OIL-WATER-MINERAL MATTER SORPTION PHENOMENA OF INTEREST IN PETROLEUM GEOLOGY.

Thesis

Submitted by

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ABSTRACT.

The types of interaction likely to be encountered in crude oil, water, fine-grained mineral matter systems have been reviewed, and current knowledge of the colloidal and interfacial properties of crude oils summarized. The principal conclusion of previous investigations of interfacial phenomena associated with crude oils was that crude oils contain small quantities of highly surface-active non-hydrocarbon components.

Interaction of the three phases, oil, water and mineral matter, was demonstrated for four different types of argillaceous mineral matter, basically two montmorillonites, illite and kaolinite, and two different types of oil, asphaltic and paraffinic. Furthermore, the extent of the interaction was found to be dependent on the hydration properties of the mineral matter, the properties and type of crude oil, and the relative proportions of the three phases in the neutral systems.

After an initial comparison of the ultra-violet absorption spectra of oil fractions, obtained by chromatography, with the ultra-violet absorption spectrum of the unfractionated oil, a method was developed, using ultra-violet spectrophotometric measurements, for investigating the part played by crude oil and its components in oil-water-mineral matter interactions. Experiments involving a given

volume of a standard hydrocarbon solution of crude oil contacted with dry, mildly water wetted, damp or water saturated argillaceous material were performed to determine the influence of water on the interactions. The results indicated that the initial water content of the mineral matter controlled the type of oil component as well as the quantity of oil adsorbed from solution by a given weight of mineral matter. The greater the initial water content the more the adsorption was restricted to non-hydrocarbon (polar) components alone, and the smaller was the quantity of oil adsorbed. Furthermore, for a given initial water content the specific adsorption of oil, i.e. weight adsorbed per unit weight of mineral matter, decreased with increase in weight of mineral matter contacted.

Following the percolation of crude-oil solutions through damp argillaceous material, the bulk of the oil components adsorbed were recovered by eluting with aromatic hydrocarbon and polar solvents, and the characteristic fluorescence of the recovered material in ultra-violet light, after the removal of the eluting solvent, was noted. Examination of the isolated components by means of infra-red absorption spectra was also carried out. The results indicated that the material adsorbed by water-wet fine-grained mineral matter consisted principally of resinous and asphaltic non-hydrocarbons, containing porphyrins and

components with carbonyl functional groups. Part of the material adsorbed could not be recovered by solvent elution and is, therefore, tightly adsorbed. The tightly adsorbed material appears to be capable of displacing the adsorbed water layer from fine-grained mineral matter, and this action may promote the formation of stabilized adsorbed films, composed of resinous and asphaltic non-hydrocarbons, at the oil-solid (clay) or oil-adsorbed water interface.

Finally, the results obtained are discussed in relation to some problems of Petroleum Geology.

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INTRODUCTION.

Petroleum geology, as for geology as a whole, is basically, applied physics, chemistry, and biology. The last science, however, may be of more importance than in general geology, since petroleum is a derivative of living organisms. The chemistry of possibly suitable living organisms, and the environments in which they existed are of prime importance in any theories which are formulated to explain the origin and accumulation of petroleum in the earth's crust. In the field of biochemistry it has been shown that surface and colloid chemistry must be considered in explaining the chemical reactions which take place in life processes; therefore this aspect of physical chemistry is involved in discussing problems connected with petroleum geology. Thus, although the organic matter from which petroleum is apparently derived is no longer in the living state, there is no reason to suppose that its entire chemical nature will change immediately on the death and deposition of the organisms concerned. Furthermore, the presence of the solid surfaces of the rocks themselves, both as unconsolidated sediments and as lithified rocks, may provide an important, if not critical, influence on the associated fluids both before and after the formation of an accumulation, as well as during production.

The American Association of Petroleum Geologists research committee (1957, Bull. A.A.P.G., Vol. 41, August, p.1856)

recently rated origin, migration, and accumulation of petroleum as the subject second out of a total of nine requiring greater research activity. Under a sub-heading suggesting the investigation of capillarity in fluid migration, both of hydrocarbons and other fluids, they list as corollaries the following two problems:

(a) Since most formations are presumably water-wet at the time of deposition, under what conditions do they become oil-wet?

(b) What is the role of the surface chemistry of the mineral constituents in migration; i.e. how does "wettability" vary with mineralogy? The clay minerals may be especially important in this connection.

Further topics they consider in need of investigation under the heading of migration are:

(1) The method or methods by which hydrocarbons migrate, e.g. en masse, as discrete droplets in water, as a colloidal dispersion, or in solution. The method of transportation may be different at different stages of the migration prcoess, i.e. in solution or colloidal dispersion in the early stages, and as discrete droplets at later stages.

(2) An overall attack on many of the problems of both oil source and migration, detailed studies of the causes and significance of variations in oil gravity and type, both generally and with respect to basin position, is suggested.

The above cited problems are typical of those which cannot be investigated satisfactorily without taking note of the

possible interaction of oil, water and fine-grained mineral matter. The effects of such interactions are not confined, however, to these fundamental problems, but they may also be involved in phenomena associated with petroliferous areas, such as reservoir bitumen deposits, tar belts, and oil seeps. A better understanding of oil, water, mineral matter relationships is also vital to the proper evaluation of subsurface fluid mechanics, so important in the efficient exploitation of a reservoir, and there is also the problem of the possibility of formation damage by invading drilling fluids during drilling. Similarly the formation and treatment of oil-field emulsions are dependent on surface phenomena often involving fine-grained mineral matter.

Indeed, there are numerous aspects of both petroleum geology and petroleum engineering in general wherein a better understanding of all aspects of the relationships of oil, water and mineral matter would help solve many of the problems which at present stand in the way of more efficient exploration for, and production of oil.

The relationship of oil, water and fine-grained mineral matter is complicated by many variables such as the relative proportions and the composition of the individual phases, and the physico-chemical factors capable of influencing either a particular phase or phases, or the system as a whole. If for oil, the word organic matter is substituted, the

relationship becomes even more complex, and at the same time it would include the situation present in certain recent and ancient non-reservoir sediments from which oil apparently is being, or has been derived. Certainly the transition from organic matter to oil in the dynamic sedimentary system resulting from the continuous deposition, burial and compaction of sediments, appears to be a function of this relationship, which in turn is probably influenced by changes in the pressure and temperature factors inherent in the system.

Realizing the extent of the problem it was concluded that limited experimental work must of necessity be an approximation, yet by first studying the relationship of an oil with different clay mineral types it might be possible to obtain some idea of the part played by the solid phase; and secondly, by investigating the oil before and after contact with the other two phases an insight into the role of the oil phase might be obtained. The water phase was kept as simple as possible in the majority of the experiments in order to avoid any unnecessary complications which would hinder the interpretation of the part played by the other two phases.

Whilst it is realized that the condition of oil during the primary migration stage ("proto-petroleum") from the source rock is very uncertain, initial studies involving the possible interaction of reservoir crude oil with water and fine-grained mineral matter may be justified in order to evaluate some of the factors that have to be taken into account when attempting

to find a satisfactory explanation of the character of "proto-petroleum". Crude oil interactions with water-wet fine-grained mineral matter will undoubtedly involve changes in the properties of the oil and mineral matter, and could, therefore, have significant consequences with regard to the wetting properties and fluid mechanics of reservoirs containing fine-grained mineral matter, i.e. "dirty sands". Furthermore, the changes taking place in the oil phase as a result of such interactions may markedly alter the properties of the oil, i.e. specific gravity and chemical character.

Other examples of problems involving crude oil-water-fine-grained mineral matter systems include the entry of oil into drilling muds during the course of drilling, and oil escaping from seepages into streams carrying sediments.

The presence of the water phase is likely to be important in a system where its influence has previously been neglected, i.e. the effect of drying out "source rocks" before solvent extraction. The drying process may cause a change in the quantity and type of extract obtained as compared with extractions of "fresh" samples, and may have some affinities with the changes observed in the wettability properties of "fresh" oilfield cores after periods of storage (ageing).

The opening chapters of this thesis review the kind of phenomena that might be expected to occur when dealing with solid-liquid systems of large surface area, and also some of the more recent investigations carried out on the surface and colloid chemistry of crude oils.

Chapter I

SURFACES AND COLLOIDS.

Perhaps the most familiar phenomenon associated with surfaces is that of the surface tension of a liquid in contact with its vapour. This results from the molecules at the surface of the liquid being attracted towards the bulk of the liquid, since the more highly dispersed vapour molecules do not exert an equal and opposite attraction. Thus, all liquid surfaces, in the absence of other forces, tend to contract to a minimum area. In order to extend the area of an interface, work must be done against the cohesive forces in the liquid to bring molecules from the interior into the surface. From this it follows that the surface portions of the liquid have a higher free energy than the bulk of the liquid. This extra surface free energy, acts parallel to the surface, and opposes any attempt to extend the interface. Surface tension is a negative force per unit length or surface pressure If the surface tension is γ, the work done on the surface in extending its area by an amount dA is

$$dw = -\gamma dA = -dF \quad \text{or} \quad dF = \gamma dA$$

where dF is the change in free energy.

Since the surface of a liquid does not have the same free energy as the bulk liquid, it cannot be said to be in the same thermodynamic state or to be part of the same phase as the bulk of the liquid. In certain instances interfacial phenomena must be taken into consideration in order to study the system at all;

this will arise when any considerable fraction of the material in the system exists at, or near, interfaces.

The degree of subdivision or particle size of a substance is usually the decisive factor determining its surface-to-volume ratio. Extremely porous materials are apparently exceptional cases, but they may often be treated as loose aggregates of very small particles. The surface area per gram of particles of density ρ, either small cubes of side s, or of spheres of diameter d, is given by

$$A = \frac{6s^2}{\rho s^3} = \frac{6}{\rho s} \quad \text{or} \quad A = \frac{\pi d^2}{\rho \pi \frac{d^3}{6}} = \frac{6}{\rho d}$$

If $\rho = 2.30$ the following results are obtained for the surface area in cm.^{2} per gram at various particle sizes:

s(cm.)	A(cm.^{2}/gm.)
10^{-1}	26.1
10^{-3}	2,610
10^{-5}	261,000
10^{-6}	2,610,000
10^{-7}	26,100,000

It is seen that the area increases enormously as the particle size decreases. The lower end of the scale, with s below 10^{-7} cm. or 10A$^\circ$, corresponds to the dimensions expected for ordinary molecules. From around 10^{-7} to 10^{-4} cm. there extends the domain of colloids, and for these particles surface phenomena play a pre-eminent role, and, indeed, much of colloid chemistry is essentially surface chemistry.

Pressure Differences across Curved Surfaces and Capillary Rise.

As a direct consequence of the existence of a surface tension, it can be shown that across any curved liquid surface there must exist a difference in pressure, the pressure being greater on the concave side. The excess pressure is $\Delta P = \frac{2\gamma}{R}$, where R is the radius of a bubble or droplet, and for a more general curved surface with principal radii of curvature R_1 and R_2 it becomes $\Delta P = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$.

