THE SEPARATION OF THE INSOLUBLE NON-TANNIN CONSTITUENTS FROM CHESTNUT EXTRACT

by

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I. INTRODUCTION

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In the preparation of tannin extract from chestnut wood chips there is present in the extract, along with the tannin, certain insoluble non-tannin constituents. If allowed to remain in the extract, these materials make the tannin solution unsuitable for use in the manufacture of leather.

To accomplish the separation of the non-tannin constituents from the tannin, the Mead Corporation of Lynchburg, Virginia, now employs a process of concentration and mechanical settling. For the past twenty years the company has been engaged in research to develop a better process. The investigations have been concentrated mainly on the idea of varied forms of mechanical separation. So far no solution to the problem has been found, thereby giving rise to the opinion that perhaps mechanical separation is the wrong approach to the problem.

In a preliminary study of this problem(6), research work has been done at V. P. I. using several new approaches, the most important of these being electrophoresis and adsorption. Of these two procedures, adsorption gave indications of having the greater potentialities. The following thesis will deal with additional research work using coals of varying grades as an adsorbing medium.

The American Viscose Company of Roanoke, Virginia has installed units for clarifying the spinning bath solutions. The units incorporate coal as an adsorbing medium. The process is extremely successful and therefore strengthens the belief that it may be applicable to the clarification of tannin extract solutions.

Adsorption methods are often applied industrially to remove impurities, especially if they are present in low concentrations. Small amounts of impurities often interfere with processes such as crystallization, filtration, and distillation, but by the application of adsorption the impurities may be separated and the fault corrected. Often times adsorbents are used to recover valuable constituents, which otherwise would be lost completely or require for more costly processing.

Separation by adsorption is made possible because of the fact that different materials differ in the degree to which they are adsorbed by a given adsorbent.

The object of the research work is to investigate the possibility of developing an economically feasible process, based on adsorption, using coal as the adsorbent, for the separation of the insoluble non-tannin constituents present in a fresh tannin extract.

II. LITERATURE REVIEW

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The Nature of Adsorption: Adsorption concerns itself with the concentration, as a result of surface forces existing on a solid, of gases, vapors, liquids or solutes (solids dissolved in a solvent), dispersed materials, or colloids(16). The nature of these surface forces is incompletely understood. The solids termed "adsorbents," may effect concentration, localization, fixation, or separation of gases from gases, vapors from gases, solutes from solution, and dispersed materials from solutions. The extent of the adsorption is large or small, depending on the nature and character of the adsorbent and adsorbate, that is, the material concentrated, localized, fixed, or separated. The adsorbent may be used only once, as in the case of carbon or chars, which remove odors or tastes from water to make it potable, then discarded; or it may be used once and then removed and treated to eliminate the adsorbate and be rendered fit for re-use, a process termed reactivation; or it may be worked in such a manner as to be used, reactivated in place, and re-used in cyclic procedures.

The Division of Adsorbents: Adsorbents are generally classified by their application as follows:

1. Separation of gases from gases, as deodorization of air, elimination of toxic gases.

2. Separation of vaporers from gases, as recovery of solvents, drying gases, dehumidification.
3. Separation of solutes from solutions, as decolorizing and clarifying of liquids.
4. Separation of ions from solutions, as concentration of metals on adsorbents.
5. Separation of dissolved gases or suspended solids from liquids, as in water treatment.
6. Concentration of dissolved materials, often toxic in nature, to eliminate them from liquids, as in the case of medicinal carbons, which make up poisonous chemical compounds.
7. Fractionation by selective-adsorption of gases from gases, vapors from gases, vapors from vapors, liquids from liquids, dissolved materials from other solutes, and then concentration of these.

Adsorption should be sharply differentiated from absorption in that adsorption is commonly without chemical reaction between the adsorbent and the adsorbate, while absorption refers to temporary, or more or less permanent, chemical reaction or phase change as function of the operation. A gas or vapor brought into contact with a solid has a tendency to collect on the surface of the solid. This phenomenon is known as "adsorption." The term "absorption," on the other hand, is used to describe the phenomenon which occurs when a gas or vapor penetrates the solid structure, producing a solid solution of the gas. Adsorption may occur alone or in combination with absorption in which case the general term "sorption" is usually applied.

The adsorbed atoms and molecules may be bound to the surface of the solid in different ways: there may be a weak interaction between solid and gas, similar to condensation, or a strong interaction, similar to chemical reaction. The former is called physical or van der Waals adsorption, since the forces involved are the same as the van der Waals forces that produce condensation in liquids; the latter, termed "chemisorption" is also known as "activated adsorption," which implies that this type of adsorption requires activated energies much the same as do chemical reactions. In physical adsorption the adsorbed gases may be easily pumped off unchanged, particularly if the temperature be raised. In chemisorption the tenacity with which the adsorbed gases are held varies. Generally, a much higher temperature necessary to remove the gases and the process is irreversible, the binding force being so strong that the gas originally adsorbed comes off in a different state (e.g., as atoms instead of molecules, or as compounds with the adsorbent).

<u>Industrial Adsorbents</u>: A few of the more important industrial adsorbents with their uses are outlined on the following page as given by Mantell(16).

Adsorbent	Important Industrial Uses
1. Fuller's earth	Refining of petroleum fractions, vegetable and animal oils, fats and waxes.
2. Bauxite	Percolation treatment of petroleum fractions; dehydration of gases.
3. Acid-treated Clays	Contact filtration of petroleum fractions.
4. Bone char or bone black	Sugar refining; ash removal from solutions.
5. Decolorizing carbons and water carbons	Sugar refining; refining of vegetable and animal oils, fats and waxes; miscellaneous decolorizing of inorganic and organic substances; water purification; purification of dry cleaning fluids; purification of food products.
6. Gas adsorbent carbon	Solvent recovery; recovery of gasoline from natural gas; elimination of industrial odors; purification of carbon dioxide and industrial gases; gas masks.
7. Alumina	Dehydration of air gases and liquids.
8. Silica Gel	Dehydration and purification of air and industrial gases; air conditioning; refining of petroleum distilates; gas masks.
9. Base exchange silicates	Water treatment.
10. Magnesia	Treatment of gasoline and regeneration of dry cleaning solvents.
11. Medicinal carbons	Elimination of bacteria and toxic poisons; an addition to animal foods.
12. Metal-adsorbent chars	Recovery of precious metals.

Adsorption from Liquids: Adsorption from liquids is usually an adjunct to other unit operations. Adsorption processes might be considered as filling a place and need in relation to distinctly chemical processes, which might have definite limitations with respect to small concentrations of substances to be removed or eliminated. Often chemical action on substances in liquids is not sufficiently quantitative to produce the desired results. Further refinement in the chemical process would entail expense disproportionate to the results obtained. Impurities of organic nature are often more economically removed by the use of a solid adsorbent in processes supplementary to the economic utilization of the chemical method.

When used for the precipitation of colloids from solutions, chemical reagents often fail to produce complete elimination. Their action cannot be considered as truly chemical in nature; hence, it does not proceed according to chemical laws. These reactions depend on closely controlled conditions of temperature, pH, etc., uncontrollable slight variations in which alter the equilibrium point in many cases in the direction opposite to that desired.

Filtration, settling and centrifuging are effective in removing undissolved solids from liquids only when the particles are of sufficient size. The diameter of the pores in a filter medium determines the completeness of separation. Colloids and many untrafine suspensions cannot be filtered, settled, or centrifuged out. Moreover, the rate of flow of a given liquid is a direct measure of the permeability or porosity of the filter medium; hence, separation of particles in an extremely fine state of division can be accomplished only at the expense of capacity and time.

The use of an adsorbent to remove solids by adsorption of particles on the surface of the particles of adsorbent allows easy filtration in many instances and increases the efficiency of filtration. In combination with filter aids, solid adsorbents make easier the filtration of liquids containing amorphous or nonrigid particles in a fine state of division.

Industrial Operation: Adsorbents must be tried out on the job; predictions as to what they will do are only of a general nature. Because adsorbents are so selective, processes function around the adsorbent, whose physical form, nature, and properties determine the equipment. Equipment design is simple; but the design and preparation of adsorbents of predetermined physical, mechanical, and chemical characteristics constitute an important problem only partly solved. The adsorbent is really part of the equipment, but at the same time is a raw material consumed slowly during the processing of liquids or gases.

Many industries employing adsorbents still fail to realize the unit-operational nature of the process. The equipment is fundamentally the same whether it be used in petroleum, sugar, water, vegetable oils, organic acids or salt in liquid processing.

Desorption and Revivification: The desorption method(12) includes:

1. The addition of some material more strongly adsorbed with resultant driving out of the adsorbed component.

2. Change of pH, where the adsorbability varies with the pH.
3. Steaming where the adsorbed body has a relatively high vapor pressure.
4. Extraction with a solvent in which the component is very soluble.
5. Chemical reaction.

The use of chemical reaction can best be illustrated by an operation on the West Coast(12) which for a number of years has produced iodine equal to one-third the total domestic consumption of the United States. The sump water from the oil wells contains iodine to the extent of about 70 to 100 parts per million; oxidizing agents convert this to free iodine which was adsorbed by activated carbon. The carbon with the adsorbed layer of iodine was separated from the liquid and treated to convert the free iodine to sodium iodide, which was extracted with limited quantity of water.

The Adsorption Characteristics of Coal: Petegov and Nyankovskii(21) sought to determine the age of coal by its adsorptive power for oxalic acid, ferric chloride, and methylene blue under the assumption that the non-oriented, unsaturated components of the coal, capable of adsorbing are present in largest amounts in soft coal, least in anthracite. While the measurements with oxalic acid are independent of whether the coal is fresh or not, the determinations with the ferric chloride and methylene blue must be carried out on freshly pulverized coal, since the adsorptive capacity for these substances greatly decreases when the coal is stored in the pulverized condition.

In the preparation of coke as an adsorbent(3), the addition of rich (highly bituminous) coals to the charge lowers the reactivity and adsorptive power of coke, but with lean (low volatine) coals the reverse happens.

Adsorption and Ionic Exchange: Phenomena of electrolyte adsorption can be explained on the basis of three main mechanisms:(26)

1. The adsorbent and electrolyte contain a common ion. The adsorption is in general a primary boundary surface process identical with the formation of an electrolyte double layer. The common ion is taken into the space lattice and the second ion is held electrostatically ("counter-ion" layer).
2. The "counter-ions" of a double layer are liberated by an equivalent number of ions of equal charge. The exchange depends on the relative ion concentrations and is independent of dilution.
3. Both ions are adsorbed, neither ion entering the space lattice of the adsorbent. Adsorption indicators operate through the exchange of the dye ion and the "counter-ion;" accurate titrations are possible only in the absence of adsorption of the dye ion.

Muller(19) relates that the existance of interfacial potentials, according to the theory of the diffuse double layer, suggests that the surfaces are the seat of electric charges. These charges may arise from ionization or from adsorption. The paucity of reliable data does not permit definite conclusions. Adsorption appears to play a definite role but the electric charge within the rigidity boundary may not coincide with the surface of adsorption range.

The taking up of salts by living plasma of plants is an adsorption phenomena according to Pantanell(20). Not the whole molecule is adsorbed but the individual ions. The adsorption of the ions is independent of the adsorption of water and the rate of adsorption varies with the nature of the ions. Those which permeate slowly by long contact aquire the property of adsorbability by the plasma. The rate of adsorption is claimed not to be a linear function.

Adsorbed particles may exist on a surface either as positive adions (adsorbed ions), negative ions, or adatoms(1). Whether a given substance will be adsorbed as an atom or a positive or negative ion, will depend on the field of force which exists near the surface and near the particle at their distance of nearest approach. The adsorbed ions produce electric fields which extend to ten or more atom diameters, which, close to the surface, may attain enormous values, and which appreciable alter the electron work function and the evaporation energy for atoms and ions. The ratio of ions to atoms which evaporate from one and the same surface is determined by the electron work function of the surface and the ionisation potential of the adsorbed particles. Within a certain range of temperature, the adsorbed particles migrate over the surface like a two dimensional gas. Adatoms and adions have chemical properties vastly defferent from those of ordinary atoms and ions.

The salts of basic and acid dyes have been employed in the study of adsorption by various substances(17). In the case of charcoal, the cations and anions are adsorbed in equal proportions. Slight deviations from this principle can be explained by the impurity of the charcoal. When insoluble salts are used as adsorbents there is an exchange of anions and cations between the adsorbents and the substance adsorbed. Insoluble basic or acid oxides have shown no perceptible adsorbing capacity. In no case was an "hydrolytic" adsorption of the salts observed, that is where the salts were split into acid and basic ions and the adsorption of only one ion took place.

Grettie and Williams(10) found that the extent of adsorption on silica of various organic compounds is roughly proportional to their basic strength and roughly proportional to their acid strength in the case of adsorption on alumina.

Adsorption of sols by freshly prepared precipitates of the same material was studied by Chaterji and Dhar(5) in 1926. For instance, a sol of lead chromate is adsorbed by a fresh precipitate of lead chromate and likewise, silver ions are adsorbed by a precipitate of silver chromate.

Adsorption processes(23,11) are often a combination of two stages. In the first, or primary stage, the charge on the adsorbent increases by reason of adsorption of ions bearing charges of the same sign as that of the adsorbent. In the secondary stage, ions of opposite charge are adsorbed and this corresponds to molecular adsorption. Secondary adsorption results from a kind of building up of molecules on the diminished surface and takes place slowly. If the adsorbate is easily soluble, secondary adsorption is negligible.

According to Shelov and Nekrassov(24), the adhesive force in adsorption are of the same magnitude as the chemical forces in the formation of complex chemical compounds.

<u>Coal as an Adsorbent</u>: The adsorption activity(7) of peat, brown and anthracite coals and coke of 0.25 to 0.5 mm. was determined with solutions of iodine, potassium iodide and oxalic acid. The adsorption fell in the following order of decreasing activity: peat, brown coal, and anthracite.

