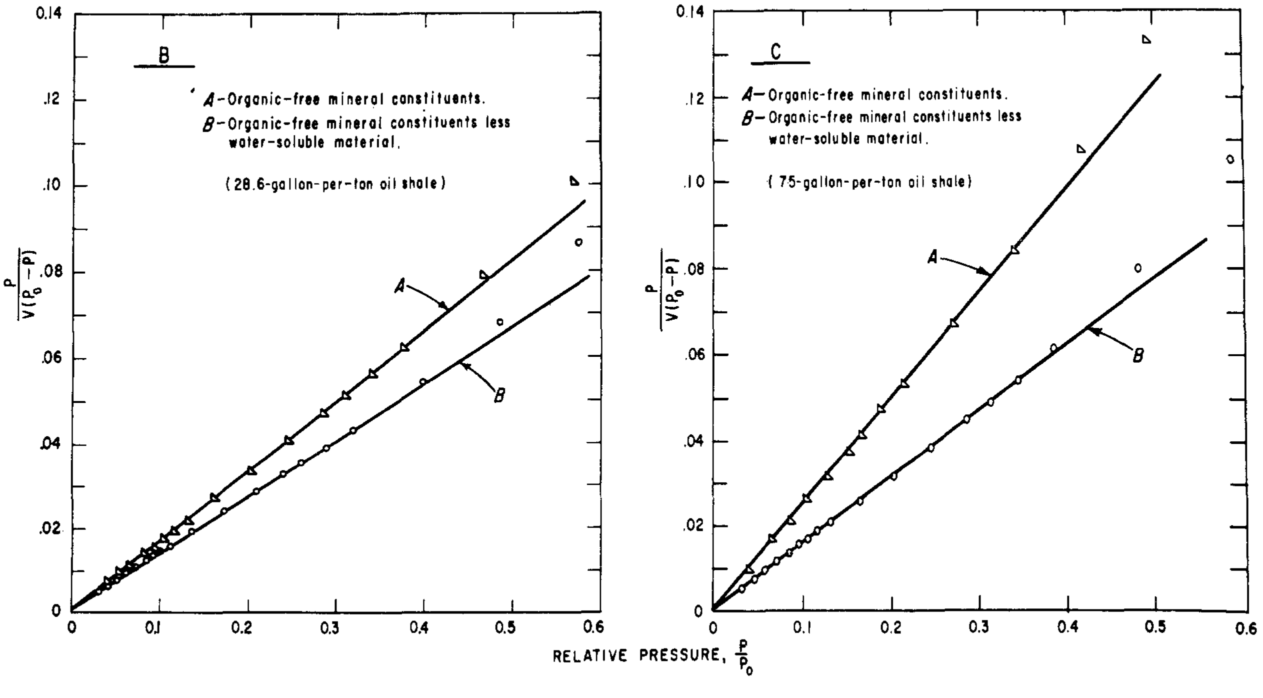

Table V. Pore Volume of Inorganic Particles

Source of Inorganic Particles[a]	Pore Volume				Intraparticle O.M.,[d] Vol. %	
	$P/P_0 = 0.96$		$P/P_0 = 0.90$			
	Ml./g.	Porosity, %	Ml./g.	Porosity, %	$P/P_0 = 0.96$	$P/P_0 = 0.90$
28.6[b]	0.0096	2.66	0.0050	1.39	6.36	3.31
75[b]	0.0086	2.36	0.0029	0.80	2.06	0.70
75[c]	0.0079	2.16	0.0048	1.31	...	...

[a] Gal. per ton of shale. [b] Initial inorganic particles. [c] Free of water-soluble material. [d] Organic matter.

Table VI. Estimated Amount of Organic Matter in Contact with the Mineral Constituents

Source of Mineral Constituents	Surface Area, Sq. M./G.	Diam. of Organic Molecule, A.	O.M.[a] Per Monolayer, Wt. %	Total O.M.,[a] No. of Monolayers
28.6 Gal./Ton Shale	4.24	20	3.11	32
	4.24	10	1.57	64
75 Gal./Ton Shale	3.12	20	0.57	175
	3.12	10	0.29	345

[a] O.M. = organic matter.

structure and that the distribution of the organic matter within the two shales is essentially inter- rather than intraparticle. Therefore, only a small part of the organic matter has to diffuse through the inorganic particles' micropore structure when it is removed from the shale.

Organic Matter in Contact with the Mineral Constituents. Using surface area data and the following assumptions, an estimate was made of the amount of organic matter in contact with the mineral constituents. The assumptions were: The organic molecules were spheres, 10 or 20 A. in diameter; the total surface of the mineral constituents was available for contact; and that the spherical molecules formed a rectangular pattern on the surface. Based on the density of the organic matter, the respective molecular weights of these molecules would be about 340 and 2700. Table VI presents the amount of organic matter represented by one monomolecular layer in contact with the surface, and it also presents the number of monolayers the total organic matter could form if evenly distributed over the surface of the mineral constituents. These estimates suggest that only a small part of the organic matter is bonded either physically or chemically to the mineral constituents.

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Polynitro Carbamates and *N*-Nitrocarbamates

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IN RECENT YEARS there has been a great deal of interest in high energy compounds for use in explosive and propellant compositions. Polynitro aliphatic compounds constitute a new class of high energy materials and the present work describes the synthesis of several classes of these substances. The preparation of polynitro carbamates and *N*-nitrocarbamates is described in this paper while the synthesis of polynitro aliphatic nitramines is presented in a following article.

Carbamates are conveniently prepared by the addition of an alcohol to an isocyanate. Utilization of nitro alcohols and nitro isocyanates leads to the formation of polynitro carbamates. The nitro alcohols, such as 2,2,2-trinitroethanol, were prepared by the condensation of the corresponding nitro alkanes and formaldehyde (2). The nitro isocyanates were synthesized by the Curtius degradation of the corresponding acid chlorides (*4*).

Nitro alcohols are more acidic and react less readily with isocyanates than ordinary alcohols. However, when the reaction is catalyzed with a trace of ferric acetylacetonate (*5*), addition occurs readily. Thus, on refluxing the reactants in chloroform for 6 to 8 hours, in most cases quantitative yields of the addition products were obtained. In those cases in which the carbamate was an oil, no attempt was made at purification through distillation because of the high oxygen content. The crude oils were nitrated directly, following the procedure of Curry and Mason (*1*), to give solid products which could be easily purified. Twenty-two new carbamates (Table I) and 25 new *N*-nitrocarbamates (Table II) were prepared. Many ot these

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