Whether a liquid rises in a glass capillary, like water, or is depressed, like mercury, depends on the relative magnitude of the forces of cohesion between the liquid molecules themselves, and the forces of adhesion between the liquid and the walls of the tube. These forces determine the contact angle θ, measured through the liquid, which the liquid makes with the tube walls. If this angle is less than 90°, the liquid is said to wet the surface and a concave meniscus is formed. A contact angle of 90° corresponds to a plane meniscus; a contact angle greater than 90° gives a convex meniscus.

The occurrence of a concave meniscus leads to capillary rise. The pressure under the meniscus is less than that at the plane surface of liquid outside the tube. Liquid rises in the tube until the weight of the liquid column balances the pressure difference.

Surface-tension Data.

Since surface tension is a measure of the work that must be done to bring a molecule from the interior to the surface of a mass of liquid, the liquids with exceptionally high surface tensions, such as water, are those in which the cohesive forces between the molecules are large.

The surface tension of solutions may be given a simple qualitative interpretation. In the case of aqueous solutions, substances that lower the surface tension of water are those that, like the fatty acids, contain both a polar hydrophilic group and a non-polar hydrophobic group. The hydrophilic group, e.g. -COOH in the fatty acids, makes the molecule reasonably soluble if the non-polar residue is not too dominant. The hydrocarbon residues in fatty acids tend to be insoluble in the interior of an aqueous solution, and little work is required to persuade them to come from the interior to the surface. This leads to the conclusion that solutes lowering the surface tension of a liquid tend to accumulate preferentially at the surface, and are said to be positively adsorbed at the interface. Thus the concentration of substances at the interface lowers the surface tension by partially compensating for the normal dissymmetry resulting from the molecules at the surface of the liquid being attracted towards the bulk of the liquid.

On the other hand, solutes such as ionic salts, usually increase the surface tension of aqueous solutions above the value

for pure water, although these increases are much smaller than the decreases produced by fatty acids and similar compounds. The reason is that the dissolved ions, by virtue of ion-dipole attractions, tend to pull the water molecules into the interior of the solution. Additional work must be done against the electrostatic forces in order to create new surface. It follows that in such solutions the surface layers are poorer in solute than is the bulk solution. The solute is said to be negatively adsorbed at the interface.

Adsorption by liquids.

Since the surface of a liquid is not in the same thermodynamic state as the bulk of the liquid, an interfacial phase is formed at the point where the homogeneity of the bulk phase changes to one of inhomogeneity. Thus, for two bulk phases in "contact", there is an interfacial region where the properties of the system vary continuously from those of one phase to those of the second phase. Because of the short range of inter-molecular forces, the interfacial region will usually be not more than a few molecular diameters in thickness. This surface or interfacial phase is parallel to the surface of the two bulk phases, and defined in this way has an area but no thickness. It is a strictly two-dimensional phase.

This change in surface tension as a result of adsorption at an interface giving a surface film, is called the surface pressure. The surface film consists of adsorbed molecules which may be either soluble or very sparingly soluble in the

bulk phase. The spreading of some sparingly soluble substances over the surface of liquids, results in the formation of a film exactly one molecule thick. These uni-molecular films may be regarded as essentially two-dimensional states of matter.

In many instances these two-dimensional uni-molecular surface films behave in a similar manner to three-dimensional states of matter of bulk solids, liquids and gases. the relationship between surface pressure and surface area is similar to the three-dimensional pressure and volume isotherms. Surface films of adsorbed fatty acids are typical examples of this analogy. At low concentration, i.e. large surface area, the pressure is small and increases very slowly with decreasing area, until a critical area is reached. The pressure then begins to increase rapidly on further compression of the film. The long chains of fatty acid are apparently highly orientated at the water surface, with their water-loving carboxyl groups buried in the water, and their water-hating hydrocarbon chains waving around above the surface. The critical area then corresponds to a tightly packed uni-molecular film or mono-layer, with fatty acid molecules completely covering the surface. Any further decrease in area can be achieved only by compressing the closely packed film, which requires a considerable surface pressure, just as in the three-dimensional case compression of a solid or liquid is much more difficult than compression of a gas. The two-dimensional "gas law" applies equally to surface films

resulting from soluble substances adsorbed at the interface, as well as to sparingly soluble substances, since in dilute solutions the lowering of surface tension (surface pressure) becomes a linear function of the solute concentration (surface density).

Adsorption from Solution.

The adsorption of components from solution on to the surfaces of solid adsorbents has not as yet received any satisfactory theoretical treatment. It is, however, a phenomenon of great practical importance. Chromatographic adsorption analysis, which is dealt with more fully in a later section, has become one of the most important methods of separating natural products such as amino acids, peptides, and plant pigments. Many of the biochemical reactions catalyzed by enzymes probably occur by virtue of adsorption from solution on to the enzyme surface.

Adsorption from solution does not, in general, appear to lead to layers more than one molecule thick. For many cases the experimental data can be fairly well represented by an empirical isotherm proposed by Freundlich: $\frac{x}{m} = k_1 c^{1/n}$. Here x and m are the masses of substance adsorbed and of adsorbent, respectively; c is the concentration of the solution when equilibrium is reached; and n is an empirical constant usually greater than unity. This equation implies that if log x/m is plotted against log c, a straight line will be obtained with slope 1/n:

$$\log x/m = \log k_1 + 1/n \log c$$

Another form of adsorption is that of electrolytes from solution, and occurs as a specific reaction between ions in the solution and localized sites on the adsorbent. The reaction involved is essentially a reversible double decomposition, in which one of the reactants is free to move throughout the solution and the other is fixed to the solid surface. For example, $Na^+ + {}^+H - S = H^+ + Na^+ - S$, where S denotes the solid surface.

These ion exchange reactions occur with a number of naturally occurring materials such as zeolites and clay minerals, montmorillonite being particularly active in this respect. In general, the cations with the highest charge and smallest ionic size are most tightly held by these adsorbents. Thus the divalent cation of calcium will replace monovalent sodium ions when present from the adsorbent surfaces.

Electrical Phenomena at Interfaces.

Across any interface separating two phases there is in general a difference in electrical potential, and since electricity is atomic in nature this potential difference may conveniently be pictured as an electrical double layer. One phase acquires a net negative charge (excess of electrons), and the other acquires a net positive charge (deficiency of electrons). This double layer is diffuse in nature. The charge on the solid is rigidly fixed, adsorbed on top of which may be a practically immobile layer of oppositely-charged ions of the liquid. Furthermore, in the solution there is a diffuse layer of charge,

which may have a sign either the same as, or opposite from that of the adsorbed layer. Only this diffuse region is free to move, for example, under the influence of an applied potential difference. The potential drop in the diffuse layer is called the zeta potential.

Summarizing, it can be seen that sorption comprises a number of phenomena, the most commonly recognized of which is accumulation of one or more substances in the interface. However, orientation of the molecules in the interface is of equal importance. Combination of the sorbed substance with a solid can take place at an interface by involving either strong chemical valence bonds or weaker physical interaction through Van der Waals forces. The first is termed "chemisorption", the latter "physical type sorption". The former is confined to surface atoms, but the latter may involve many successive layers of molecules.

Sorption occurs wherever there is a surface or an interface, the most important, and also the most complex, being the interfaces between solutions and solids, such as the surfaces of all colloidal particles in any liquid medium. Thus the study of interfaces between liquids and solids is most significant for the study of colloids.

The substances sorbed in such interfaces are sometimes products of reaction or of hydrolysis, sometimes unaltered molecules, and sometimes particular ions. The last cause electrification of the surface, but surface potentials or

differences in potential between contiguous phases may also be conditioned by orientated sorbed dipole molecules, either of the adsorbent surface itself or of the sorbate (the material sorbed). Surface tension at the interface may be greatly affected by sorption, and the external properties of a liquid or solid are correspondingly modified, sometimes to a surprising extent.

Sorption is often complicated, not only by diffusion into a solid, but also by the property of surface mobility exhibited by many sorbed molecules whereby they are able to move about freely on the surface, including any pores or channels in the solid.

Another factor which must be taken into account when discussing sorption, is the effect of time. Owing to the inaccessibility of the fine pores of solids and the competition between solvent and solute, sorption may require long periods, even years, for completion. It is common experience that a stain may be removed if it is washed off immediately, but delay may make it permanent.

Finally, temperature affects sorption phenomena, because sorption is basically a "condensation" at an interface, with the heat of adsorption being equivalent to the latent heat of vaporization of a liquid; an increase in temperature reduces the sorption in the same way that it reduces condensation of vapour at a constant pressure.

Surface-Active Agents, Surface Activity and Interfacial Processes.

Substances which alter the conditions prevailing at interfaces are referred to as surface-active agents. They include cleansing materials such as soaps and detergents, water-proofing agents such as greases and tallows, and dispersing or emulsifying agents such as glue, egg white, natural gums, and synthetic surface-active agents.

Surface-active agents owe their interesting physico-chemical behaviour and their technical merits, to their property of being adsorbed at the interfaces between liquids (usually aqueous solutions) and external gaseous, liquid, or solid phases. This adsorption may profoundly alter the characteristics of an interface, the most general effect being a lowering of the prevailing interfacial tension. Lowering of the interfacial tension between a liquid and another phase (gaseous, liquid, or solid) may promote the dispersion of one phase in the other. A typical example of this is the formation of emulsions of solids in liquid media, or liquids in liquid media, both involving a great increase in the area of the interface between the two phases. Alternatively, the displacement of one fluid phase which is not miscible with the first, may be helped (or even made possible) by the fact that a surface-active agent decreases certain interfacial tensions relatively more than others. In such displacement phenomena certain types of interfaces (e.g. liquid-solid, or gaseous-solid) tend to increase in area at the expense of other interfaces of the same or different types.

The tendency for surface-active agents to be adsorbed at interfaces is due to a property named "amphipathy"; i.e. the occurrence in a single molecule or ion, with a suitable degree of separation, of one or more groups which have an affinity for the phase in which the molecule or ion is dissolved, together with one or more groups which are antipathetic to the medium (i.e. which tend to be expelled by it). These two types of groups are referred to as "lyophilic" and "lyophobic", respectively, or "hydrophilic" and "hydrophobic" if the solvent is water. In the absence of special directive forces acting in the opposite sense, the ions or molecules of the agent will be adsorbed in the interface and will be so orientated that, on the whole, they turn the majority of their hydrophilic groups towards an aqueous phase, and a majority of their hydrophobic groups away from the water and perhaps even into the non-aqueous medium. Such a phenomenon is called amphipathic or non-specific adsorption, i.e. a form of physical adsorption; it causes a reduction in the interfacial tension, because the dissymmetry in the forces on the molecules near the surface is now diminished. The surface active molecule, or ion, can be looked on as a sort of bridge between the two phases, which makes the transition between them less abrupt.

The orientation just referred to, does not imply that the molecules are necessarily closely packed in a solid film. Generally, most films of soluble surface-active agents at

liquid-air interfaces are of the so-called gaseous type, in which the molecules are free to move laterally on the surface, with a highly dynamic equilibrium between molecules in the interface and those in the solution below, the exception being foams, which may contain liquid or even solid films at the interfaces. Many interfacial films at liquid-liquid interfaces will also be of the gaseous type, though efficient emulsifying agents are usually characterised by their tendency to form films of a more condensed type. The state of adsorbed surface-active molecules at solid-liquid or solid-gas interfaces is more a matter for conjecture. Generally speaking, where the function of the surface-active agent is dynamic, i.e. where it helps a process in which fresh interfaces are being created, then it should form films of the gaseous type at the interface in question; where a surface-active agent is present and is stabilising a particular state of extension of one or more interfaces, it tends to form a more condensed type (liquid, condensed liquid, or solid). This principle means that the presence of lateral forces between adsorbed molecules or ions, may sometimes be nearly as important as their behaviour with respect to the two media which meet at the interface.