Kleinert(14) found that treatment of coal with a 15 percent HCl solution increased its affinity for phenol by 40 percent. Lignite and bitumen-rich coals act likewise.

Bituminous coals from Alabama, Indiana, Kentucky, Virginia, and West Virginia have been used in the preparation of carbonaceous hydrogen exchanges by treatment with sulfur trioxide at 150° C.(2) The working capacities are from 9,500 to 12,800 grains of calcium and magnesium per cubic foot of exchanger bed. A study of the physical properties and chemical constituents of the coals reveal no definite characteristics or property upon which exchange capacity is dependant. Narrow particle size range (- 28 + 35 mesh) material is used in determining exchange capacities. Krenlin(15) found that the adsorption capacity is dependent on grain size as well as on the porosity of a coal.

When coal is subjected to the action of fuming sulfuric acid, the reaction product exhibits ionic exchange properties to a remarkable degree(8). The product is most suitable for water softening operations.

Swieloslawski(25) published an article in the "Polish Institute of Arts and Sciences in America" in which he correlated the adsorption of methyl blue by different grades of coal, as follows:

Origin of Coal	Class or Group	Volatile %	Milligrams of M.B. Adsorbed per gram coal
South Wales (Britain)	Anthracite	5.27	7.0
Charleroi (Belgium)	Low Volatile	13.43	5.3
Ruhr (Germany)	Medium Volatile	26.97	5.0
Durham (Britain)	Medium Volatile	26.97	4.9
Pas de Calais (France)	High Volatile A	35.66	5.2
Upper Selesia (Poland)	High Volatile A	35.48	5.4
Northumberland (Britain)	High Volatile A	37.64	6.9
Ruhr (Germany)	High Volatile B	39.23	7.1
Upper Selesia (Poland)	High Volatile B	-----	11.7
Dabrowa (C) (Poland)	High Volatile C	40.2	17.5
Dabrowa (F) (Poland)	High Volatile C	40.98	20.9
Cracow District (Poland)	Sub-Bituminous C	50.79	98.0

<u>Other Adsorbents:</u> The adsorption by certain Asiatic clays is high especially when boiled with two-normal hydrochloric acid for one hour and drying at 105° C. The activated clays are applicable to the purification of petroleum products.(27)

According to Javel(4), activated sludge has a high adsorption coefficient for many organic dyes.

Metallic surfaces adsorb many soils as noted by the fact that surfaces to be electroplated become extremely inactive after being in contact with certain soils. The effect was found to be due to a fine film of adsorbed material.(13)

III. EXPERIMENTAL

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Purpose of the Investigation

The purpose of the study is to investigate the possible separation of the insoluble non-tannin constituents from a tannin extract by adsorption of the material using coal as the adsorbent. Success of such a process will lead to the development of a more economical separation process than that now employed by the Mead Corporation of Lynchburg, Virginia.

Plan of Investigation

The plan of investigation may be outlined as follows:

1. The acquisition of a number of samples of coal to be used as the adsorbent.
2. Preparation of the coal samples by grinding and size separation with the following mesh sizes:
   - a. Minus 4 plus 8
   - b. Minus 8 plus 16
   - c. Minus 16 plus 30
   - d. Minus 30 plus 40
3. The construction of a suitable piece of test equipment to permit controlled flow of tannin solution through the chambers containing coal as an adsorbent.

4. Approximate analysis of the various coal samples to determine the grade and also to aid in an attempted correlation between coal analysis and adsorption power.
5. Analysis of the treated samples of tannin solution for total solids, soluble solids, and insoluble solids to determine the degree of separation of the insoluble constituents.

Materials

The following materials were required for the investigation:

Tannin solution: Forty-five gallons "leach house" liquor obtained from the Mead Corporation, Lynchburg, Virginia, used as test solution.

Adsorbent coals: One-hundred pound samples of Buffalo Creek, Freeport, Thacker, and Winifred seams. Obtained from the Pond Creek Colliery, Williamson, West Virginia.

One-hundred pound samples of Alma, Pond Creek, and Chilton seams. Obtained from Eastern Coal Sales Company, Stone, Kentucky.

One-hundred pound sample of Brush Mountain seam. Obtained from M. C. Slusher & Company, Blacksburg, Virginia.

Apparatus

The apparatus used in the preparation of the coal samples is located in the Unit Operations Laboratory of the V. P. I. Department of Chemical Engineering, and may be listed as follows:

Crusher, Jaw, Blake type, 6" Jaws, manufactured by Universal Crusher Company, Cedar Rapids, Iowa. Used for primary crushing.

Mill, Attrition, size 13, manufactured by Robinson Manufacturing Co., Muncy, Pa. Used for secondary size reduction.

Riddle, Combs Gyratory, manufactured by Great Western Manufacturing Company, Leavenworth, Kansas. Used to vibrate screens.

Screens, U. S. Std., 8-inch, manufactured by Precision Scientific Co., Chicago, Ill., nest of five, meshes 4, 8, 16, 30, and 40. Used to size the coal samples.

Test Equipment: The test equipment used in the adsorption experiments was constructed according to Drawing No. 1. A 1/2" bar iron stand was used to support the individual pieces of equipment. By the use of laboratory clamps, the constant head weir (B) (see drawing No. 2 for details), a 1/2 gallon glass recycle bottle (C), a 1/8" bronze globe valve (D), a small rotameter (E) capable of measuring liquid flows as low as 10 ml. per minute, and two Liebig condenser jackets (F,G) used as adsorbent chambers, were fastened to the bar iron stand. A 1/2-gallon glass feed bottle (A) was located on a shelf above the bar iron stand to permit the tannin solution to flow by gravity into the constant head weir (B). Samples of treated tannin solution were collected in 250 ml. sample bottles (H). The air for operation of the air lift recycle (See Drawing No. 3 for details) first passed through a moisture trap (I) before flowing to the air lift located in the recycle bottle (C).

A Nash-Hytor Compressor, size MD-2L, manufactured by the Nash Engineering Company of South Norwalk, Conn., located in the Unit Operations Laboratory was used to operate the air lift.

Equipment for Coal Analysis: The equipment used in the coal analyses is located in the coal laboratory of the V. P. I. Mining Engineering Department and may be listed as follows:

Oven, Allied No. A 64 - 630. Obtained from Phipps &Bird, Richmond, Virginia. Used in moisture determinations.

Furnace, Hoskins Electric. Manufactured by Hoskins Manufacturing Co., of Detroit, Michigan. Obtained from Burrell Technical Supply Co., Pittsburgh, Pa. Used for ash determination.

Furnace, Hoskins electric tube, Hoskins Manufacturing Company, Detroit, Michigan. Obtained from Fisher Scientific Company, Pittsburgh, Pa. Used for volatile determinations.

Control, Wheelco electronic, Wheelco Instrument Company, Chicago, Ill. Used to control furnace temperatures.

Calorimeter, Adiabatic oxygen bomb, manufactured by Parr Instrument Co., Moline, Ill. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used in determination of heating values.

Balance, analytical, manufactured by Wm. Ainsworth & Sons, Inc., Denver, Colo. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used for weight determinations.

Crucibles, platinum, four required. Used for firing samples.

The analysis of the tannin solutions required the following laboratory equipment which was obtained from the V. P. I. Chemistry and Chemical Engineering stock rooms:

Beakers, glass, 250 ml., five required.

Funnels, glass, 4" size, five required.

Paper, filter, Munktell Co. 1F, package of 100 required.

Stands, iron ring, with necessary clamps to support the five funnels in a line.

Kaolin, one pound required. Used as a filter aid.

Dishes, porcelain evaporating, 50 ml. capacity, eighteen required for drying samples.

Oven, electric drying, obtained from Phipps & Bird Co., Richmond, Va. Used for drying samples of tannin solution.

Pipette, glass, 50 ml. capacity. Used for measurement of samples.

Balance, analytical, manufactured by Seederer Kohlbusch Inc., Jersey City, N. J. Obtained from Phipps & Bird Inc., Richmond Va.

Procedure

Preparation of Coal Samples: Each 100-pound sample of coal was first reduced in size from 4" lumps to 1/8" particles by means of the jaw crusher. The fines produced were sufficient to obtain 15-pound samples of both - 4 + 8 and - 8 + 16 mesh of each coal.

The product from the jaw crusher was then fed to the attrition mill which produced 15-pound samples of both - 16 + 30 and - 30 + 40 mesh of each coal.

The sizing of the samples was accomplished by means of a set of 4, 8, 16, 30, and 40 mesh U. S. Std. screens and gyratory riddle.

Coal Analyses: The coal samples were analyzed according to the procedure adapted by the A.S.T.M.(11), the work being carried out in the Coal Laboratory of the V. P. I. Mining Engineering Department. The constituents and properties determined were moisture, ash, fixed carbon, volatile matter, heating value, and sulfur. Iron was determined qualitatively by color indication of the ash.

An analysis was made of the minus 8 plus 16 mesh samples of each coal. An analysis was also made of all four mesh sizes (- 4 + 8, - 8 + 16, - 16 + 30, - 30 + 40) of the Buffalo Creek coal to determine whether or not the analysis varied appreciably with the particle size of any one sample.

Adsorption Experiments: The assembly of the test equipment and the adsorption experiments using coal as the adsorbent and tannin solution ("leach house" liquor) as the adsorbate were carried out as follows:

1. The adsorption test equipment was assembled as shown in Drawing No. 1.
2. The two adsorbent chambers (F, G) were filled with a sample of coal using a 1/2" layer of glass wool to support and block the coal particles from being carried out of the chambers by the flow of tannin solution.

3. The tannin feed and recycle bottles (A and C) were filled about three-fourths full with "leach house" tannin extract. A 250 ml. sample of the feed solution was taken for analysis at this time to be used in the comparison with the treated samples.

4. The pinch cock (J) on the feed line to the constant head weir was opened allowing the weir to fill and overflow into the recycle bottle.

5. The air valve of the air lift (Dwg. No. 3) was opened to begin the recycle process.

6. The control valve (D) was opened to permit the tannin solution to flow through the rotameter (E) and into the adsorption chambers (F,G).

7. The rotameter reading was adjusted by means of the control valve, to a predetermined level which indicated a flow of 15 ± 2 ml. per minute of tannin solution or the equivalent of 12 ± 2 ml. per square inch of empty chamber cross section.

8. In the first trial run, four consecutive 250 ml. samples were collected from the outlet of the adsorption chambers.

9. Due to results obtained after analysis of the samples from the trial run, the run was repeated using the following revision in method of sampling.

The first 250 ml. to overflow was collected as sample Number (1). Then 500 ml. were allowed to collect in a beaker before 250 ml. of overflow was collected for sample Number (2). This process was repeated until four samples had been taken. By allowing 500 cc. to overflow between samples thereby increasing the span between samples it was possible, in the results, to determine the inflection point in the adsorption power of the coals.

11. Runs on all samples of minus 8 plus 16 mesh coals were carried out.

12. After getting results on these samples, it was decided to run all mesh sizes of the Brush Mountain coal, since it was the only sample which varied widely in analysis from the other samples as shown on page 28 , and also all mesh sizes of any one of the other coals, the Freeport sample being chosen.

13. All the runs after the trial run were carried out using the revision indicated in step Number (9).

<u>Treated Sample Analyses:</u> The analysis procedure was that adapted by the American Leather Chemists Association(21). Constituents analyzed were for total solids, soluble solids, and insoluble solids.

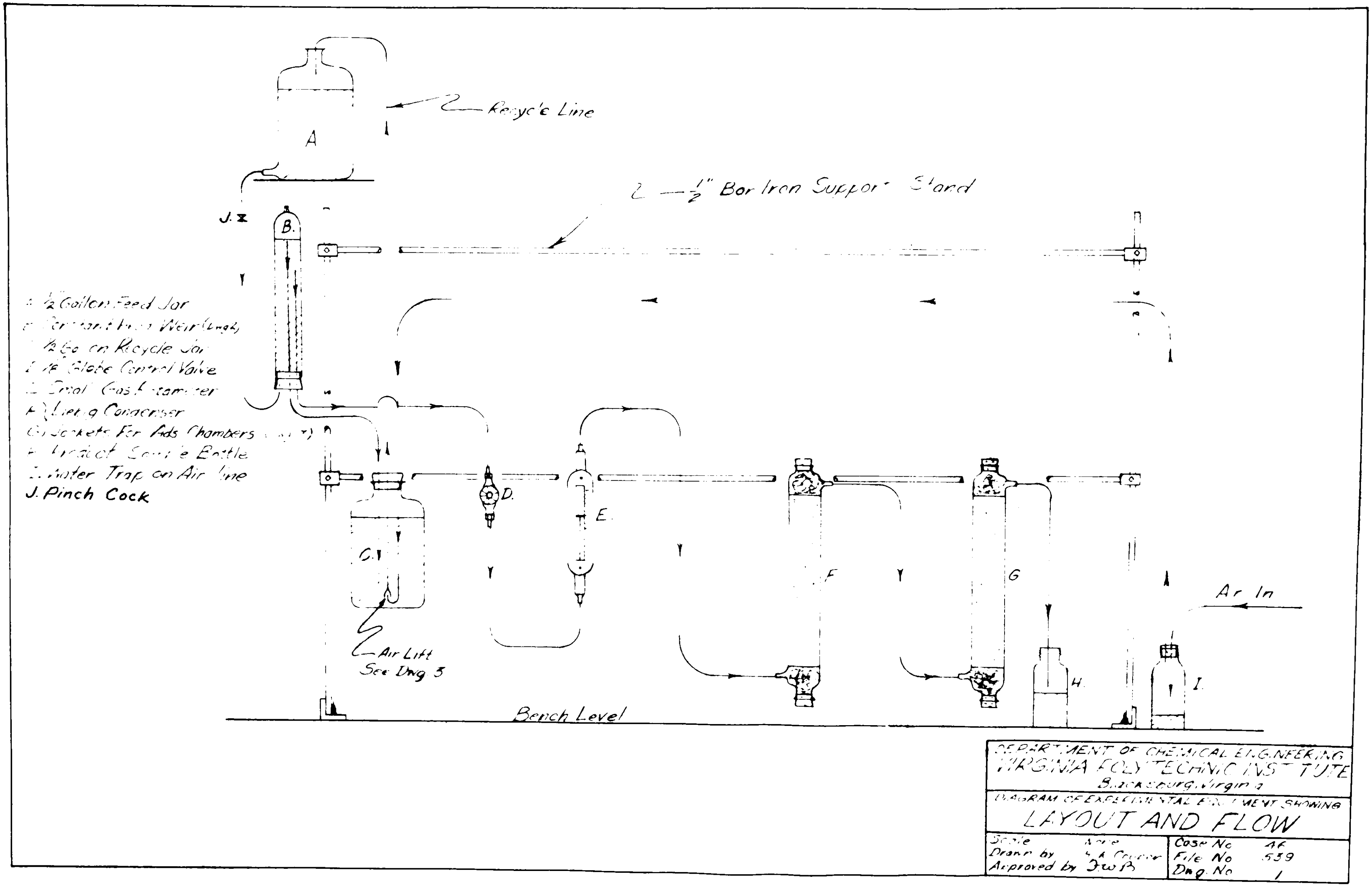
Results

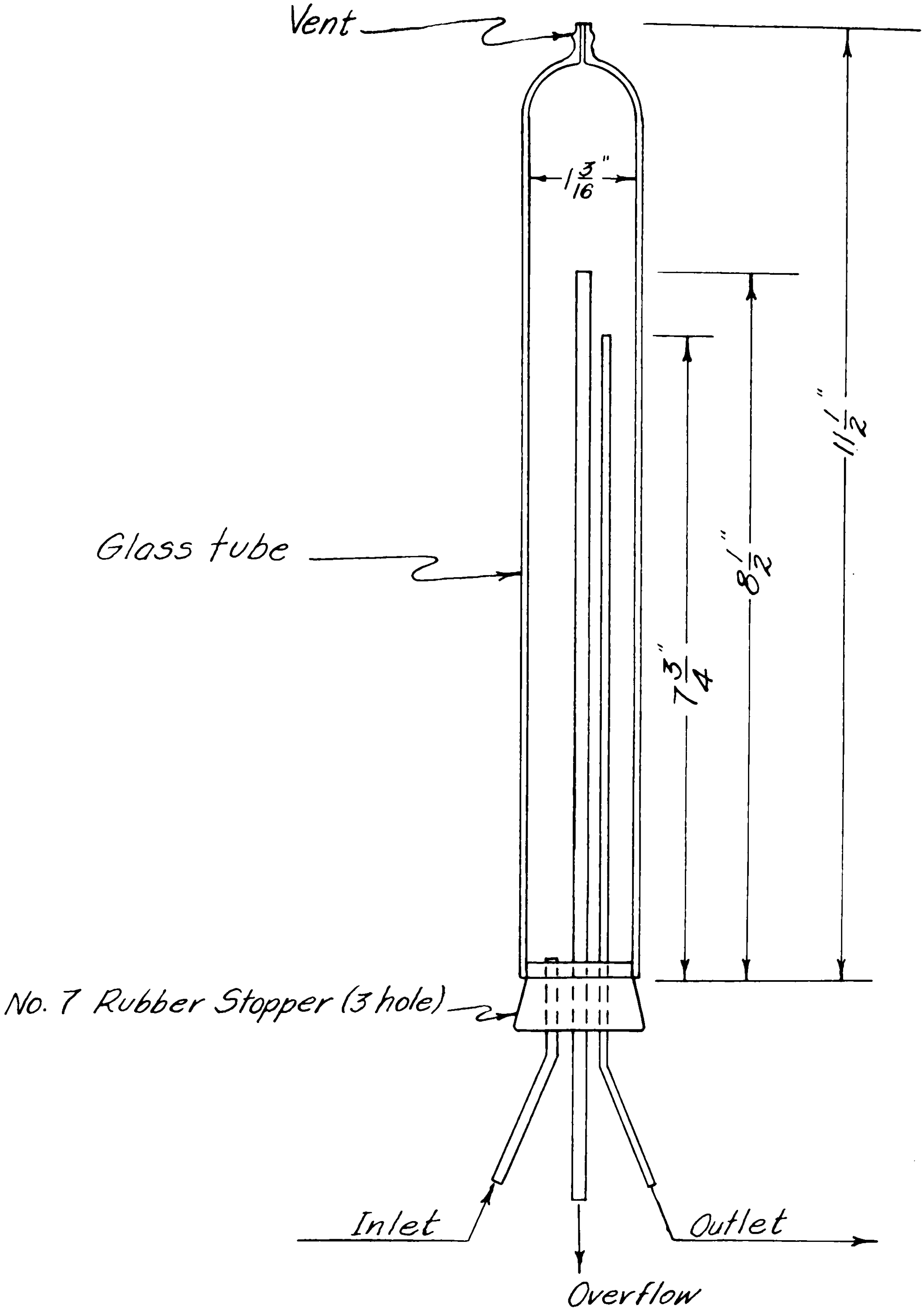
The results in the form of tables and graphs, will be found on the following pages and arranged as outlined below:

1. Table of results of the coal analyses.
2. Tables of results on the analysis of the untreated and treated

tannin solutions on coals which indicated a positive tendency toward the separation of the insoluble constituents followed by graphs prepared using the tabulated data.

3. Tables of results on the analysis of the untreated and treated tannin solutions on coals which indicated a negative tendency toward the separation of the insoluble constituents followed by graphs prepared using the tabulated data.


Recycle Line
A
J.X
B.
1/2" Bar Iron Support Stand
A ½ Gallon Feed Jar
B Constant Head Weir (Dwg 2)
C ½ Gallon Recycle Jar
D ½" Globe Control Valve
E Small Gas Flowmeter
F } Liebig Condenser
G Jackets For Ads Chambers (Dwg 7)
H Product Sample Bottle
I Water Trap on Air Line
J. Pinch Cock
C.
D.
E.
F
G
H.
I.
Air Lift
See Dwg 3
Air In
Bench Level
DEPARTMENT OF CHEMICAL ENGINEERING
VIRGINIA POLYTECHNIC INSTITUTE
Blacksburg, Virginia
DIAGRAM OF EXPERIMENTAL EQUIPMENT SHOWING
LAYOUT AND FLOW
Scale None
Drawn by
Approved by J.W.B.
Case No 46
File No 539
Dwg. No 1



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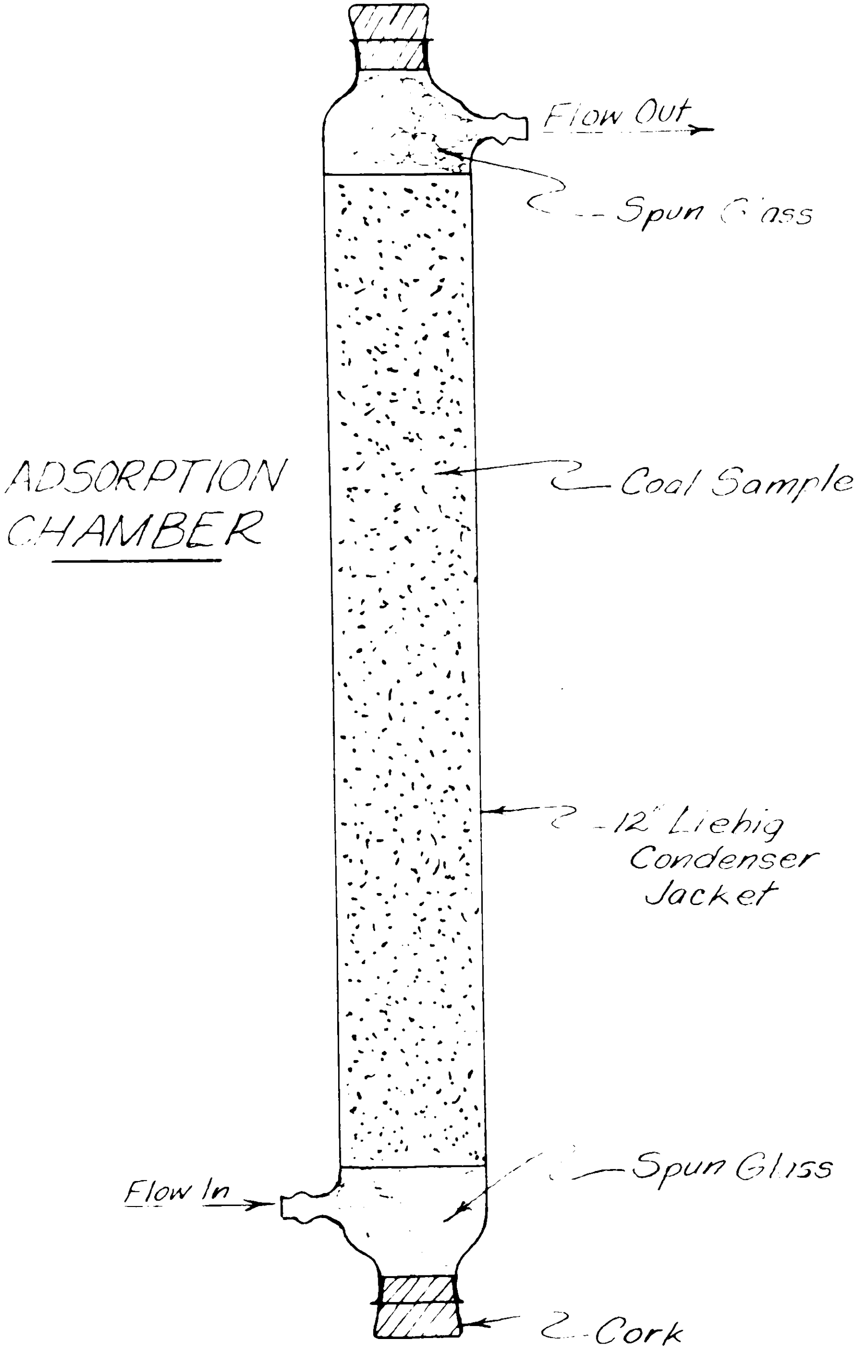
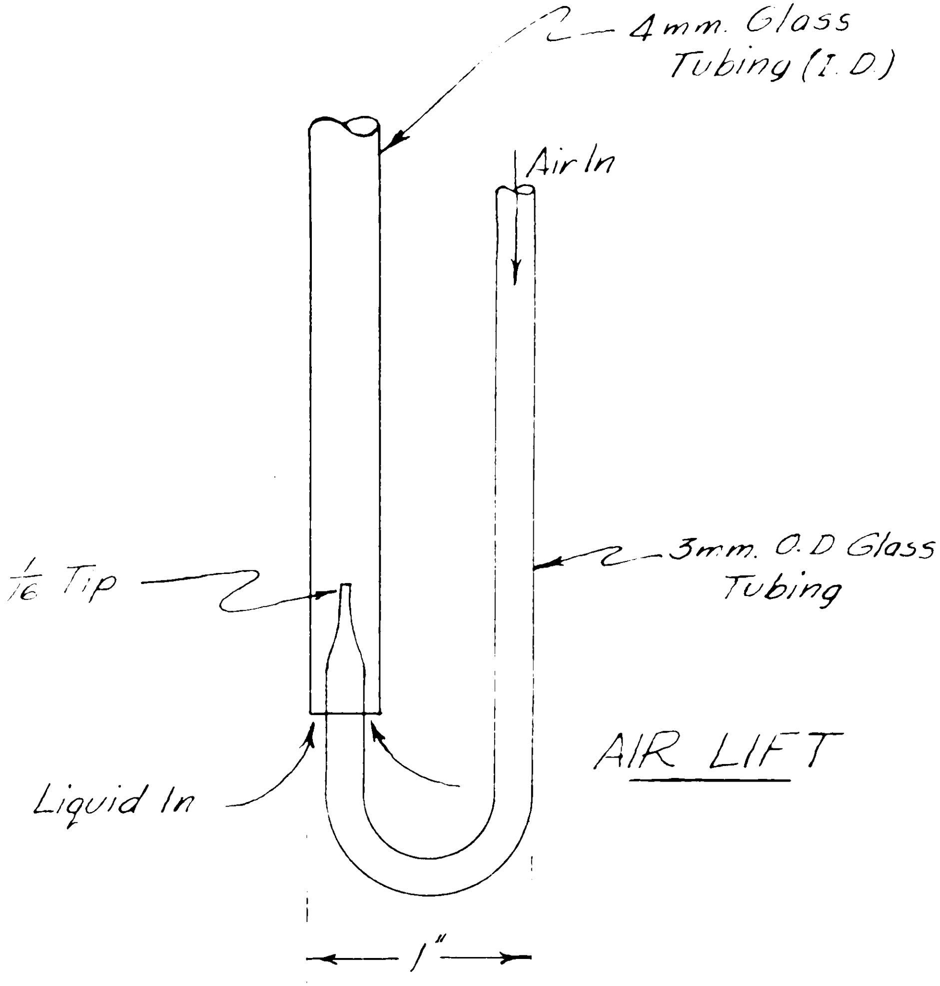
Blacksburg Virginia

DETAIL OF
CONSTANT HEAD WEIR

Scale	½" = 1"	Case No.	46
Drawn by	H.R. Couper	File No.	539
Approved by	JWB.	Dwg No.	2





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Blacksburg, Virginia

DETAILS OF
ADSORPTION CHAMBER & AIR LIFT

Scale	None	Case No.	46
Drawn by	H. R. Couper	File No.	539
Approved by	LWB.	Dwg. No.	3