The orientation of amphipathically adsorbed surface-active molecules or ions is subject to there being no special directive forces of a more powerful nature acting in the opposite sense. In many instances, however, adsorption with orientation in the

reverse sense takes place, in which it is the hydrophilic group which is bound to the surface of a solid external phase, and the hydrophobic groups are orientated towards the aqueous phase. These cases are frequently "chemisorptions" in which the polar group is bound to certain groups in the surface of the solid by chemical linkages. The result of such a specific adsorption is that the surface of the solid often becomes more rather than less hydrophobic, so that it is more difficult to wet by aqueous media. A typical example of this phenomena is the action of flotation agents on minerals. The decreased "affinity" between the surface of the solid and the liquid medium in the case of wetting is due to a decrease in the work of adhesion liquid-solid, the magnitude of which is determined by all three of the interfacial tensions, solid-liquid, solid-air, and liquid-air.

The term specific adsorption may be used to include those cases in which adsorption is due to a positive attraction, or an actual linkage between specific polar groups in the adsorbent and in a surface-active molecule or ion, i.e. it does not necessarily imply that the surface-active agent is amphipathic, but that the configuration of the adsorbent surface has a preferential affinity for the polar groups. A considerable number of technically important surface-active agents cannot in fact be termed amphipathic, because their ultimate particles (molecules, macromolecules, or colloidal aggregates) do not have

well-defined, separate lyophobic and lyophilic regions. The lyophobic groups may even be absent. In such cases it appears that certain of the lyophilic groups are adsorbed by virtue of attractive forces or specific bonds between them and groups in the surface, especially if the surface is that of a solid. These agents may be designated as specific surface-active agents, and are often characterised by high molecular weights. In many instances surface-active agents are on the "border-line" between the amphipathic and specific types.

On an electro-chemical basis, surface-active agents fall naturally into three types, according as the surface-active unit (in aqueous solution) is an unionised molecule, an anion, or a cation, and this grouping corresponds with many of the properties of surface-active agents.

An important factor in determining the behaviour of a surface-active agent is its state of solution in the medium in which it occurs. The characteristics which confer surface-activity on a molecule or ion (notably the property of amphipathy), may also cause the individual units to aggregate into micelles. It appears that these micelles are so organised that their exteriors are made up of the hydrophilic groups in the individual molecules or ions, the hydrophobic portions being directed inwards; they are, therefore, usually non-amphipathic. In general, micelle formation causes a loss of effective surface-activity, especially if the adsorption of the

surface-active agent is simply amphipathic. In such a case the technical efficiency of the agent may represent a compromise between two opposing effects. When dealing, however, with surface-activity phenomena which are based on the highly specific adsorption of a surface-active agent (e.g. by virtue of its polar group), then it is possible that micelles could be more effective than single ions, and the formation of micelles may actually be favourable, even though it may cause a decrease in the amount of adsorption. In either event, the state of solution of the surface-active agent is obviously important.

This aspect of the behaviour of surface-active agents and the consequences arising from it will be dealt with more fully in a later section, since it appears that it may play an important role in some of the problems associated with petroleum geology.

Before attempting to discuss the action of surface-active agents on wetting properties, a brief summary of wetting phenomena and the forces controlling them must be made.

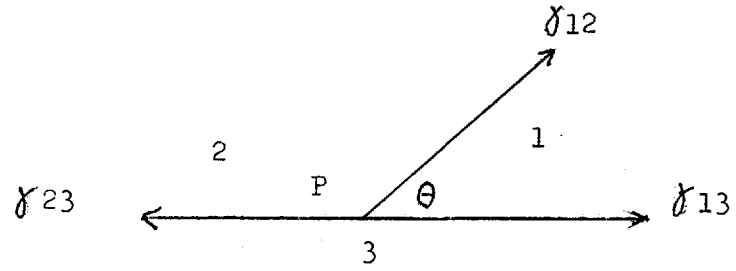
Wetting Phenomena.

"Wetting" can be defined as the process in which one fluid phase is displaced, completely or in part, by another fluid phase from the surface of a solid or liquid, although a certain amount of mutual solution of the components is not only possible but usual. In general, it is convenient to speak of "wetting" in terms of the advancing or displacing fluid phase, but

remembering that the recession of the displaced fluid phase is also taking place.

Wetting processes may be classified in terms of the changes of the total interfacial free energy which take place during the process. Thus spreading wetting, in which a layer of fluid (1) (e.g. a liquid) spreads over the surface of a solid (3), and displaces another fluid (2) (e.g. a gas), is characterised by the fact that a certain area of (3) - (2) interface (e.g. solid-gas) disappears and is replaced by equal areas of interfaces (1) - (3) and (1) - (2) (liquid-solid and liquid-gas, respectively). When one fluid completely displaces another as the result of interfacial forces, only the spreading will be spontaneous. The condition for spontaneous spreading is that there shall be a net decrease in the total free energy of the system, and is given by $dG = SdA$, where dA is the area over which spontaneous spreading occurs, and S is Harkins' "spreading coefficient", defined by $S = \gamma_{23} - \gamma_{12} - \gamma_{13}$, being the spreading coefficient of the fluid (1) against fluid (2), on the surface of a third phase (3) (e.g. a solid). For spontaneous spreading to be possible S must be greater than zero, and it may therefore be considered as the driving force behind a simple spreading process. If other influences such as gravity or mechanical work are also appreciable, then S represents the contribution of the interfacial tensions (through which surface-active agents will exert their influence) to the total process.

If the fluid (1) does not spread spontaneously and displace the fluid (2) completely, then (in the absence of other forces) a state of equilibrium may be reached in which both (1) and (2) remain in contact with the solid (3) and meet at a three-phase boundary marked P in following sketch, which represents a cross-section at the junction of the three phases. The relative wetting tendency of (1) against (2) is conveniently measured by means of the contact angle θ, which is the angle (measured inside fluid (1)) between the surface of the solid and the tangent to the boundary between (1) and (2) at P.



Treating the interfacial tensions as forces acting parallel to the surfaces a vector diagram results and the following equation is obtained: $\gamma_{23} = \gamma_{13} + \gamma_{12} \cos \theta$

It may be rewritten as $\gamma_{23} - \gamma_{13} = \gamma_{12} \cos\theta = A_{13} - A_{23}$

where A_{13} is the adhesion tension of fluid (1) for solid (3)

and A_{23} is the adhesion tension of fluid (2) for solid (3)

The above relationships are not strictly valid unless equilibrium is reached, and unless $180^{\circ} > \theta > 0$; a contact angle of zero (or more correctly disappearing) means only that S is not negative.

An alternative method of characterising wetting behaviour is by means of the work of adhesion, i.e. the work required to separate reversibly the fluid phase (1) from solid phase (3), over unit area of contact, in the presence of fluid phase (2). This is given by $W_{13} = \gamma_{12} + \gamma_{23} - \gamma_{13}$, and if $180^{\circ} > \theta > 0$, this can be rewritten $W_{13} = \gamma_{12}(1 + \cos\theta)$.

The work of adhesion, W_{13}, can be seen to be a measure of the resistance which (1) offers to being displaced by (2) from the surface of (3).

The above treatment only deals with perfectly smooth surfaces, a condition which will practically never be completely satisfied by actual solid surfaces, and a correction has to be introduced to compensate for the roughness of a surface.

This is divided into simple roughness, which has the effect only of increasing the effective areas of the two solid-fluid interfaces (the "valleys" being completely filled by the respective fluids), and a roughness which is accompanied by the formation of composite surfaces (in which the "valleys" are incompletely filled by one of the fluids).

Wenzel (1936) obtained the following equation for simple roughness: $\cos\theta_r = f_{13}\cos\theta$, where f_{13} is the "roughness factor", or the actual area of solid-liquid interface per unit area of rough surface, which will always be greater than 1. The work of adhesion to a rough surface is therefore:

$$W_{13}' = \gamma_{12}(1 + f_{13}\cos\theta).$$

The effect of this is to accentuate any differences in wetting behaviour already present. If $\theta > 90^{\circ}$, θ_r will be greater still, and if $\theta < 90^{\circ}$, θ_r will be reduced: this results in a decrease and an increase in the work of adhesion, respectively.

For composite surfaces formed as a result of porosity, the type of surface roughness has been discussed by Cassie and Baxter (1945). They consider the case in which pores in the solid-liquid interface remain filled with air, so that the apparent solid-liquid interface is in reality a composite interface containing an area f_{13} of true solid-liquid interface, and an area f_{123} of air-liquid interface, per unit area of apparent solid-liquid interface. They obtained and experimentally verified the following relationship:-
$\cos\theta_r' = f_{13}\cos\theta - f_{123}$, where θ_r' = contact angle on the rough surface. If the pores are completely filled with liquid, $f_{123} = 0$, and $\cos\theta_r' = f_{13}\cos\theta$ as above. Similarly the work of adhesion on a composite surface is given by
$W_{13}'' = \gamma_{12}(1 + f_{13}\cos\theta - f_{123})$.

The prediction here is that for a finite true contact angle , the effective or apparent contact angle θ_r' will always be increased, and the work of adhesion will always be decreased, i.e. that liquid (1) will be more readily detached from the surface than if either (a) the surface were substantially smooth, or (b) the air were completely displaced from the pores in the rough surface.

These conditions might apply in intermediate or preferentially oil-wet petroleum reservoirs where waterflooding was taking place below the bubble point, and it has been shown by Bass and Crawford (1956), Kyte et al. (1958) and others, that the presence of a free gas saturation reduces the percentage of residual oil remaining after flooding. Thus this relationship may aid the purely volumetric effect of the free gas in reducing the residual hydrocarbon content in reservoirs of intermediate wettability.

As mentioned previously the true contact angle θ is only attained when a state of equilibrium is reached. This "true" contact angle, however, varies depending whether fluid (1) is advancing across (3) or receding; a "hysteresis effect" is therefore in evidence. It seems likely that one cause of this contact angle variation is the result of an ageing effect caused by prolonged contact of the surface with a fluid. Apparently this is due to the molecules of the solid becoming re-orientated during contact with the liquid so as to reduce the interfacial tension as far as possible. This in turn may be the result of diffusion towards the solid surface of small quantities of surface-active impurities, as well as reorientation of any amphipathic molecules present.

The Effect of the Adsorption of Surface Active Agents on Wetting Properties.

The adsorption of a surface-active compound at any interface can generally be assumed to be accompanied by a decrease in

the interfacial tension, as has already been stated.