TABLE I

Proximate Coal Analyses of Each Sample (- 8 + 16 Mesh)

Coal Sample	% Moisture	% Ash	% Volatile	% Fixed Carbon	% Sulfur	Btu. Heating Value	Iron indications from ash color
Buffalo Creek - 8 + 16	1.27	3.32	39.19	56.22	0.583	12,374	Slightly Red
Brush Mt. - 8 + 16	0.47	12.98	12.49	74.06	0.449	13.983	No Red
Freeport - 8 + 16	1.47	2.05	40.04	56.44	0.618	13,586	Very Slightly Red
Pond Creek - 8 + 16	0.98	4.38	36.07	58.57	3.20	13,662	Red
Thacker - 8 + 16	0.97	3.68	44.58	50.77	2.02	12,444	Red
Chilton - 8 + 16	1.02	4.32	42.45	52.21	0.852	13,603	Slightly Red
Winifred - 8 + 16	1.34	2.37	40.9	56.29	0.479	14,711	No Red
Alma - 8 + 16	0.43	3.69	38.23	57.65	0.530	17,466	No Red

TABLE II

Proximate Analyses of Four Mesh Sizes Of Buffalo Creek Coal

Mesh Size	% Moisture	% Ash	% Volatile	% Fixed Carbon	% Sulfur	Btu. Heating Value	Iron indications from ash color
- 4 + 8	1.22	3.78	39.60	55.40	0.575	12,700	Slightly Red
- 8 + 16	1.27	3.32	39.19	56.22	0.583	12,674	Slightly Red
- 16 + 30	1.31	3.34	38.69	56.66	0.553	12,558	Slightly Red
- 30 + 40	1.42	3.54	38.83	56.21	0.560	12,650	Slightly Red

TABLE III

Tannin Analyses of Samples

Showing Positive Tendency Toward Separation

Coal Sample and Size	% Con-stituent	Untreated Sample	Treated Samples				Appearance of Samples
			1	2	3	4	
Brush Mt. - 8 + 16	T.S.	3.0842	3.0272	3.0014	3.0612	3.0768	Samples 1 and 2 Dark 3 and 4 Light
	S.S.	2.9070	2.6684	2.7310	2.8164	2.8832	
	I.S.	0.1772	0.3588	0.2704	0.2448	0.1936	
Brush Mt. - 8 + 16	T.S.	3.0018	3.2216	3.0450	3.1068	3.2788	Samples 1 and 2 Dark 3 and 4 Light
	S.S.	2.8238	2.9220	2.8604	2.9364	3.1174	
	I.S.	0.1780	0.2996	0.1846	0.1704	0.1614	
Buffalo Creek - 8 + 16	T.S.	3.4326	2.9970	3.0856	3.1454	3.2812	No Color Change
	S.S.	3.1536	2.7084	2.8182	2.8886	3.0056	
	I.S.	0.2790	0.2886	0.2674	0.2568	0.2756	
Winifred - 8 + 16	T.S.	2.9970	2.9962	3.0364	3.1492	3.2156	No Color Change
	S.S.	2.7554	2.7234	2.7804	2.8864	2.9188	
	I.S.	0.2416	0.2728	0.2560	0.2328	0.2968	
Freeport - 8 + 16	T.S.	3.0628	3.0008	3.0896	3.1886	3.2026	No Color Change
	S.S.	2.9512	2.8736	2.9592	3.0838	3.1016	
	I.S.	0.1116	0.1272	0.1304	0.1048	0.1010	
Freeport - 30 + 40	T.S.	3.1972	3.2552	3.2300	3.2764	3.2898	No Color Change
	S.S.	2.9034	2.9298	2.9642	2.9964	3.0020	
	I.S.	0.2938	0.3254	0.2558	0.2800	0.2878	