In a case of spreading wetting, the likelihood of the spreading coefficient being positive, and hence spontaneous spreading occurring, is increased if an added surface-active solute is adsorbed at the interface (1)-(3) and/or (1)-(2) (e.g. solid-liquid and for liquid-air). It is therefore, not surprising that most surface-active compounds which cause water to spread on solids, or which favour the maintenance of stable films of water on solids, also lower the surface tension of water (against air), although the converse does not necessarily hold. Following from this any tendency for the spreading coefficient to become more positive (or less negative) as a result of such an adsorption at the solid-liquid interface will also, if it is finite, tend to decrease the contact angle.

Adsorption at the (1)-(2) (e.g. liquid-air) interface will also decrease the contact angle if it is already less than 90°, but will increase it if it is greater than 90°.

In the case of adhesional wetting of a solid by a liquid, adsorption of a surface-active agent at the solid-liquid interface again favours wetting, i.e. increases the reversible work necessary to separate the liquid from the solid. Adsorption at the liquid-air interface, on the other hand, is always unfavourable to adhesional wetting, i.e. γ_{12} is reduced. It is seen, therefore, that both types of

wetting are favoured by adsorption at the solid-liquid interface, but contrary to the usual assumption, adsorption at the liquid-air interface, or in the case of two liquids, the liquid-liquid interface (and hence lowering of the liquid-air or liquid-liquid interfacial tension) is not always favourable, but depends on the type of wetting involved. The same observations apply equally to rough surfaces, with the proviso that the presence of a surface-active agent will possibly change a composite surface into a simple rough one by the complete displacement of phase (2) from the pores.

Chapter II

THE COLLOIDAL NATURE OF PETROLEUM AND ITS SURFACE ACTIVE CHARACTERISTICS.

Introduction.

Of the three phases involved in the oil-water-mineral matter relationship the first is without doubt the most complex and least understood. Crude oils exhibit a wide variation of physical properties from the heavy, black viscous oils, comparatively poor in hydrocarbons (sixty per cent) as found in the Pliocene of California, to the very light low-viscosity oils, almost wholly hydrocarbon in composition (neglecting the condensate reservoirs which for the sake of this discussion are classified as natural gas). They are often classified as paraffinic-base, naphthenic base, mixed-base (naphthenic-paraffinic) oils according to their relative richness in hydrocarbons of these groups, although a fourth classification of asphaltic-base crudes, if the distillation residue consists largely of asphalts, is also used. For the most part, however, the elemental analyses of these various types of crude do not differ appreciably and they have 83 to 87% carbon, 11 to 14% hydrogen, oxygen, nitrogen and sulphur in amounts varying in general up to 2 or 3%.

The differences that exist between crude oils result from the relative proportions of the light, medium and high-molecular-weight hydrocarbons present, and also from differences in the

relative proportions of the hydrocarbon groups (paraffins, naphthenes, aromatics) within equivalent molecular weight fractions. Thus Smith et al. (1959) point out that Miocene crude oils from the Gulf Coast contain a large proportion of the total hydrocarbons (40%) in the gas oil distillation range (200 - 300°C) in marked contrast to oils from other areas of the United States (average 25%). This fraction from the Gulf Coast crudes is high in aromatic components, and in this respect is similar to the naphtha fraction (distillation range up to 200°C). The gas-oil fraction of the Tertiary oils of California, on the other hand, although having a high aromatic content like those from the Gulf Coast, represents only 25% of the total oil on average, whilst its naphtha fraction is relatively deficient in aromatics. In spite of this seeming disorder, however, a reasonably consistent and systematic relationship has been found within the hydrocarbon type groups in different crude oils. Thus the ratios of the various members of the paraffin-type hydrocarbons in one crude are very similar to the ratios of these compounds in other oils, and similar consistent relationships exist within the naphthene and aromatic groups (Forziati et al., 1944; Cady et al., 1952; Smith and Rall, 1953; Hood et al., 1959).

This systematic relationship, which appears to bring order out of chaos, has led Baker (1959, 1960a, 1960b) to formulate a theory that the hydrocarbons dispersed in fine-grained

non-reservoir rocks, have accumulated to form crude oils as a result of their transportation to the reservoir rock in colloidal solution. The solubility of a homologous series of hydrocarbons in the interior of the colloidal partilces or micelles, formed from the association of colloidal electrolyte ions (e.g. soaps), is very much greater than that in water, and is comparable, in fact, to their solubility in a hydrocarbon solvent. The relative micellar solubilities of the various members of a series are similar to the systematic relationships found within crude oils.

Although this theory has its drawbacks, the principal one being the mechanism of hydrocarbon release from the micelles, it is consistent with the composition of the various hydrocarbon groups. According to Baker's theory, the differences in overall composition of oils are accounted for by the nature of the original source material and the variations in colloidal electrolytes available to solubilize the hydrocarbons. One of the important features of the theory is the association it provides between crude oil origin and colloid chemistry.

The Colloidal Nature of Crude Oil.

It is not suggested, however, that the only association of crude oil with colloid chemistry is connected with the peculiarities of hydrocarbon distribution. Although the presence of colloidal particles in crude oils has long been debated, it is only since the work of Witherspoon (1958),

using an ultracentrifuge, that the colloidal nature has been finally confirmed. The oil components which exhibit colloidal properties are the resinous, asphaltic, and non-hydrocarbon material. The presence of complex non-hydrocarbon polar material forms the link between the hydrocarbon components and any interfacial activity associated with external solid or liquid phases.

Various fractions of the asphaltic material from petroleum have been separated by their differential solubility in a light aromatic-free petroleum ether, such as pentane. The insoluble materials are called asphaltenes and the soluble material the maltenes. The latter have been separated by O'Donnell (1951) into saturates containing naphthenic oils of 2 to 5 condensed ring structures, and wax, monocyclic and dicyclic aromatics, substituted benzothiaphenes, and resins consisting of nitrogen-, sulphur- and oxygen-containing aromatics. The precipitated asphaltenes are similar in composition to the resins, but appear to be generally of greater molecular weight, which accounts for their insolubility. The structure of the asphaltenes appears to consist of a mixture of aliphatic chains intermixed with fused aromatic ring sheets (Erdman, 1961), their x-ray patterns being similar to that obtained from blending a polyethylene (chains) and a carbon black (condensed aromatic sheets) (Yen et al., 1961). They are not unlike the synthetic rubber Buna-S,

produced by the emulsion polymerisation (in the micelles of colloidal electrolytes) of butadiene, and the aromatic styrene (phenyl ethylene) found in coal tar (which is readily polymerised in sunlight or oxygen, but can be stored in light petroleum if an antoxidant such as quinol is added).

Based on solubility, viscosity, and ultracentrifuge studies, the asphaltenes appear to be relatively small (2,000--5,000 molecular weight) discrete colloidal particles with a strong tendency to associate even in good solvents, resulting in apparent molecular weights of the order of 40,000 (Winniford, 1960). The general concept of the asphalts present in oils is that the asphaltenes are the centres of micelles, with the various maltene materials adsorbed on the surface of the asphaltene particles. According to Pfeiffer and Saal (1940) the structure of the micelle is such that the substances with the greatest molecular weight and most pronounced aromatic nature form the nucleus around which are arranged lighter and less aromatic constituents with a gradual transition to preponderantly aliphatic compounds, i.e. there is no distinct interface either within the micelle or between it and the surrounding environment. Thus the asphaltenes are fully peptized so long as there are sufficient constituents for the formation of the outer regions of the micelle. The action of the non-aromatic solvents appears to remove part of the peptizing layers of maltenes, and the adsorptive forces that

cause the formation of the micelle are then not fully compensated, resulting in the mutual attraction of asphaltenes, with their subsequent flocculation and precipitation. Heithaus (1960) has shown that the concentration of asphaltenes depends not only on the relative quantity and physical properties of the asphaltenes and maltenes present, but also on the solubility or peptizability of the asphaltenes in a solvent medium. The corollary to this is that the concentrations of asphaltenes in crude oil are dependent on the source and type of asphaltenes available and the combined solvent properties of the remainder of the crude oil, i.e. a solubility equilibrium exists within a given oil between the asphaltenes and the solvent medium.

Eldib et al., (1960) have correlated asphaltene concentration with nitrogen, carbon residue, vanadium, nickel, sulphur and non-hydrocarbon content of an oil, based upon the separation by ultracentrifuge of the colloidal materials present in the oil, showing that the colloidal particles of petroleum are rich in these components. No sedimentation of colloidal asphaltenes was observed when a de-asphalted oil was ultracentrifuged; this supports the evidence that the material precipitated by petroleum ether is colloidal. However, the results of precipitation methods prove only that the substances are physically similar, that is polar. The centrifugation results indicate a physical or chemical

association of asphaltenes with much of the nickel, vanadium, and nitrogen present in crude oil.

The non-hydrocarbon Constituents of Crude Oils.

These include the nitrogen, sulphur and oxygen compounds amongst which are the acids and bases present in petroleum.

Most of the nitrogen content is in the material distilling above 275°C, with an average of almost 90% in the residium obtained from Bureau of Mines distillation at 300°C at 40mm. pressure of mercury. The nitrogen content of crude oil is quite low and usually between 0.01 and 0.3% by weight, but in a few cases rises to as much as 0.8%. As most of the nitrogen is present in the asphaltic fractions it has been found that for oils from formations of the same geological age, but from widely different localities, there is a relationship between the nitrogen content and carbon residue of the crude oil, the latter being roughly representative of the asphaltic components present. This is further confirmation of the association of nitrogen-containing compounds with the colloidal material present.

In general the oils from the younger formations (Tertiary and Cretaceous) have a higher nitrogen-carbon residue ratio (0.07 and 0.05, respectively) than those from older formations which appear to have reached a lower and more constant value (approximately 0.04), and this suggests a preferential removal of the nitrogen compounds. These are

speculative conclusions and certainly must be considered in the light of geographical variations as well as geological conditions. An alternative conclusion is that source materials and environment as well as time, have a role in the maturation of petroleum.

The form in which nitrogen is combined is also important, and the work of Bailey in A.P.I. Research Project 20 has been reported by Lochte and Littman (1955). A large number of basic nitrogen compounds, including pyridines, quinolines, benzoquinolines, tetrahydroquinoline, indoles and pyrroles, have been identified. The basic nitrogen compounds account for one quarter to one third of the total nitrogen, regardless of total nitrogen and crude oil source (Richter et al., 1952). The quantity of basic nitrogen increased with boiling range, but the ratio of basic to total nitrogen remained constant, except for some fractions in the middle distillate range where it increased. The only non-basic nitrogen compound so far positively isolated and identified is a carbazole.

Porphyrins are also nitrogen compounds, being a complex of four pyrrole rings joined by methyl groups. They are derived from plant and animal pigments (chlorophyll and haematin), and have the ability of forming stable complexes with several metals, usually vanadium, nickel, and iron. They are present in very small amounts associated with the asphaltic residues of crude oils in which they occur. The porphyrin contents

of American oils of low asphalt content, such as Bradford, Oklahoma City "Wilcox", and Bartlesville crude oils are very small. Their presence in the asphaltic components of crude oils supports the contention that the asphaltic components are of a primary character, and that porphyrin complexes are related to the organic matter deposited during the sedimentation phase of formations which subsequently act as source rocks.

Not all the vanadium and nickel present in crude oils is associated with porphyrin complexes, possibly only 3 to 10% of the vanadium present being thus associated (Dunning et al., 1960). There is, however, some evidence that a large part of the vanadium in many oils is present as nitrogenous complexes. A total of 43 elements have been identified in crude petroleum in trace amounts, many of which appear to be present in the form of oil-soluble organo-metallic compounds, including possibly such compounds as metallic salts of organic acids.

The sulphur content of crude oils varies from 0 to 4% by weight, the average being about 1%. Only a limited number of sulphur compounds have so far been isolated from petroleum, the light distillates having either a thiol group (sulphur-hydrogen) as a side-chain or a sulphur atom replacing one or more carbon atoms (thia group) in the normal hydrocarbon types found in crude oil, i.e. normal and iso-paraffins, naphthenes,

aromatics, and naphthene-aromatics. The structure of the sulphur compounds in general appears to parallel the structure of the predominant hydrocarbon group in a given fraction. Thus alkanethiols and thiaalkanes are present in the naphtha fraction, and sulphides of penta- and hexa-cyclic naphthenes above 200°C, with a gradual transition from mono- to bi- to tri-cyclic compounds with increasing molecular weight of the gas oil range. Similarly the aromatic sulphur compounds appear to predominate in the heavier fractions, with a trend from benzothiophenes through dibenzothiophenes to polybenzothiophenes.

Finally the non-hydrocarbon constituents of petroleum also include oxygen-containing compounds, the oxygen content of petroleums varying from 0.1 to 4.5% by weight. The only oxygen compounds which have received detailed attention are the petroleum acids. These are present mainly in the form of naphthenic acids, and reach their maximum concentration in the gas-oil fraction. They range from 0.03% by weight of total crude for an Iraq sample to 3.01% for a crude oil from Kettleman Hills, California (Pliocene). Phenols and aliphatic fatty acids are also present, the latter mainly in the naphtha fraction. However, palmitic, stearic, myristic, and arachidic acids have also been separated as solids, from Japanese and Polish petroleums.

The origin of these acids is closely linked with the

organic origin of petroleums, some of them being optically active. One acid 2,2,6-trimethyl-cyclohexane-carboxylic acid is related rather simply to the carotenoids found in Californian petroleum. According to Lochte and Littman (1955) there may be a genetic relationship between the naphthenic acids and the nitrogen bases in petroleum, since the Californian oil containing the above mentioned acid also contains 2,2,6-trimethylcyclohexyl pyridine as the most plentiful of the higher bases separated from it.

Other oxygen-containing compounds present occur as esters, alcohols, aldehydes and ketones, but little work has been done so far in characterising them. The resinous and asphaltic components of petroleum also contain a considerable proportion of the total oxygen present combined in some form other than the functional groups already listed. A Russian crude, for example, contains 8.2% of natural resins with an empirical formula $C_{41}H_{57}O_2$ (Gruse and Stevens, 1942). The asphaltenes on analysis show approximately the following composition C 85.2%, H 7.4%, S 0.7%, and O 6.7%.

Surface and Interfacial Tension.

In general the surface tension values for crude oils, as measured at surface conditions, lie between 24 and 38 dynes/cm., an average value being 30 dynes/cm. These values are markedly reduced by dissolved hydrocarbon gas and carbon dioxide, and also by a rise in temperature. Muskat (1949) has estimated

that for pressures and temperatures in excess of 3,000 psi. and 150°F, respectively, the surface tension may be of the order of 1 dyne/cm.

The measurement of interfacial tension of oil against brines gave values of 13.6 to 34.3 dynes/cm. for the thirty-four crudes examined, compared with 50 dynes/cm. for pure straight-chain, and cycloparaffins, and 34 dynes/cm. for the simple aromatic hydrocarbons (Livingston, 1938). Under subsurface conditions an increase in dissolved gas increases the interfacial tension against water, the rise being of the order of 3 dynes/cm. for pressure rises of 1,000 psi. For pressure increase with a fixed content of dissolved gas the interfacial tension decreases.

Although the interfacial tension of an oil fraction against water may change markedly after refining, its surface tension is often not greatly altered, thus it has been observed:-

Table I

	Interfacial Tension dynes/cm.	Surface Tension dynes/cm.	
Raw kerosene fraction	35.5	26.1	Gurwitsch,
Refined kerosene fraction	42.4	26.7	1926.
Raw lubricating oil fraction	29.4	31.3	Johansen,
Refined lubricating oil fraction (after filtering through Fuller's Earth)	42.6	31.7	1924.

The reduction of the interfacial tensions of crude oils and its unrefined distillates is a result of surface-active substances concentrating at the limiting surface of water or salt solution, this concentration effect being the principal cause of crude oil emulsions. The formation of emulsions is caused by the concentration of resinous and asphaltic substances, together with naphthenic soaps, at the limiting surface of the two liquids, which in turn reduces the interfacial tension. At the same time this concentration allows thin films to form which are of sufficient stability to withstand the disruptive action of the already lowered interfacial tension. As stated by McBain (1950) "a low interfacial tension or a high viscosity, or the inevitable electrical charges are each insufficient factors to stabilize an emulsion. A solid coating, a polar compound, or a film is best. Sometimes it is evident that the stabilizing agent is present in the form of a tough coherent, or plactic film". He goes on to cite as an example a brine emulsified in natural petroleum from Fitts Pool, Oklahoma, and draws attention to the wrinkled skin around the droplets and the crystals of salt in the droplets of saturated brine as shown in microphotographs of the emulsion.

An empirical rule which has been found to rest on a strict thermodynamic basis is that of Bancorft. This rule states that the continuous medium is that in which the

stabilizing agent is more soluble. A corollary to this rule which appears to be valid for solid stabilizing materials is that the continuous medium is that which preferentially "wets" the solid. Thus the stability of emulsions formed by resinous compounds is a function of the type of oil in which the resins occur as is shown by the following Table.

Table II

Interfacial Tension Against Water. dynes/cm. (after Gurwitsch 1926).

	Pure.	0.1% resin.
Benzene	32.6	28.8
Refined lubricating oil	28.9	26.9
Refined kerosene	42.4	38.6
Refined gasoline	48.1	35.5

The change in interfacial tension resulting from the addition of resins decreases as the initial interfacial tension of the refined oil decreases. This is in accord with the theory of Gibbs, since the resins are more strongly concentrated at the interface for gasolines than for kerosenes, and kerosenes more than for lubricating oils owing to their decreasing solubility in successively lighter fractions. The stability of emulsions formed by shaking these solutions with water bears this out, the gasoline-resin-water emulsion being the most stable, the lubricating-resin-water emulsion the least.

More recently Greenlee (1960) has corroborated these

observations with simulated crude oil emulsions of 25% water-in-oil composition, the oil phase consisting of various proportions of toluene and heptane with 1 gm. of asphalt per 100 ml. of oil. The rate of breakdown of these emulsions increased with the increase in the percentage of toluene present, the fastest breakdown occurring with 100% toluene. He states that a large amount of asphaltene may be ideally dispersed as "sol" particles (size of particles based on ultracentrifuge studies is 40Å, Ray et al., 1957), when substantial quantities of petroleum resin (or protective colloid) and/or oil aromatics (for solvation) are present. In other cases, when the amount of resin or oil aromatics is very small, relatively little asphaltene can be dispersed in the oil. Thus oils may be either "saturated" or "undersaturated" with respect to their asphaltene content, depending on the quantity of resins and/or aromatics present, and may be in a state either near to or far from dispersion equilibrium. If the oil is near saturation with asphaltenes, i.e. where minor changes such as the addition of paraffinic solvents would initiate some bulk flocculation, then this incipient flocculation may be sensitized in the "hydrous" vicinity of the water-oil interface. Here, aqueous surfaces initiate flocculation by providing an antagonistic local environment. The resulting films, capable of stabilizing the water droplets around which they are formed, may vary in

thickness from a mono-layer to a heavy pellicle, depending upon factors which are probably very complex.

Finely divided matter, such as moderately fine sand, will adhere to the limiting surface of an emulsion, assisting in the formation of very strong and stable films. This is a result of the preferential wetting of the grains by one or other of the liquids present; a very stable emulsion is formed in this way. Emulsions of this type have been found in fluids produced from Russian and Roumanian oil fields. Under the microscope it is seen most clearly that these emulsions consist of countless irregularly shaped oil droplets, suspended in water, their surfaces being covered by minute sand grains. Their stability is such that neither heating nor the addition of naphthenic soaps will cause breakdown. The oil can only be separated from them, and by no means completely, by agitation with a small amount of coarse sand which mechanically breaks down the films (Gurwitsch, 1926).

The Nature and Properties of the Interfacially-active Components in Crude Oils.

The stability of crude oil-water emulsions and the association of emulsion formation with the asphaltic and resinous components present in the oils has led to detailed studies of the interfacially-active components causing stability. One of the first attempts made to characterise these components was carried out by Bartell and Niederhauser (1949) as part of

A.P.I. Project 27 which was concerned with "The Function of Water in the Production of Oil from Reservoirs."

Using a pendant-drop method, i.e. a droplet of oil attached to a capillary opening and extending upwards in water, they observed tough membranous films which formed a folded and wrinkled skin on retraction of the droplet into the capillary. Thus the material adsorbed at the interface did not return into the oil phase as the droplet was reduced in size, but became more concentrated until the film became solid, followed by rigid resistance to any further decrease of the interfacial area. If, after the wrinkling had started, the oil was again forced out of the capillary an elongated cylindrical cigar-like shape was formed, similar in diameter to the bore of the capillary. As these elongated "sacs" gradually became filled out with oil, they decreased in length whilst they grew in volume, until after a short time they again assumed the regular shape of an ordinary drop. If the oil was re-emitted more slowly the wrinkles of the skin unfolded and the drop gradually returned to a normal shape. The drops continued to expand smoothly with further additions of oil, the thin film never perceptibly resisting expansion, thus suggesting spontaneous spreading over any new surfaces formed.

The formation of these films was time-dependent on the formation of the original drop and varied widely for different

crude oils and solutions of crude oil constituents. This time effect indicates that the adsorption of the film-forming material is a slow process. A partially retracted drop giving a wrinkled form, gradually returned to a normal rounded shape if allowed to stand, possibly due to resolution of film-forming material or to redistribution of the material at the interface. The films formed in the case of crude oils were tough and pliable, and could be folded and unfolded repeatedly. The fact that the observed behaviour of the solid interfacial films was due to an adsorption process and not a chemical reaction occurring at the interface, was supported by the accompanied lowering of the interfacial tension.

The film-forming tendency was assessed by considering the ratio of the length of the residual drop when wrinkling of the surface started, to the original length of the drop before retraction, expressed as a percentage. This ratio was determined after various time intervals because of the increase in film-forming tendencies with the age of the drop.

Bartell and Niederhauser (1949) extracted these film-forming materials from a Californian crude oil (Rio Bravo) by means of a water spray process which sedimented the materials in a water-in-oil emulsion. The emulsion recovered was centrifuged, the oil layer extracted with benzene, and the interfacially-active material concentrated by further

water spray extractions of the oil-in-benzene solution. The weight of material finally separated was 0.007% of the total crude, and it showed the following general properties:

1) It was a hard black, non-crystalline material, which when heated, swelled, and gradually charred without melting. In transmitted light it appeared as black particles embedded in a reddish, translucent, resinous-appearing film.