T. S. - Total Solids
S. S. - Soluble Solids
I. S. - Insoluble Solids

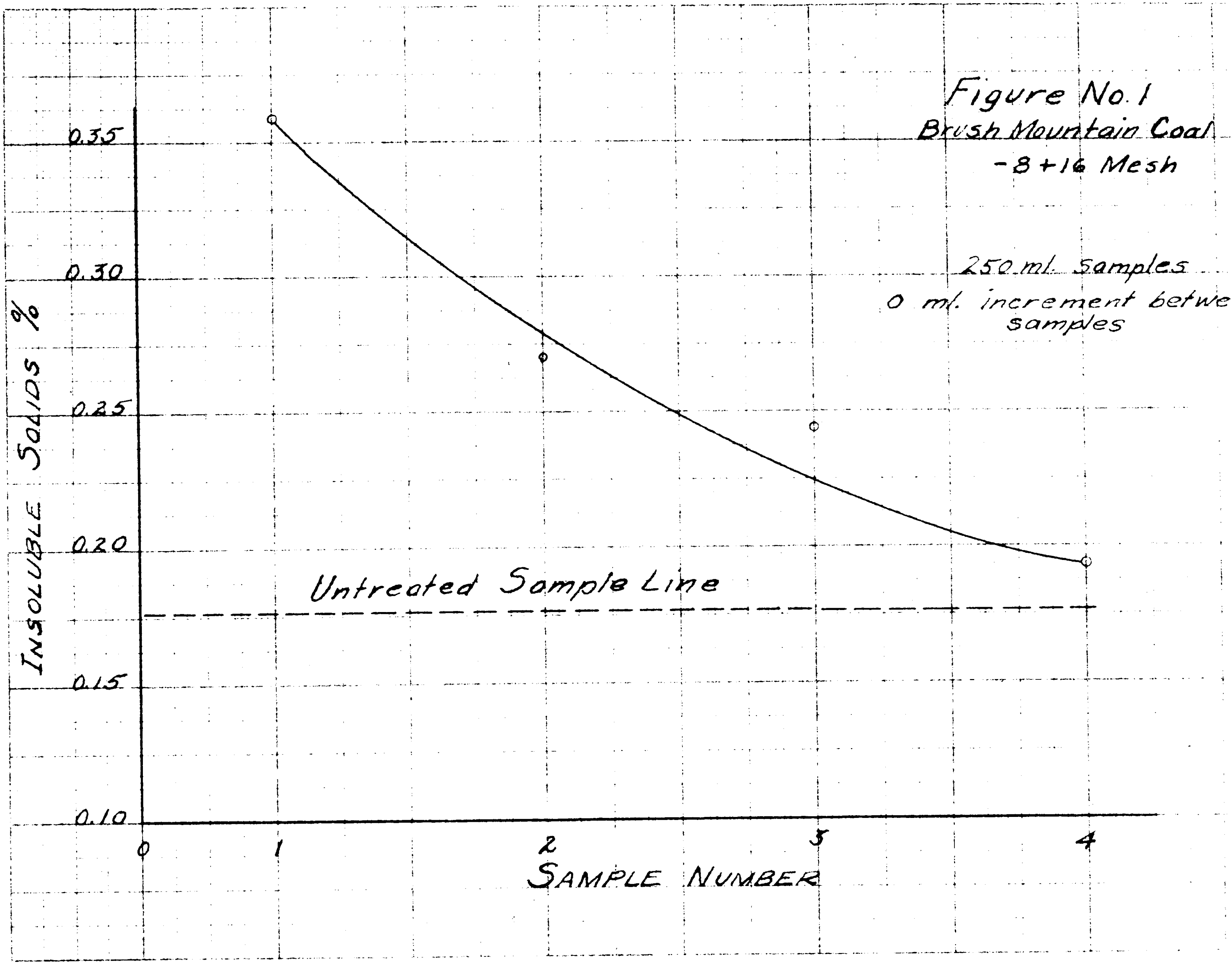

Figure No. 1
Brush Mountain Coal
-8+16 Mesh

250 ml. samples
0 ml. increment between samples

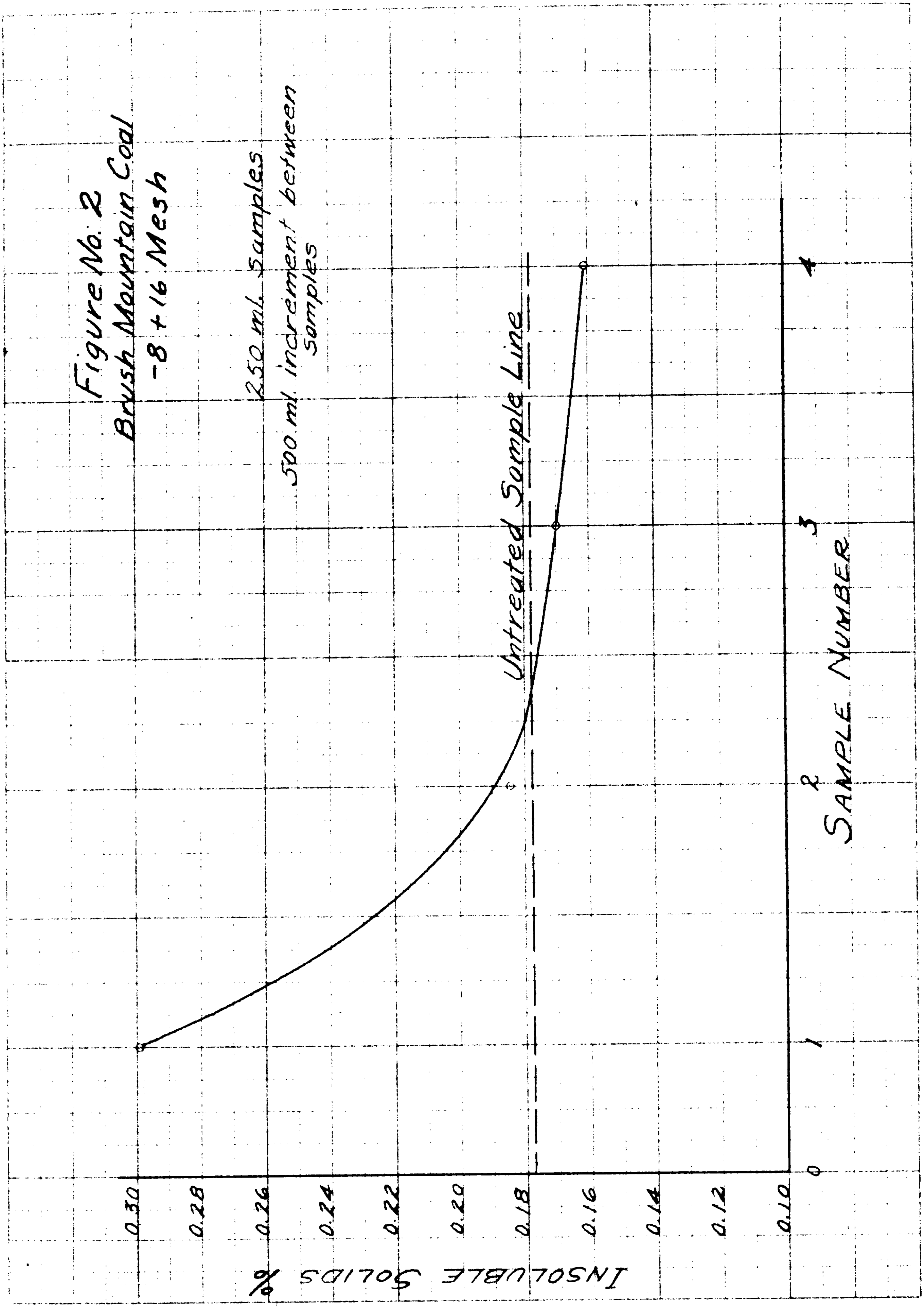

Figure No. 2
Brush Mountain Coal
-8 +16 Mesh

250 ml. Samples
500 ml. increment between samples

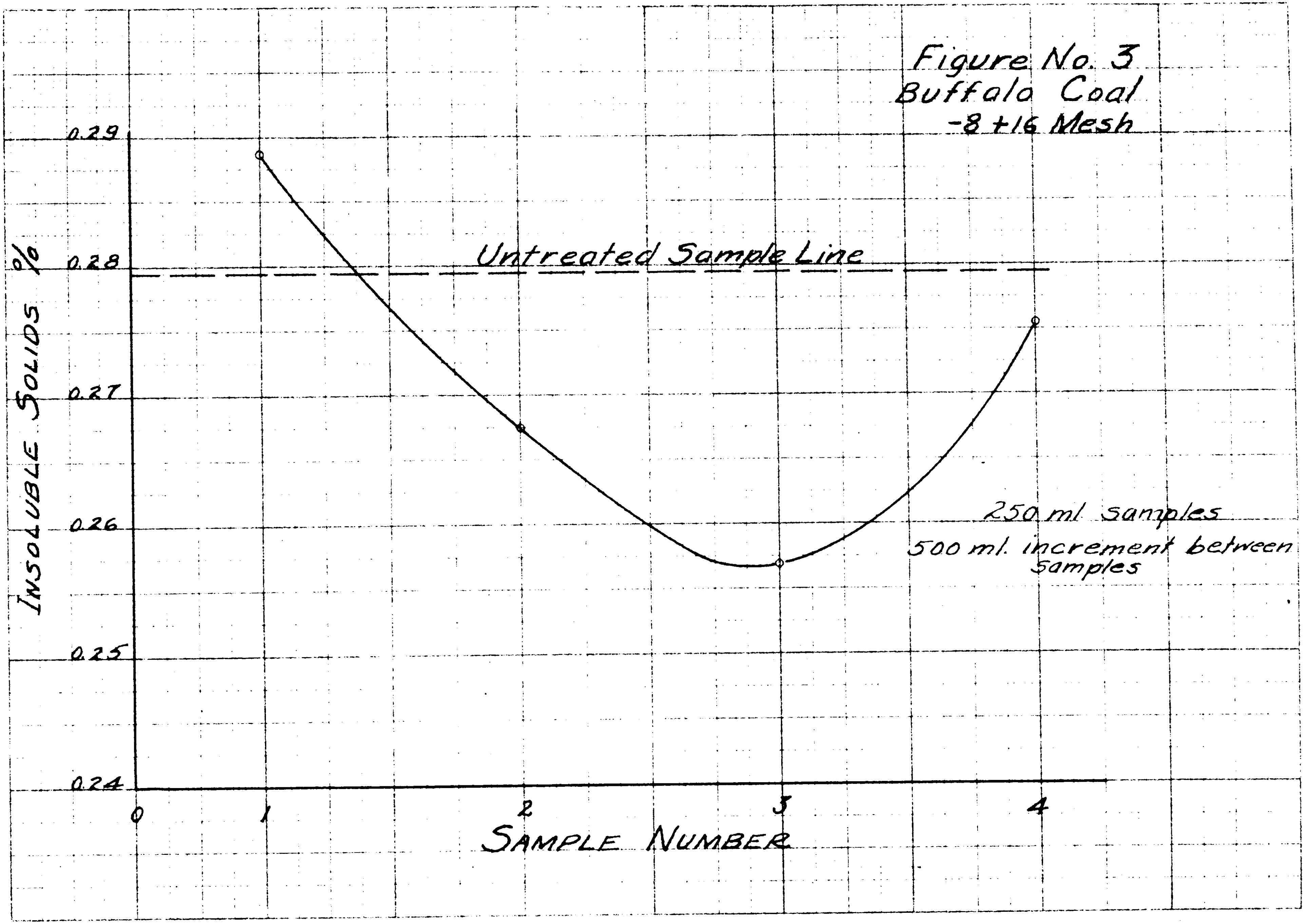

Figure No. 3
Buffalo Coal
-8 +16 Mesh

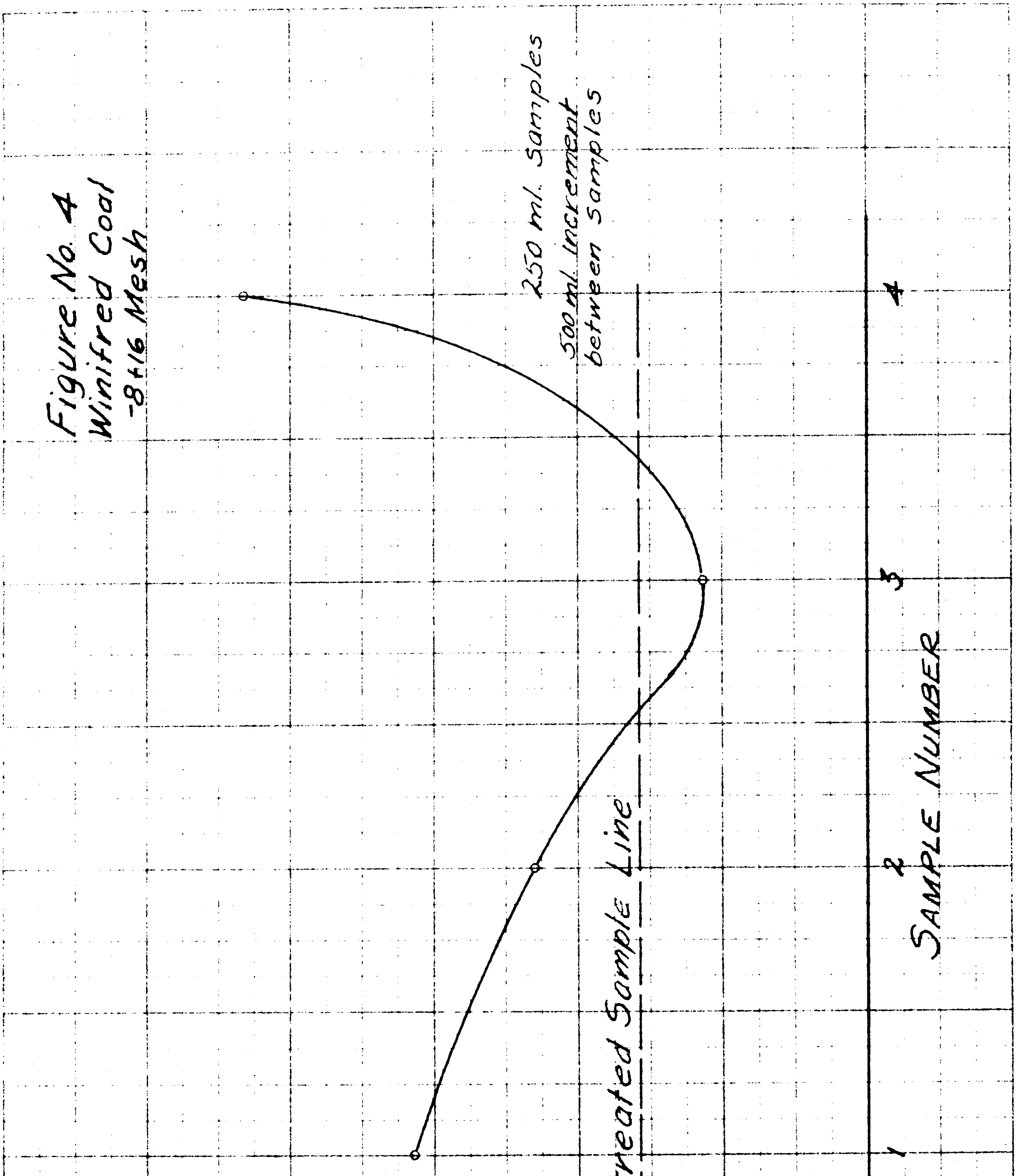

Figure No. 4
Winifred Coal
-8+16 Mesh

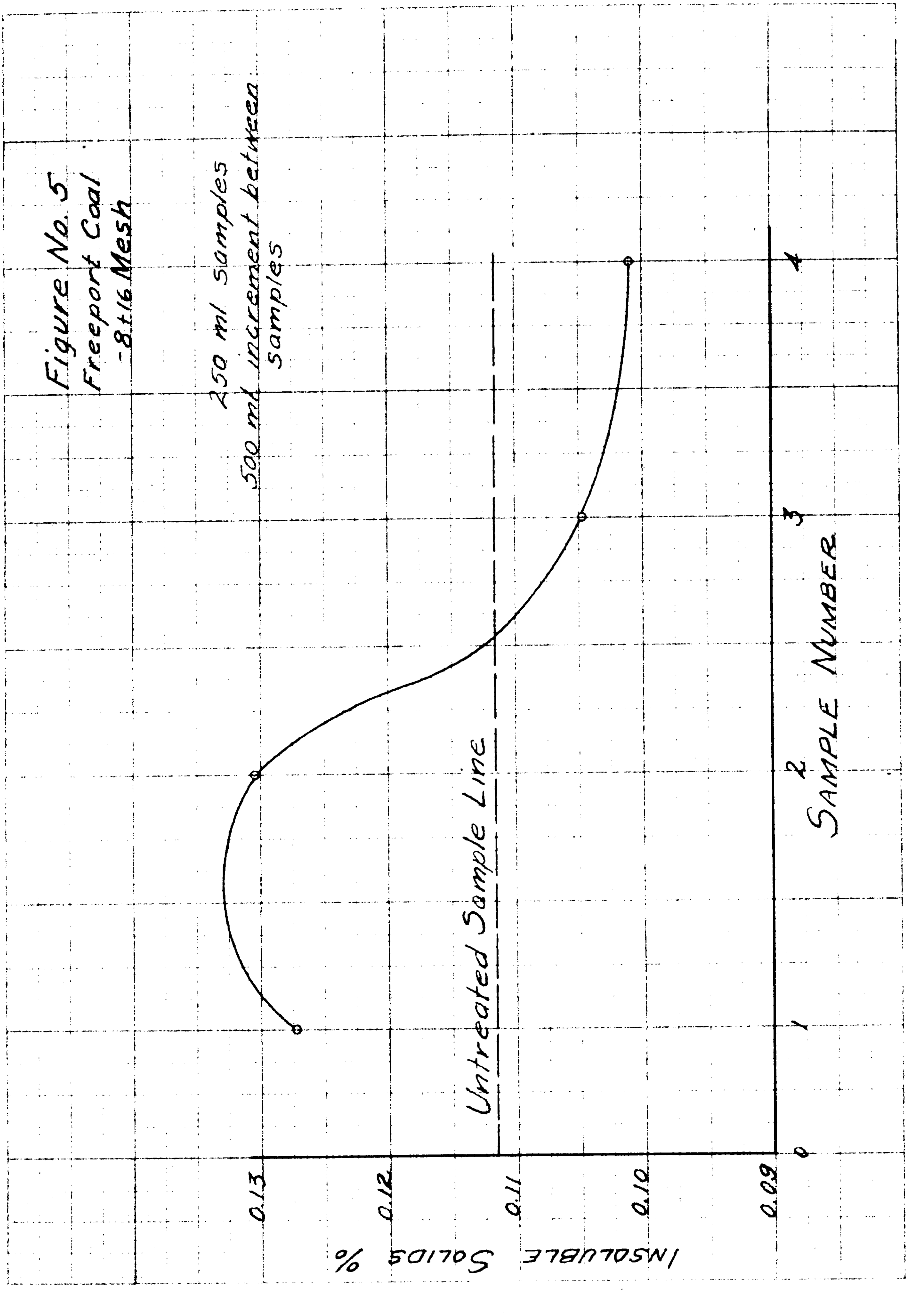

Figure No. 5
Freeport Coal
-8+16 Mesh

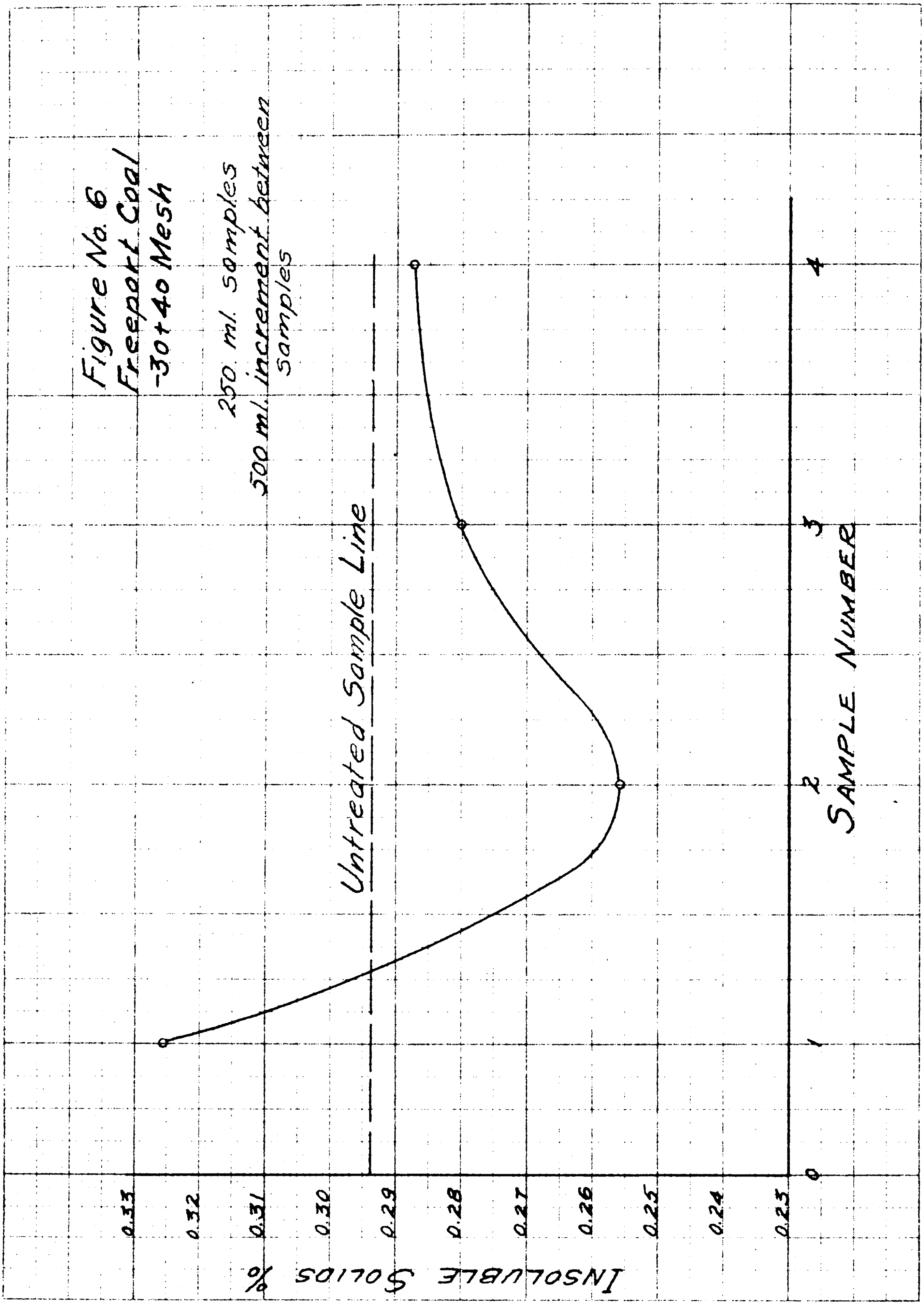

Figure No. 6
Freeport Coal
-30+40 Mesh

TABLE IV

Tannin Analysis of Samples

Showing a Negative Tendency Toward Separation

Coal Sample and Size	% Constituent	Untreated Sample	Treated Samples 1	2	3	4	Appearance of Samples
Thacker - 8 + 16	T.S.	2.9882	2.8556	2.9926	3.0748	3.1332	1 & 2 very dark, 3 & 4 slightly dark
	S.S.	2.8500	2.4458	2.8498	2.9092	2.9624	
	I.S.	0.1382	0.4092	0.1428	0.1656	0.1708	
Pond Creek - 8 + 16	T.S.	3.1774	3.1360	3.2240	3.2992	3.3400	No Color Change
	S.S.	2.8498	2.8412	2.8814	2.9436	2.9968	
	I.S.	0.3276	0.2948	0.3426	0.3556	0.3432	
Alma - 8 + 16	T.S.	3.0408	3.0244	3.0656	3.1226	3.1218	No Color Change
	S.S.	2.7684	2.7972	2.8266	2.8216	2.2816	
	I.S.	0.2724	0.2272	0.2390	0.3010	0.2602	
Chilton - 8 + 16	T.S.	3.0220	2.8920	3.0468	3.0640	3.1028	No Color Change
	S.S.	2.7610	2.6216	2.7902	2.7940	2.8184	
	I.S.	0.2610	0.2704	0.2566	0.2700	0.2844	
Brush Mt. - 16 + 30	T.S.	3.2476	3.3124	3.3346	3.3132	----*	1 & 2 dark 3 & 4 light
	S.S.	2.9686	3.1438	3.0280	2.9680	----*	
	I.S.	0.2792	0.1686	0.3066	0.3452	----*	
Brush Mt. - 30 + 40	T.S.	3.1696	3.1968	3.1388	2.9876	----*	1 dark 2, 3 &4 light
	S.S.	2.9912	2.9124	2.8462	2.6916	----*	
	I.S.	0.1784	0.2844	0.2926	0.2960	----*	
Freeport - 16 + 30	T.S.	3.2716	3.3294	3.3414	3.3708	3.4300	No Color Change
	S.S.	2.9640	3.0218	3.0044	3.0098	3.1028	
	I.S.	0.3076	0.3076	0.3370	0.3610	0.3272	

*Coal bed became clogged, stopping flow and preventing collection of sample for analysis.

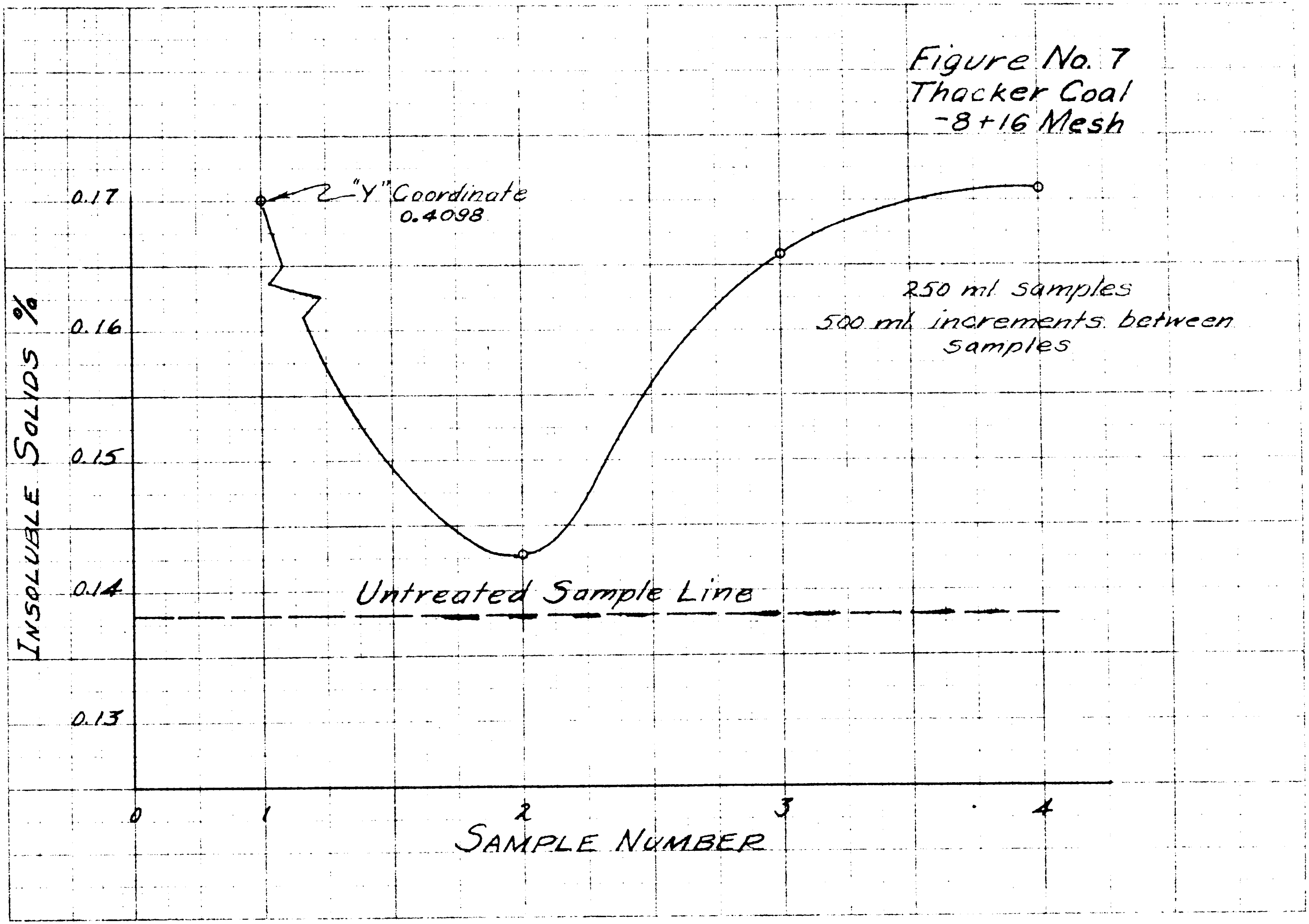

Figure No. 7
Thacker Coal
-8+16 Mesh

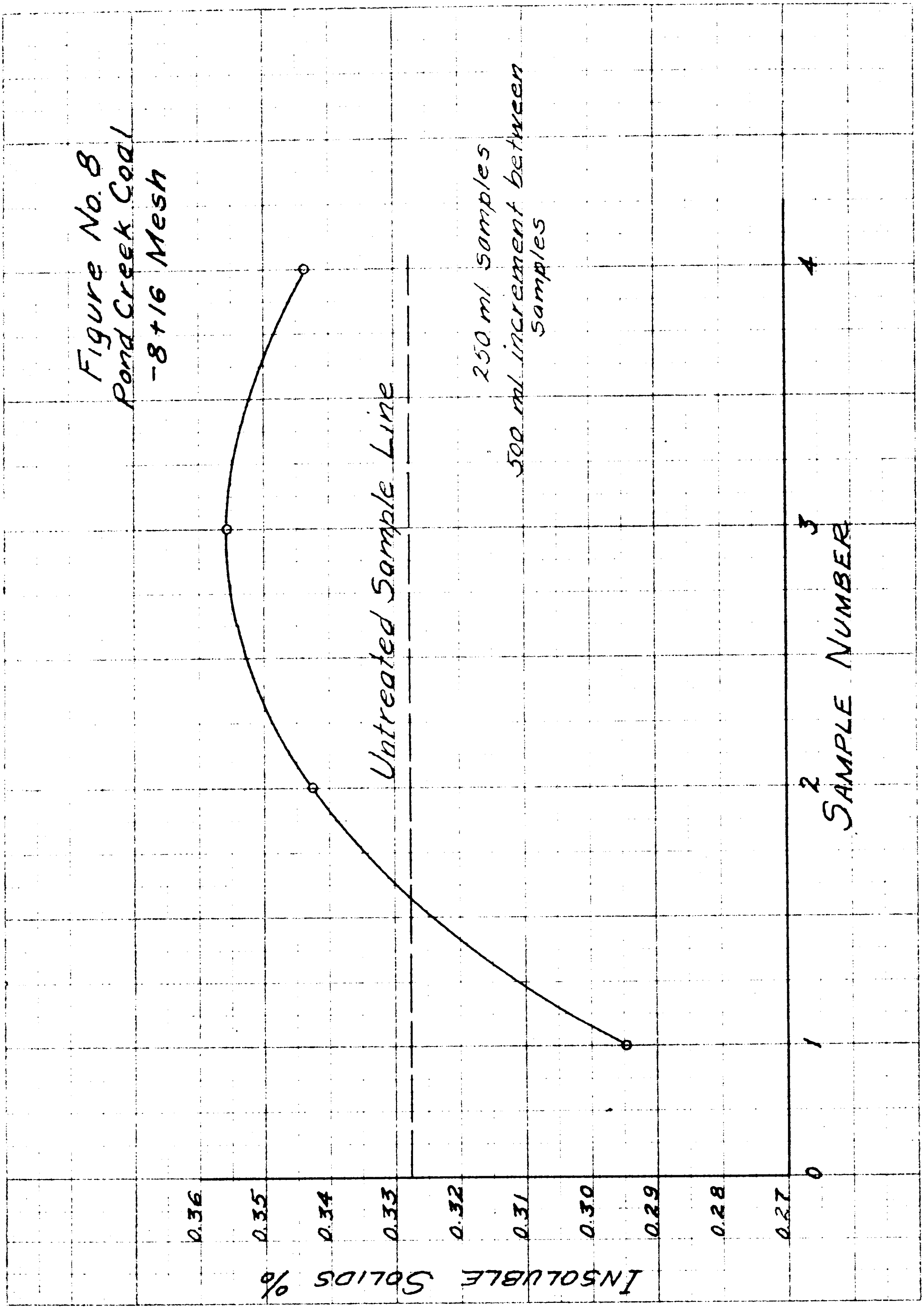

Figure No. 8
Pond Creek Coal
-8+16 Mesh

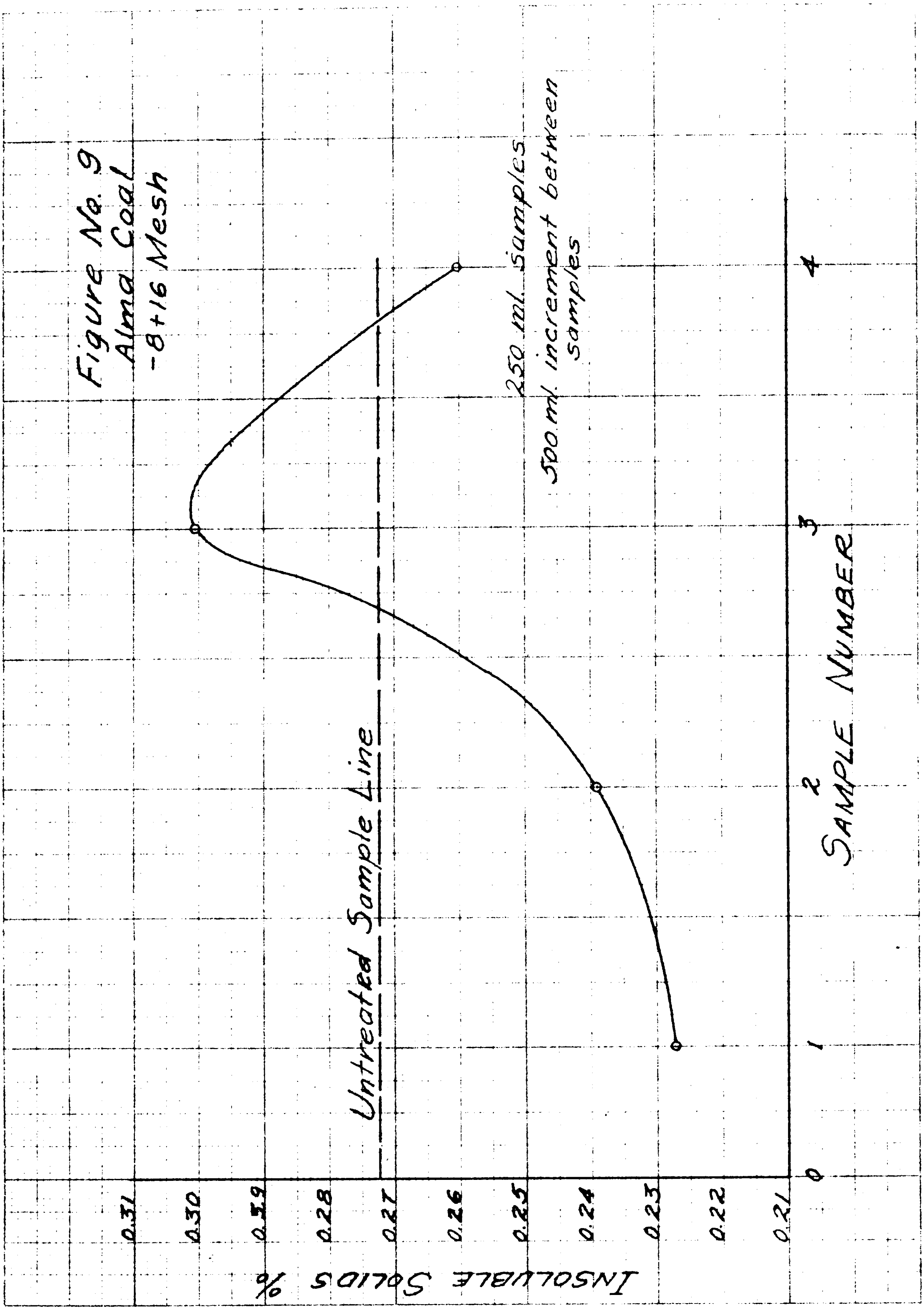

Figure No. 9
Alma Coal
-8+16 Mesh

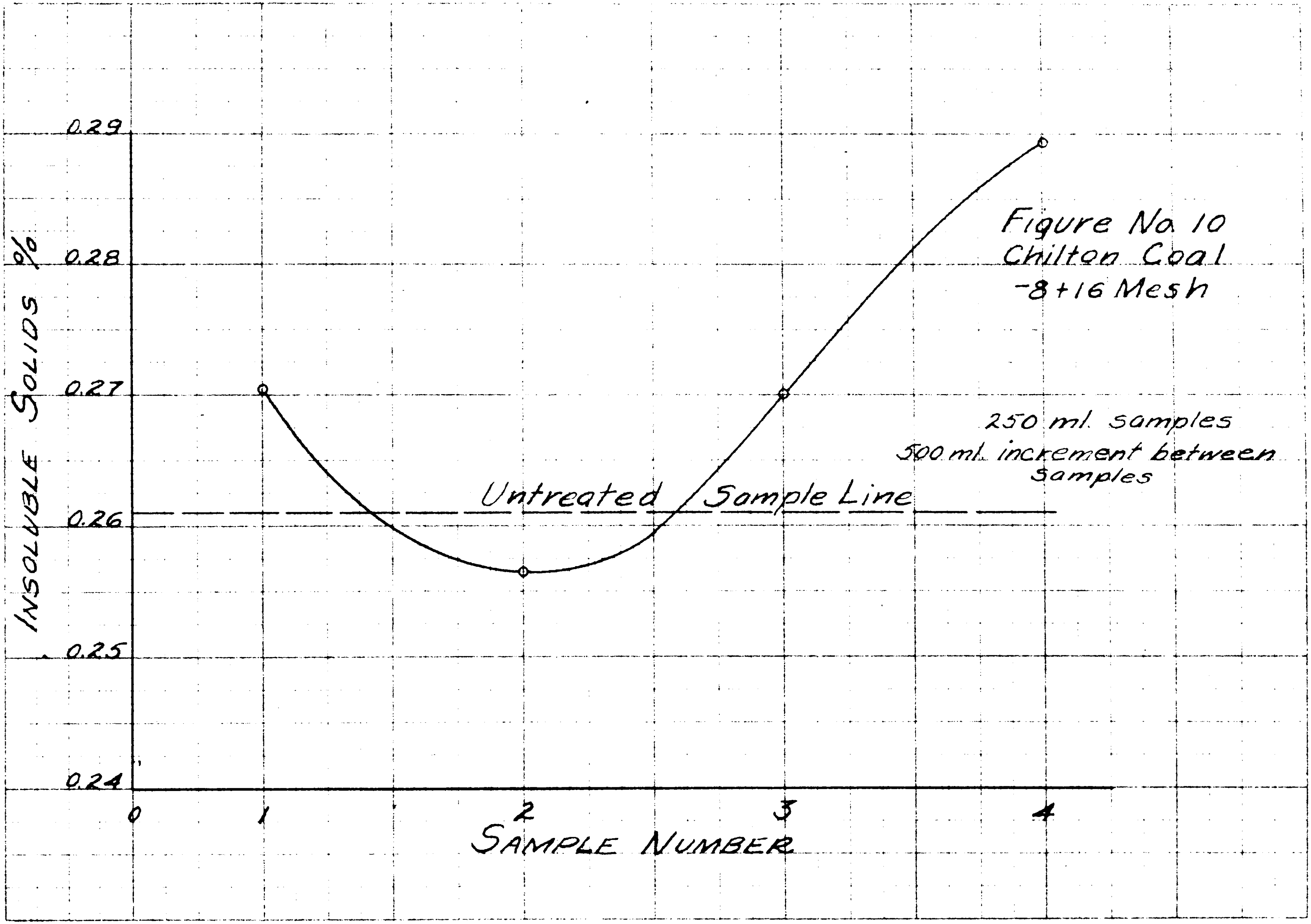

Figure No 10
Chilton Coal
-8+16 Mesh

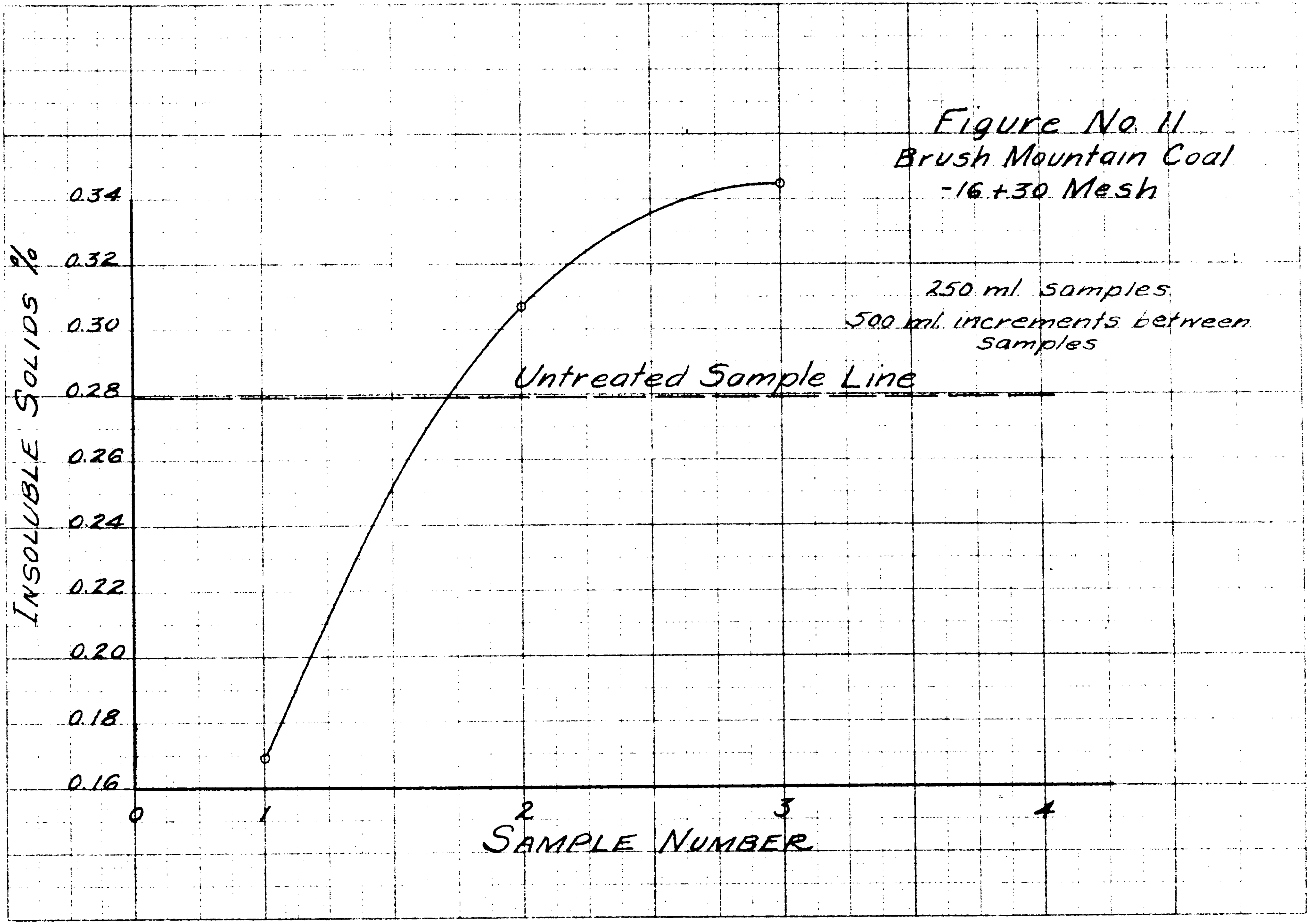

Figure No 11
Brush Mountain Coal
-16+30 Mesh

250 ml samples
500 ml increments between samples

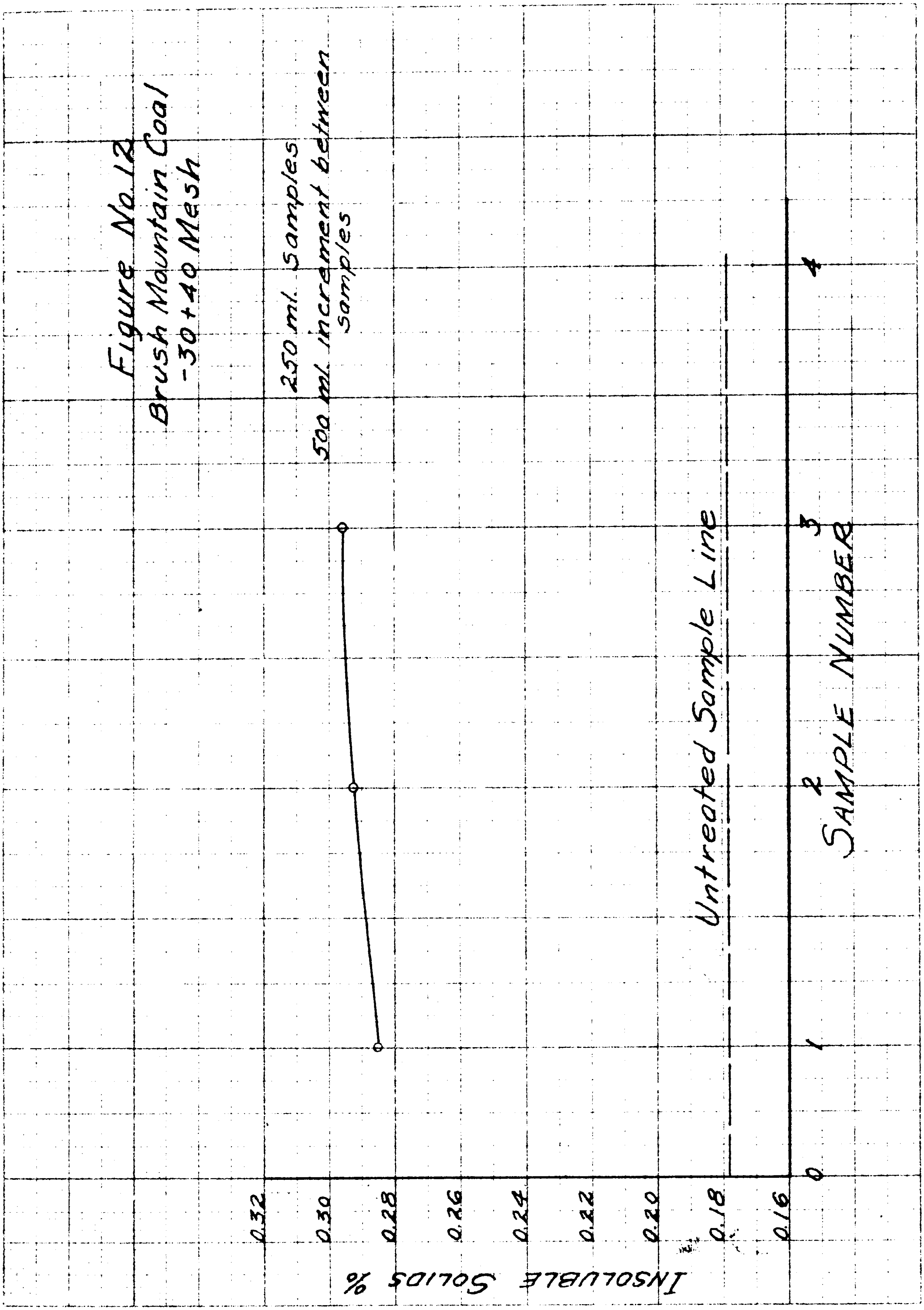

Figure No. 12
Brush Mountain Coal
-30+40 Mesh

250 ml. Samples
500 ml. increment between samples