2) The density of the material was 1.35 gm./ml., and its molecular weight was 1,600. The thickness of the interfacial films formed by the material were 30 ± 3Å.

3) It was insoluble in pentane, but was increasingly soluble in benzene, carbon tetrachloride, carbon disulphide, chloroform, and pyridine in the order given.

4) Although of an apparently colloidal nature, colloidal particles could not be detected by ultra-filtration due to the adsorption of the material by the collodion membrane used.

5) For a given weight of activated adsorbent (charcoal and silica gel) it was preferentially adsorbed by the finely ground as opposed to large particles, suggesting that the material does not penetrate the very fine porous structure of the adsorbents, but is adsorbed only on the external surfaces.

6) Its general properties classify it among the resinous

and asphaltic materials, but it represented only 1.17% by weight of the asphaltene content of the oil; the asphaltene content being 0.6% of the oil.

7) Very strong film-forming tendencies and an advancing contact angle of oil against water on silica of 180°, i.e. oil-wet, by a 0.1 mgm./cc. solution of the material in benzene indicated its highly surface-active nature.

Benzene solutions of the resins and asphaltenes separated from the crude were found to become more interfacially-active with time of exposure to air (several months) in spite of their storage in darkness. Similar behaviour was found for benzene solutions of the residual crude oil after water-spray extraction. This led Bartell and Niederhauser to the conclusion that oxidation during storage was the principal cause of the film-forming tendencies of crude oil. This belief was supported to some extent by the poor to moderate film-forming tendencies of anaerobically-collected crude oil samples against their associated reservoir brines and against distilled water. Generally speaking, however, the film-forming tendencies and the interfacial tension of the oils against their associated brines were less than against distilled water. This suggests that the lack of surface activity was due, in part at least, to surface-active materials in the brines reducing the interfacial tension values and at the same time inhibiting in some way the formation of stable

films. It was further indicated that the reduced interfacial tension values and possibly the film-forming tendencies of the oils against their associated reservoir brines, were due to a reaction taking place between the constituents of the oils and brines (e.g. the formation of a complex naphthenic acid with calcium or magnesium ions). Although the prolonged ageing of an oil in air resulted in increased film-forming tendencies and a reduced interfacial tension against distilled water, equivalent to 0.01% by weight of film-forming material, the actual weight of oil oxidized was 0.3%, i.e. only 3.3% of the material oxidized was interfacially active.

A contrary view to that of Bartell and Niederhauser regarding the presence, under reservoir conditions, of film-forming material and its effectiveness in anaerobic conditions, has been presented by Reisberg and Doscher (1956). According to these workers the fact that drops of crude oil pendant up in distilled water exhibit ageing curves, i.e. a relatively rapid decrease in interfacial tension followed by a gradual attainment of equilibrium, is merely a characteristic of systems containing adsorbable constituents. They also found that after ageing, sudden retraction of the pendant drop to the point just prior to that where the drop appears to be encased in a membraneous structure resulted in an abrupt decrease of interfacial tension. The ageing of the compressed interface produced by this sudden retraction produces a

relatively rapid increase in interfacial tension, followed by a slow attainment of the final equilibrium value, i.e. that just prior to the retraction. In one example this decrease was of the order of 45% of the original interfacial tension before retraction.

Like Bartell and Niederhauser (1949) they also noted the pronounced wrinkling effect of the membrane encasing the pendant drops on further retraction beyond that necessary to demonstrate the sudden reduction of interfacial tension. They noticed, however, that when an aged drop was withdrawn completely into the orifice and then re-expelled various unpredictable angular forms appeared which were stable for at least several days. As before, if the volume of the drop was increased after the development of such rigidity, a normal-shaped drop formed, but the interface, viewed in reflected light, appeared to have remnants of the membraneous material suspended in it.

Film rigidity was observed at temperatures as high as 90°C, and with 50% solutions of crude oils in such solvents as carbon disulphide, benzene, and carbon tetrachloride. The particular significance of these observations is that they were made under rigorously anaerobic conditions, and that similar conditions were maintained during the collection of the oil samples from wells; photochemical effects were also minimized by the use of a low-actinic glass wherever possible.

Reisberg and Doscher, therefore, concluded from the above observations that a film of material is irreversibly produced upon compression of the interface. This monomolecular insoluble film formed by the retraction of pendant oil drops after ageing in contact with water may be used to measure the concentration and molecular diameter of material adsorbed at the interface by the application of the Gibbs adsorption equation to the system (Harvey, 1960).

Having noted that Bartell and Niederhauser (1949) were unable to isolate the interfacially-active materials by adsorption upon activated carbon and silica gel because desorption of the most strongly adsorbed fraction was not possible by prolonged soxhlet extraction with such solvents as alcohol, acetone, ether, benzene, toluene, and carbon tetrachloride, Reisberg and Doscher further concluded that the adsorption was not a reversible process. They made use of this irreversibility by using finely divided sugar as the adsorbent which, after washing successively with benzene to remove the oil, and 1 : 1 benzene and isopropyl alcohol to remove the less strongly adsorbed polar material, was dissolved in water in the presence of benzene. A benzene-insoluble fraction collected at the interface, and a benzene-soluble fraction was recovered by evaporation of the solvent. A separation of one litre of Ventura D-7 crude from California using this technique yielded 650 mg. of material eluted by

benzene and isopropyl alcohol (fraction 1), 450 mg. insoluble in benzene after dissolving the column in water (fraction 2), and 350 mg. of benzene-soluble material extracted from the water solution of the column (fraction 3).

The association of these fractions with the resins and asphaltenes was again suggested by their high carbon-to-hydrogen atomic ratios of 0.7 to 0.9. The two soluble fractions were also found to be very rich in ester and carboxylic groups, and had oxygen contents of 4% (1) and 16% (3), the acid numbers being 16 and 13 (mg. KOH per gm.), resepctively. The oxygen content of the benzene-insoluble fraction was 7%, the asphaltene fraction of the crude containing less than 2% oxygen by comparison. The acid numbers of the entire asphaltene and resin fractions were less than one and seven, respectively. The average molecular weights of (1) and (3) were 700 and 400, respectively, compared to 1200 for the resins and 3400 for the asphaltenes. Vanadium, sulphur, and nitrogen were present in all three fractions. The interfacially-active materials, therefore, appear to constitute a highly oxygenated, low-molecular-weight fraction of the resins and asphaltenes.

Tests performed on glass with benzene solutions (1 mg./cc.) of these surface-active materials showed, as expected, an increase in the equilibrium contact angle of sessile water drops as a result of continued exposure to these solutions,

i.e. they rendered the solid surface progressively more hydrophobic.

Bartell and Niederhauser (1949) had noted that the film-forming tendencies and interfacial tensions of crude oils were quite sensitive to slight changes of pH of the aqueous phase with which they were in contact. This observation led Reisberg and Doscher (1956) to investigate the influence of pH on the interfacially-active material. They tested the interfacial properties of the crude oil over the pH range from 1 to 12, and found that at a pH in excess of 8 rigid film formation became negligible. The interfacial tension over this range varied from 27 dynes/cm. between a pH of 5 to 9 down to 7 dynes/cm. at pH 1 and 12. At a pH of 12.7 the interfacial tension had dropped to 0.02 dynes/cm.

These results indicated that a water-soluble surface-active material had been produced in situ by the action of the alkali on the crude oil. At concentrations of sodium hydroxide below 0.5%, the addition of salt to the aqueous phase lowered the interfacial tension to less than 0.01 dyne/cm. The surface-active material that caused this lowering of interfacial tension was extracted by shaking the oil for several days with a 0.5% solution of sodium hydroxide. It was found to be a black highly viscous material with an acid number of 160, an equivalent weight of 350, an average molecular weight of 700, and a carbon-to-hydrogen atomic ratio of 0.7. Its surface

tension was intermediate between that of oleic and naphthenic acid. The interfacial tension of the residual oil remaining after the extraction of this material was 26 dynes/cm. as against 0.02 dyne/cm. for the original unextracted oil when measured against a 0.5% sodium hydroxide solution, demonstrating its highly surface-active nature. Benzene solutions of the extract formed rigid films at acid and neutral aqueous interfaces. Emulsions of water and the residual oil were very unstable compared with emulsions of water in the unextracted oil.

The fact that the surfactant produced by the reaction of crude oil with an alkaline solution was capable of displacing the interfacially-active asphaltic aggregates responsible for the rigidity of the neutral interfaces led Reisberg and Doscher to the use of synthetic surfactants in an attempt to reproduce this effect. They found, however, that the solutions of commercially available surfactants investigated were incapable of lowering the interfacial tension significantly below 1 dyne/cm., although these substances eliminate the rigidity of the crude-oil-water interface. The interfacial tension of alkaline solutions ($pH > 12$) of nonionic surfactants in contact with the oil was also higher than that of the corresponding alkaline solution alone.

Denekas et al. (1951) used the water-spray technique to separate surface-active substances from an Oklahoma City crude

obtained from the Wilcox sand of Ordovician age, and which is responsible for the preferential oil-wetting of the reservoir rock by creating a hydrophobic surface on the sands with which it comes in contact. From 7.5 litres of oil, only 1.1 gm. of surface-active material was obtained. The main constituent was one gram of an acetone-insoluble, brown, waxy powder, shown on analysis to be normal-paraffins ranging from fifty to eighty carbon atoms per molecule and only slightly soluble in hot chloroform or hot benzene. Thus it is likely to be present in crude oil as finely divided micro-crystals, possibly stabilized by a protective colloid which might be oxidized to a hydrophilic state.

A second carbon tetrachloride-soluble fraction of 90 mgm. consisted of a pitch-like substance which appeared to be a mixture of saturated hydrocarbons of lower average molecular weight than the first fraction. The third fraction, carbon tetrachloride-insoluble and acetone-soluble (10 mgm.), was shown to have olefinic-type unsaturation; its solubility characteristics placed it in a group of neutral compounds including ketones, esters, quinones, ethers and unsaturates.

Dodd et al. (1952) continued work on the above oil and performed a similar type of extraction of the Californian oil used by Bartell and Niederhauser and on a Venezuelan sample. The extracts were fractionated by means of chromatography using pure calcite granules as the adsorbent, any material

not eluted by a series of solvents of increasing polarity being obtained by dissolving the adsorbent in hydrochloric acid and recovering the insoluble residue. Arc-emission spectroscopy was used to detect the trace metals present in the various fractions. Interfacial tensions and film-forming tendencies of the crudes, water-spray extract solutions and fractionated extract solutions were determined by the pendant drop method.

Although vanadium, iron, zinc, copper, nickel, titanium, calcium and magnesium were present in the water-spray extracts as a whole, only vanadium was present as a major constituent of all three oils.

The extraction technique did not remove all the surface-active constituents from the oils, and the film-forming tendencies remained strong in the Oklahoma and California extracted crudes, in spite of the rise in interfacial tensions. The film-forming tendencies of the North American crude oil water-spray extracts were strong as would be expected, but they were only moderate in the Venezuelan extracts, correlating with the respective interfacial tensions of the extracted solutions.

The trace metals associated with the chromatographic fractions showing the greatest lowering of interfacial tension were zinc, copper and calcium. The film-forming tendencies of the fractions on the other hand, showed no such correlations,

and in one case the fractions with the greatest film-forming tendencies had the least effect in lowering interfacial tension. Another point of interest was the concentration of all the titanium and most of the magnesium in the residue recovered by dissolving the adsorbent, i.e. it was associated with the most surface-active material.

Evaporation of the pyridine-eluted fraction from one of the extracts gave blue-green water-soluble, prismatic needles containing large amounts of copper (around 10%), and showed considerable ionization in aqueous solution. Their absorption spectra indicated that they were copper salts of fatty acids and copper complexes of proteins similar to bovine albumen. Micro-analysis of part of the water-spray extracts from the Californian oil suggested a nitrogen-metal ratio similar to that of porphyrins.

Confirmation that metal-porphyrin complexes make a considerable contribution to the surface-active properties of crude oil was obtained by Dunning and his associates (1953, 1954). Using the same technique as that employed by Skinner (1952) for isolating a vanadium porphyrin complex from a Californian oil, Dunning et al. (1953) investigated the interfacial properties of fractions extracted from another Californian oil of Pleistocene age (Tulare Formation).

The method consisted of initially precipitating the asphaltic material with propane under pressure, followed by

successive solvent extraction of the precipitated material with pentane, hexane, heptane, iso-octane, cyclohexane, benzene and pyridine. The interfacial tensions against water decreased and the film-forming tendencies increased with successive extracts, paralleling the increase in the complexity of the asphalts in the extracts. Nickel and vanadium porphyrin complexes were identified in the extracts and, with the exception of the pyridine-soluble extract, their interfacial activity correlated with their respective concentrations of porphyrins.

Dunning et al. (1954) also extracted the Tulare oil by means of a water-spray, followed by successive solvent extraction of the water-spray extract with pentane, hexane, iso-octane, cyclohexane and benzene. Metal-porphyrin complexes were associated as before with all the extracts; a considerable amount of nickel, with lesser amounts of vanadium, being the principal types of complex in the hexane and iso-octane extracts. The water-spray extraction procedure caused a decrease in the interfacial tension but not in the film-forming tendency of the crude oil.

The surface activity of the porphyrins appears to be dependent on the polarity of any side chains present, as well as on metal-complex formation. The surface-active properties of porphyrins also vary with changes in the hydrogen-ion concentration of the aqueous phase with which they are in contact (Dunning, 1953).

By isolating vanadium and nickel complexes from the raffinate of a de-asphalted crude oil, Dunning and Rabon (1956) demonstrated that these constituents are not entirely restricted to the asphaltic material. They separated 30 p.p.m. of porphyrins from the raffinate (83% of the crude), compared with 200 p.p.m. for the total crude oil. Their ability to lower the interfacial tension of a standard benzene solution against water, and their film-forming tendencies, however, were reduced as compared with those of a solution of the total oil porphyrins. This reduced surface activity correlated with the finding that the porphyrins involved were mainly decarboxylated types, and therefore less amphipathic than the carboxylated complexes occurring in the asphaltic material. The occurrence of these normally hydrocarbon-insoluble metal porphyrin complexes in the raffinate of crude oils appears to be the result of solubilization, i.e. colloidal solution, by naturally occurring substances which have been observed in association with them.

Further evidence for the wide distribution of surface-active components in crude oils has been provided by an investigation of their occurrence in eight lubricating oils from different crudes (Groszek and Palmer, 1961). The surface-active material, separated by chromatography on magnesium oxide, followed by dissolving the adsorbent in

acid and solvent extraction of the residual solution, varied from 0.1 to 0.65% by weight of the lubricating oil. Its molecular weight was of the order of 1,000, and its elemental analysis indicated that it contained between 6 and 7% oxygen, suggesting the presence of more than one oxygen-containing group per molecule. The infra-red spectra of the materials were essentially those of a hydrocarbon type oil containing hydroxyl, carbonyl, and sulphoxide groups. The peak heights for the carbonyl groups in the benzene-acetone fractions eluted from magnesium oxide were less than those in the surface-active materials, and the same applied to the peaks characterizing the hydroxyl groups. The strong retention of the surface-active materials by the alkaline oxide and their acid values indicated that they had acidic properties. The properties of their mono-molecular films on water suggested that they contained either more than one polar group per molecule or that they had a high degree of branching in the hydrocarbon group above the polar group attached to the water surface. Their behaviour on an alkaline aqueous surface was typical of films formed by acids or phenols, the end groups of which ionize and repel one another by virtue of their ionic charges. The saponification values were higher than the acid values, indicating the presence of ester or other saponifiable groups. The quantity of carbonyl groups present in the

surface-active material was further correlated with their ability to disperse carbon black in n-heptane.

Adhesion of Oil to Solid Surfaces.

A possible correlation between the surface-active material indigenous to the various distillation fractions of crude oils and their ability to wet initially hydrophilic solid rock surfaces (sandstone and limestone) has been investigated by Denekas et al. (1959). Thirty oil fractions obtained by molecular distillation up to 200°C at pressures down to three microns of mercury and the residues (20 to 40%), together with oil fractions of varying polarity and molecular structure fractionated by chromatography, were dissolved in a non-polar solvent (xylene) and diluted to their concentrations in the original crude oils. Their ability to wet an initially hydrophilic porous rock was measured as the "relative rate" of imbibition of water by the porous rock after prolonged contact with an oil-in-solvent fraction, and expressed as a percentage of the initial imbibition rate of water by the hydrophilic porous rock, i.e. prior to contact with the oil solution. Thus 100% would be zero wetting to oil, whilst zero per cent would be 100% oil-wet. In certain instances the contacting of the hydrophilic rock with oil residues and the unfractionated oils resulted in no water imbibition, but did allow oil to be imbibed; this was expressed as a negative value.

For the distillation fractions the wetting capacity increased in general with molecular weight, i.e. the higher the boiling point of the fraction the greater was its effect in reducing water wettability of the rocks. Sandstone was generally more prone to a reduction of water wettability by the fractions than limestone. The distillation residues either reduced the wettability of both sandstone and limestone to a neutral or near neutral state, or caused a reversal (negative rate); similar results were obtained for the unfractionated oils. This further confirmed what had previously been demonstrated by other workers, namely that a considerable portion of the surfactants in crude oils are very high-molecular-weight compounds. However, many of the relatively low-boiling fractions significantly reduced the water wettability of the rock samples.

A hydrophilic sandstone column on which a Pennsylvanian oil had been fractionated retained 1% of the oil after successive washing with n-heptane. Of the oil retained 70% was eluted by benzene, and this fraction (in xylene) reduced the relative imbibition rate of a sandstone to near neutral wettability. The oil remaining after benzene elution was recovered by successively more polar solvents (chloroform, methanol, methanol-pyridine, acetone), and the fractions obtained were similarly examined with respect to their effect on sandstone wettability. Each of these solvent fractions,

which eluted successively less material, also reduced the relative wettability, but not to the same extent as the benzene-eluted fraction. Thus, in spite of the weakly polar nature of the material in the benzene fraction its relatively high concentration caused a marked decrease in sandstone wettability. Taken on a unit weight basis, however, the more polar fractions, as might be expected, were successively more efficient in reducing the relative imbibition rate with the increasing polarity of their constituents. It is, therefore, not essential to have highly polar surface-active materials in a crude oil for it to cause the preferential oil-wetting of a rock, so long as there is a sufficient quantity of less polar surface-active material available.

The influence of the type of polar group present in a crude oil on its oil-wetting characteristics was investigated by separating the basic organic material (mainly nitrogenous compounds) from a Miocene oil. The effect of this basic material was to cause near neutral wettability of both sandstone and limestone. The residual oil remaining after the extraction of basic material was similarly tested, causing oil-wettability of sandstone, but having little effect on the wettability of limestone. This result was somewhat surprising since the residual oil should contain all the acidic components initially present in the oil, but in spite

of this, the basic surface of limestone was apparently unaffected; limestone is, on the other hand, sensitive to the basic nitrogenous components. Similarly sandstone, which has an acidic surface, was nearly as sensitive to the acidic components as to the basic components of the crude. It appears, therefore, that the adsorption of surfactants to rock surfaces is not a simple acid-base reaction, and that those surfactants which have the most effect on the wettability of limestone are probably nitrogenous organic compounds.

The residual oil, after extraction of the basic components, was further spearated chromatographically on alumina, and six fractions were obtained, each eluted by a successively more polar solvent. These fractions were tested for their influence on the wettability of sandstones and limestones. As for the unseparated residual oil, limestone was only very mildly affected by two of the fractions (benzene eluted, -fraction 4, and methanol eluted, -fraction 6), the remainder being completely ineffective. Sandstone on the other hand, was affected by five of the six fractions, one fraction (the second eluted, 10% benzene in pentane) having a mild effect, whilst the other four caused near-neutral wettability (fractions 3, 4, 5, 6,), the fifth fraction (50% benzene in propanol) actually causing a negative imbibition of water. The only fraction not affecting sandstone wettability was the

first fraction eluted (4% benzene in pentane). Thus the selective adsorption of different types of surfactants by sandstones and limestones was positively demonstrated.

The complexity of the relationship between surface-active materials present in crude oils and rocks, particularly sandstones, was therefore shown, as was the widespread occurrence in crude oil of different types of surfactants capable of adsorption by the rocks. It does appear, however, that the wettability of sandstone reservoirs may be governed by the total concentration of the surfactants in a crude oil rather than by the presence of a specific type. This is in direct contrast to limestones which are apparently particularly sensitive to the basic nitrogenous type of surfactants.

Summarizing the findings of the various workers in this field, it has been found that the majority of the most surface-active materials present in crude oils are associated with the high-molecular-weight components in distillation residues. Furthermore, they are closely allied in their physical properties to the resinous and asphaltic materials present in the residues, and like these materials appear to exist in colloidal suspension in crude petroleum. They contain trace metals combined as metal prophyrin complexes, and as the metal salts of fatty acids. As well as neutral and acidic surfactant components, many of the basic nitrogenous

components associated with these residues have highly surface-active properties. Although the bulk of the surface-active material is of a non-hydrocarbon nature, containing nitrogen, sulphur and oxygen, there is evidence that some high-molecular-weight paraffin waxes also contribute to the surface-active properties of petroleum.

Two effects of these surface-active materials have been observed which normally occur together, but on occasions are capable of an independent action. The first is their ability to lower the interfacial tension of petroleum hydrocarbons against water, and the second their ability to be irreversibly adsorbed at interfaces, forming stable insoluble films. It is not suggested that each specific type of surfactant is capable of producing both these effects, but rather that the specific types present are able to produce one or other, and that they are complementary in their overall action. Their total concentration in petroleums is generally of the order of less than 1% by weight.

The Influence of Water on the Adhesion of Oil to Solid Surfaces.