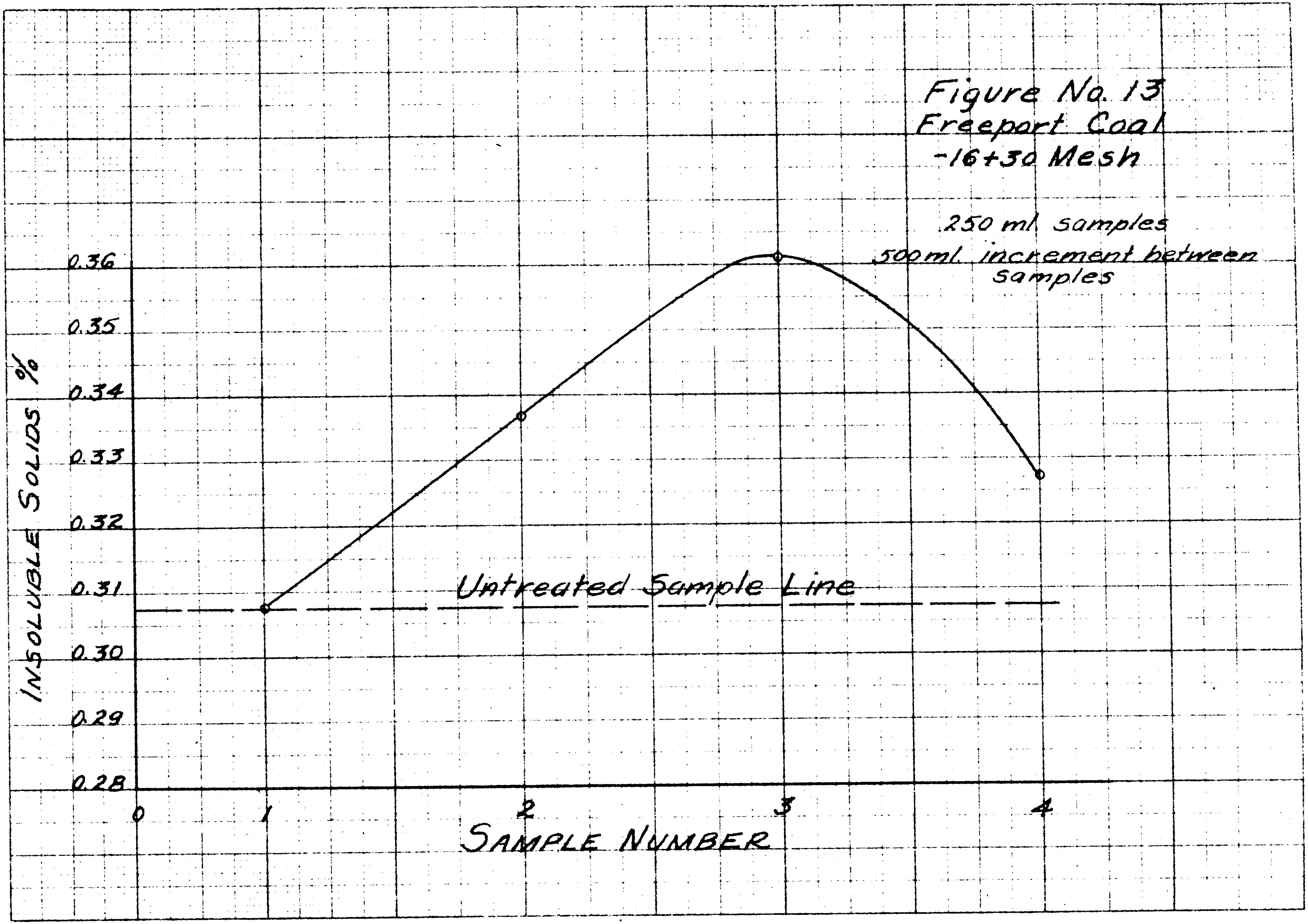

Figure No. 13
Freeport Coal
-16+30 Mesh

.250 ml samples
500ml increment between samples

IV. DISCUSSION

IV. DISCUSSION

<u>General</u>: In the adsorption tests using - 8 + 16 mesh samples of each coal, no trouble was experienced in the procedure, but in the tests using the finer mesh samples (- 16 + 30 and - 30 + 40) of Brush Mountain coal it was found impossible to collect the fourth treated sample solution in each case. This may be attributed to the fact that the spaces between the particles of coal became clogged with insoluble material.

<u>Microscopic Appearance of Brush Mountain Coal</u>: It was noted during the preparation of the coal samples, that the Brush Mountain sample was extremely soft and produced a much higher percentage of fines than did any of the other coals. Any handling of the sample tended to cause powdering from friction between the particles. At the completion of all the adsorption tests samples of untreated coal were viewed under a Spencer binocular microscope employing 3X objective lenses and 12X eyepiece lenses. The Brush Mountain coal exhibited several types of particle structure, some of which were fibrous, some angular, with the surface composed of numerous granular particles, giving the appearance of having a spongy structure, and others were angular particles with surfaces, smooth and regular. Of these types present, the fibrous and granular surfaced particles were predominant

and were structurally weak as evidenced by shattering or powdering when they were touched with the point of a pencil. The fine particles tended to cling to the larger particles and it is quite possible that the combination of these very fine particles with the insoluble non-tannin constituents, being adsorbed in the adsorption tests, produced a mass much more apt to clog the free space between the coal particles than either factor alone.

Microscopic Appearance of Other Coals: All of the other coals, with the exception of the Freeport sample, when viewed under the binocular microscope, exhibited angular particles with regular and smooth surfaces predominating. The Freeport sample exhibited angular particles with very irregular surfaces but the small irregular surfaces appeared to be smooth.

All of these coals exhibited a higher structural strength than the Brush Mountain sample in that they resisted shattering or powdering when moved about on the slide with the point of a pencil.

High Insoluble Content of Initial Treated Tannin Samples: In many of the curves it may be noted that the first one or two treated samples show an insoluble percent above that of the untreated sample. The effect may be caused by any one of the three factors or a combination of the three listed below:

1. Evaporation during the adsorption tests or during analysis of the samples.
2. Coal dust clinging to the coal particles being freed by the

tannin solution and carried over into the treated samples.

3. The formation of insoluble tannin compounds with iron or other constituents in the coal.

Of these factors, evaporation may be eliminated from consideration since the air to the air lift recycle in the tests was supplied by a Nash Hytor Compressor which delivers air nearly saturated with water vapor, and in the analyses of samples, the filter funnels were kept covered as well as the filtrate bottles which were supplied with covers with holes in them just large enough to admit the funnel stems.

Since coal dust tends to agglutinate and cling to the surface of larger coal particles and since the coal samples were not washed prior to being subjected to the adsorption tests, the tannin solution was certain to have loosened some of the agglutinated particles and carried them over into the treated tannin samples.

The third factor of chemical combination of tannin with constituents present in the coal was noted in a few of the initial treated samples as indicated by a dark color and listed in the tables of results under the heading "appearance of samples."

Indications of Insoluble Separation: The separation appears to be a combination of two effects. First, there is the adsorption effect and secondly, a filtration effect which seems to come into prominence toward the latter part of the individual tests.

The curves of results are separated into two groups, those showing a more or less positive tendency toward the separation of the insoluble constituents from the tannin solution by coal, and those showing no change or in some cases a negative tendency toward the separation.

In the case of most curves showing a tendency toward negative separation, the curves pass through an inflection point in favor of separation toward the end of the respective tests, most probably due to the filtration effect coming into prominence as the free spaces between the coal particles became filled with the adsorbed material.

One coal sample, namely, the Brush Mountain - 30 + 40 mesh exhibited no tendency toward the separation as indicated by a nearly flat curve. This phenomenon may be explained by the extreme friability of the sample as discussed previously and a consequent carrying over of the fine particles into the treated samples.

The curves showing a positive tendency toward the separation appear to pass through a definite inflection point where the separation effect begins to decrease due probably to the diminishing of the adsorption effect. A continuation of the tests on these samples might exhibit a second inflection point in the favor of separation as the effect of filtration came into prominence as was noted in the curves of samples showing a negative separation tendency.

From previous research work(6), however, it was concluded that separation by filtration or any existing mechanical means is not practical since the separation may only be accomplished at the rather disastrous expense of capacity.

Of the coals tested, the maximum separation was exhibited by the Freeport - 30 + 40 mesh sample. The separation reduced the insoluble solids percent from 0.2938 to 0.2558 percent or an effective separation of 0.038 percent. In order to be of commercial importance(22) the percentage must be reduced to 0.0375 or a reduction of 0.2563 percent. This indicates that the Freeport sample mentioned above was only 14.8 percent effective in the insoluble separation.

<u>Effect of Coal Composition on Separation</u>: It was found impossible to correlate the adsorptive power of the coal with any chemical constituent as shown in a proximate analyses of the coal samples.

Recommendations

The use of coals as an adsorbent for the insoluble constituents present in a fresh tannin extract still requires study. All of the coals used in this investigation were of the bituminous and semi-bituminous types. Any further investigation should incorporate tests on coals varying from anthracite through lignite or brown coals obtained from widely different sections of the country.

Planned Future Investigations: In discussions dealing with the problem, Mr. P. H. Porter (graduate student, 1946) decided to continue the investigation using coals as adsorbents. His plan of investigation incorporates the use of coals varying from anthracite through lignite. Tests are planned to determine the relative surface area of the adsorbents by measurement of the pressure drop of water through a vertical glass chamber packed with the various coal samples. Tests will also be made to determine the relative roughness of the particle surfaces by means of the intensity of reflection of a beam of monochromatic light. The intensity of reflection is known to vary inversely to the roughness of the reflecting surface.

It is also planned by Mr. Porter that the effect of the roughness on the adsorptive power shall be investigated by smoothing the surfaces of a sample of coal mechanically and comparing the adsorption effect of this sample with an untreated sample of the same coal.

Any change of surface area with the use of coal as an adsorbent will be investigated by backwashing the samples of coal after being subjected to the adsorption tests and again checking the relative surface area by the pressure drop method.

<u>Test Equipment</u>: It is suggested that Mr. Porter design his equipment so that the chambers used in the relative surface determinations may also be used as the adsorption chambers. Since the manner in which the coal samples are packed in the adsorption chamber has considerable effect on the free space and exposed surface area between the coal particles, this revision would enable adsorption tests to be run on samples of known relative surface area.

<u>Preparation of Coal Samples</u>: Since the grinding and sizing of the coal samples produces many very fine particles which tend to adhere to the surface of the larger particles, it is suggested that the samples be washed thoroughly before the adsorption tests are run. Possibly some liquid with a greater wetting power than water will prove more successful in loosening the adhered dust particles.

<u>Other Adsorbens</u>: Other types of adsorbents including chemically treated coals (such as sulfonated coals) should also be investigated for their effect on the separation.

In many separation processes where the material to be separated consists of finely divided non-rigid particles in suspension, an adsorbent in the form of irregular particles is agitated in the solution. The insolubles to be separated are adsorbed on the adsorbent surfaces and the solution may then be filtered successfully, whereas, filtration alone would not be economically feasible due to the necessity of employing a filter medium containing extremely fine pores. It is, therefore, recommended that future research be carried out employing adsorption on the surface of pulverized activated particles followed by filtration. The Mead Corporation of Lynchburg, Virginia uses copper tube heat exchangers to cool the tannin extract before the separation of the insoluble materials is attempted, and it was noted that the insoluble constituents formed a heavy coating on the surface of the copper tubes requiring them to be cleaned every few weeks. Active adsorbent materials in further investigations might, therefore, include materials such as copper or aluminum which are not attacked by tannin solution.

In the literature it was noted that many precipitates exhibit strong adsorptive tendencies toward sols or colloidal suspensions of the same material. It is, therefore, suggested that the use of a fabricated form of the insoluble material present in the tannin extract as an adsorbent for the material in suspension be incorporated in further research work.

<u>Use of Concentrated Tannin Solution</u>: The Mead Corporation of Lynchbourg, Virginia concentrates the "leach house" liquor before attempting a separation of the insoluble material by settling. The use of this concentrated liquor or a similarly concentrated liquor may react more readily to the separation by adsorption.

Recommendations Offered During Oral Examination: The suggestion was made that further investigation using adsorption should include a material balance for each test as an aid in the determination of the efficiency of separation.

The idea was advanced that the adsorption effect may be a linear function of the exposed adsorbent surface. In the case of the Freeport -30 + 40 mesh sample of coal, an effective separation of 14.8 percent was accomplished using two adsorption chambers. If the above theory is true, the use of 12 chambers or an equivalent amount of adsorbent surface may effect a separation of almost 90 percent. It was recommended that the theory be investigated.

It was further suggested that the treated samples exhibiting a dark color be examined for suspended colloidal particles of coal by passing a beam of light through them and observing the presence or absence of the "Tyndall effect".

V. CONCLUSIONS

V. CONCLUSIONS

On the basis of results of the adsorption tests using the insoluble constituents present in the "leach house" tannin extract produced by the Mead Corporation of Lynchburg, Virginia as the adsorbate and coals of the bituminous and semi-bituminous types mined by the Pond Creek colliery of Williamson, West Virginia, The Eastern Coal Sales Co. of Stone, Kentucky, and M. C. Slusher & Co. of Blacksburg, Virginia as the adsorbents, using a tannin solution flow of 12 ± 2 ml. per square inch of adsorption chamber cross section at 68 ± 5 degrees Fahrenheit, the following conclusions may be postulated:

1. The coal samples as adsorbents may be arranged in two groups: first, those showing a positive tendency toward the separation, including Brush Mountain, Freeport, Buffalo Creek and Winifred samples of - 8 + 16 mesh and also the Freeport sample of - 30 + 40 mesh size; second, those showing no separation or a negative tendency toward separation including Thacker, Pond Creek, Alma and Chilton samples of - 8 + 16 mesh, Freeport and Brush Mountain of -16 + 30 mesh, and the Brush Mountain sample of - 30 + 40 mesh size.
2. The Freeport sample of - 30 + 40 mesh effected a reduction of the insoluble material from 0.2938 to 0.2560 percent

which is 14.8 percent of the required reduction to make the process commercially practical. The next in rank of effective separation was the Buffalo Creek coal sample of - 8 + 16 mesh size and exhibited an effective separation of only 9.5 percent of the required.

3. The proximate chemical analysis of the coals revealed no chemical constituent which could be correlated with the adsorptive power.

VI. SUMMARY

VI. SUMMARY

The Separation of the Insoluble Constituents from a Fresh Tannin Solution

In the preparation of tannin extract from chestnut wood chips, there is present in the extract, along with the tannin, certain insoluble non-tannin constituents which must be separated in order to make the extract suitable for the manufacture of leather.

This investigation was undertaken to determine the feasibility of using coal as an adsorbent in the separation of the insoluble constituents.

The effective separation is indicated by a comparison between the insoluble constituents present in the untreated sample with the insolubles present in the treated samples as determined by analysis.

By making a proximate analysis of the coal samples used in the adsorption tests, it was hoped that a correlation could be made between the adsorptive power and the chemical constituents present.

Test Equipment: The adsorption test equipment was designed and constructed by the investigator, employing two glass tubes as adsprption chambers, and a means of controlling the flow of tannin solution to 12 ± 2 ml. per square inch of chamber cross section.

Adsorption Tests: Adsorption tests were run using - 8 + 16 mesh samples of each coal. Since the Brush Mountain coal mined by M. C. Slusher & Co. of Blacksburg, Virginia was the only sample which varied widely from the others in proximate analysis, the - 16 + 30 and - 30 + 40 mesh samples of Brush Mountain Coal and any one of the other samples (Freeport coal was selected) were subjected to adsorption tests.

Results: It was found possible to separate the coals into two groups: (1) those showing a positive tendency toward the separation, and (2) those showing no effect or a negative tendency toward the separation.

Of the coals tested, the Freeport sample of - 30 + 40 mesh size exhibited a separation of 0.038 percent of the total insolubles present which is only 14.8 percent of the required separation to make the process commercially practical. The next in rank was the Buffalo Creek sample which exhibited only 9.5 percent of the required separation.

No correlation could be found between the adsorptive power of the coal and any chemical constituent as shown in the proximate analysis.

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