It will be recalled that the interfacial tension between two liquid phases does not in itself give direct information concerning the strength of the adhesion of either phase to a third solid phase. The measurement of a contact angle in conjunction with the interfacial tension is necessary before

adhesion tension values can be obtained, and these measurements have been made by Benner et al. (1942) for crude oil-water-silica systems. For the eight crude oils examined they found that the pressure of displacement of oil by water and of water by oil from silica, calculated from contact-angle measurements of crude-oil-water systems on silica plates, agreed with actual measurements of pressures for the same crude-oil-water systems in packed-silica powder plugs. With all the crude oils investigated there was hysteresis of the interfacial contact angle, i.e. the oil-water interface gave one angle against silica when water was advancing, and a different angle when water was receding. All of the water-receding angles measured were less than 90°, whereas the majority (7 out of 8) of water-advancing angles were greater than 90° (measured through the water). It was further shown that spontaneous displacement of oil by water occurred only when both angles were less than 90°, and that no spontaneous movement occurred when the angles were on opposite sides of 90°. The most significant fact brought out by the work was that so large a percentage of the oils gave advancing interfacial contact angles greater than 90°, indicating that the surface underlying the oil had become hydrophobic as a result of the adsorption of surface-active materials from the crude oil.

Further light has been thrown on the mechanism and

conditions of oil retention and displacement from initially water-wetted solid surfaces by the work of Reisberg and Doscher (1956). Using a simple qualitative test involving the upward drainage, due to buoyancy, of oil adhering to a glass microscope slide, after its immersion in water, they found for a clean, dry microscope slide that its retention of oil after immersion was dependent on the time the slide was in contact with the oil prior to immersion in water, i.e. if briefly contacted with oil the oil was quickly displaced, but if exposed for several days, little or no displacement occurred. This applied for both distilled water and 5% sodium chloride solution as the aqueous phase. When the slide was initially contacted with distilled water prior to its contact with crude oil (Ventura D-7) and then re-immersed in the same distilled water phase as the initial wetting phase, it was found that the oil was not readily displaced, in spite of oil contact of only a few minutes. When a sodium chloride solution was used in place of distilled water similar results were obtained, except that a longer exposure of the solution-wetted slide to the oil was necessary (10 days) for the retention of an unbroken film of oil on re-immersion in the solution.

They extended these experiments to include pre-wetting aqueous phases of varying pH (2, 6, and 11), and found that an alkaline solution induced a high degree of oil displacement

whereas an acidic solution (which had the same interfacial tension against crude oil as the alkaline solution, 12 dynes/cm.) and a neutral solution (interfacial tension 27 dynes/cm.) caused no displacement. Even when the pre-wetting aqueous phase was neutral, the immersion of the oil-covered slide in an alkaline phase caused displacement, whilst an acidic phase was ineffective. These results suggested that the formation of stabilized rigid films at the interface between oil and water-wetted solid, responsible for the apparent wetting of the latter by crude oil, is dependent on the pH of the aqueous phase.

Whilst a solution of a non-ionic commercial surfactant (Triton x-100) showed a slightly higher displacement rate of oil from a slide pre-wet with distilled water than a 0.5% sodium hydroxide solution (approximately 2 hours), a combination of the two solutions accomplished an almost instantaneous displacement. The interfacial tensions of the three solutions against the oil were 0.9 dyne/cm., 0.02 dyne/cm., and 0.7 dyne/cm. respectively, showing that instantaneous oil displacement is not dependent on a low oil-aqueous phase interfacial tension alone. An important observation made in connection with the alkaline surfactant solution was that it discoloured rapidly, probably owing to solubilization of some material from the crude oil.

The difference in behaviour of the alkaline solution alone

and the alkaline surfactant solution indicated that there was some factor unrelated to the oil-water wetted solid. In order for this process to occur, it is necessary for the contact angle (measured through the oil) to be raised from a value below 90° to a value above 90°. From an examination of the equation $\gamma_{sw} = \gamma_{so} + \gamma_{ow}\cos\theta$ it was realized that either γ_{sw} must decrease or γ_{so} must increase.

According to Reisberg and Doscher γ_{so} will increase if either or both of two processes occur:

1) The alkali reaction product or the surfactant present in the aqueous phase finds its way into the oil phase and is therein negatively adsorbed, or

2) A component of the oil which is initially positively adsorbed at the oil-solid (water wetted) interface becomes solubilized in the aqueous phase.

The first of these alternatives is unlikely to occur. It is likely, however, that the alkaline surfactant solution promotes solubilization in the aqueous phase of oil-soluble polar components, and especially of the material formed by reaction of the alkali with the crude oil, thus rendering these components unavailable to the oil-solid (water wetted) interface. If the polar material produced by the interaction of crude oil with an alkaline solution is responsible for the very low interfacial tension between the oil and the aqueous phase, then the addition of a non-ionic surfactant, capable

of inactivating the above material through solubilization, should result in a higher interfacial tension against oil. As noted previously this was found to be the case.

γ_{sw} for the alkaline surfactant will be less than for either of the separate solutions, alkaline and surfactant, only when the water-soluble micelles are more strongly adsorbed at the aqueous phase-solid interface than the individual components of the micelle. However, no argument can be presented in support of such an effect.

This phenomenon of stabilized interfacial films at oil-solid (water wetted) interfaces accounts for the very stable emulsions formed when moderately fine sand adheres to the limiting surface of crude oil-water emulsions, and for the Russian and Roumanian oilfield emulsions already described, which were exceedingly difficult to break down. Similar aggregates of sand, water, and asphalt-rich petroleum occurred in the tubing and flowlines of Ventura D-7 producing wells. Physicochemical examination of the aggregates suggested that they had been formed as a result of the adsorption and stabilization of rigid films at the surfaces of the water-wetted sand grains (the concentration of water in the aggregates was always greater than the concentration of water in the produced fluids). Injection of an alkaline surfactant solution, as used in the above experiments, into the annulus of the wells so that it mixed with the produced

fluids as they entered the tubing, prevented any further formation of these aggregates.

Conductivity measurements of the thickness of water films in a water-filled glass capillary into which a slug of oil had been injected supported the view that a film of water lies between the rigid films of the oil and the glass surface, since the conductivity was much higher than for a corresponding system in a siliconed (hydrophobic) capillary (no measurable water film). The thickness of the aqueous film of a surfactant solution (0.8Å) was greater than that of water (0.2Å; actually sodium chloride solutions in all cases) and an alkaline solution had an even thicker film (10×10^3Å).

The thickest aqueous film of all, however, existed for the oil slug and an alkaline surfactant solution as might be expected (40×10^3Å). The presence of sodium hydroxide is the common factor in all systems for which a very large value of the water film thickness was calculated, and is probably related to the strong adsorption of hydroxyl ions on glass and similar surfaces.

Similarly an interesting comparison was made between the effect of an alkaline solution and surfactant solutions on crude oil adhering to water-wetted solids and the effect of similar solutions on a crude oil adhering to a hydrophobic solid. It was found that crude oil adheres strongly to a

hydrophobic lucite slide whether or not the slide is first immersed in water, and the crude oil was not readily displaced by an alkaline solution. The significant difference in behaviour of the hydrophobic solid was attributed to the low value of γ_{so} by virtue of the non-polar nature of the crude. Reaction of the polar components with alkali possibly led to a further decrease in γ_{so}. Although hydroxyl ions and water-soluble reaction products probably lower γ_{sw}, the reduction is insufficient to offset the low value of γ_{so}. Raising the concentration of commercial surfactant in the aqueous phase did, however, eventually lower γ_{sw} sufficiently to cause a slow displacement of oil from the lucite slide.

The hysteresis of interfacial contact angle in crude oil-water-silica systems first noticed by Benner et al., was confirmed by Reisberg and Doscher for the flow of crude oil in a single non-uniform capillary. It was observed for Ventura D-7 crude flowing from a capillary section into a large diameter pore that the meniscus of the oil-water interface suggested a preferentially water-wet system for neutral and acid solutions (water receding). This situation remained only so long as the oil was moving into an area not previously contacted by the oil. If the direction of flow was reversed so that the oil moved on to an area previously in contact with oil, then the meniscus suggested that the system was preferentially oil-wet.

Results comparable to those obtained from the retraction and ejection of aged pendant oil drops were obtained when oil was allowed to age in the section of largest diameter, and then retracted into the constricted section of the capillary, i.e. marked wrinkling occurred as the interface was compressed, and on ejection into the enlarged portion of the capillary the oil entered it in the form of long slugs of the same diameter as the constricted capillary. If, however, the capillary was first filled with an alkaline solution, the contact angle always remained less than 90° (through the water) regardless of the flow direction, and no wrinkling or slug formation was observed. It appears that once oil has moved through a capillary and formed a rigid interfacial film with the water present in the capillary, a continuous flow channel to oil bounded by these rigid films is formed.

From waterflood displacement experiments, the use of alkaline surfactant brine solutions appears to result in 100% recovery, compared with 54% for an alkaline brine solution and only 46% for a neutral brine.

Chapter III

PRELIMINARY INVESTIGATIONS OF SORPTION PHENOMENA IN CRUDE OIL-WATER-FINE GRAINED MINERAL MATTER SYSTEMS.

Materials.

In case any sorption effects were small and therefore not easy to observe, together with the importance of fine-grained argillaceous rocks in petroleum geology, the solid materials used throughout have been clays; their small particle size and consequent large specific surface would increase the chances of detecting sorption.

The argillaceous materials used were as follows:

Table III

Name.	Principal Mineral Constituent.	Source.	Formation.	Age.
Fuller's Earth.	Calcium montmorillonite.	Redhill, Surrey.	Lower Greensand.	Cretaceous.
Aquagel.	Sodium montmorillonite.	Wyoming.	Mowry.	Cretaceous.
Gault clay.	Illite.	Dunton Green, Kent.	Gault.	Cretaceous.
China clay.	Kaolinite.	Cornwall.	Weathered Granite.	

These materials are not made up entirely of pure clay minerals; they also contain other minerals, mainly of silt size. Nevertheless, any differences in properties of the materials may be attributable largely to the nature of the clay minerals present.

In order to provide experimental material approximating

to a crude oil, yet without some of the disadvantages of crude oil, samples of residual oil were obtained by distillation of crude oils under a pressure of 1mm. of mercury at 100°C. This is equivalent to a boiling point of between 280 to 300°C at atmospheric pressure, and the raffinate includes all fractions above the gasoline and kerosene range, or normal paraffins with sixteen or more carbon atoms per molecule. These "topped" crude oils avoid the difficulties arising from the use of the more volatile original crudes, ensuring better reproducibility of the oil samples, both before and after the tests. Distillation under reduced pressure, and at low temperature, precludes any likelihood of extensive breakdown of the constituents due to thermal cracking, and thus the oils are likely to resemble crude oils closely, apart from the absence of the more volatile components. Quantitatively they represented over 60% of the original crude oils.

Details of the two "topped" crude oils are given in Tables IV and V. Both oils are of Tertiary age, but quite different in character, the Mercedes residue being black and very viscous, whilst that from Ancon is brown and quite fluid; they also differ markedly in asphalt, sulphur and ash contents.

For convenience in what follows the topped crude oil will generally be referred to as oil.

Table IV

Country of Origin	Field	Well no.	Producing Formation	Age
Venezuela	Las Mercedes	M-253	Upper C sand	Miocene or Oligocene
Ecuador	Ancon	1002	Socorro sand	Upper Eocene

Table V

Properties of Residue After Vacuum Distillation at 1 mm. of mercury to a temp. of 100° C.

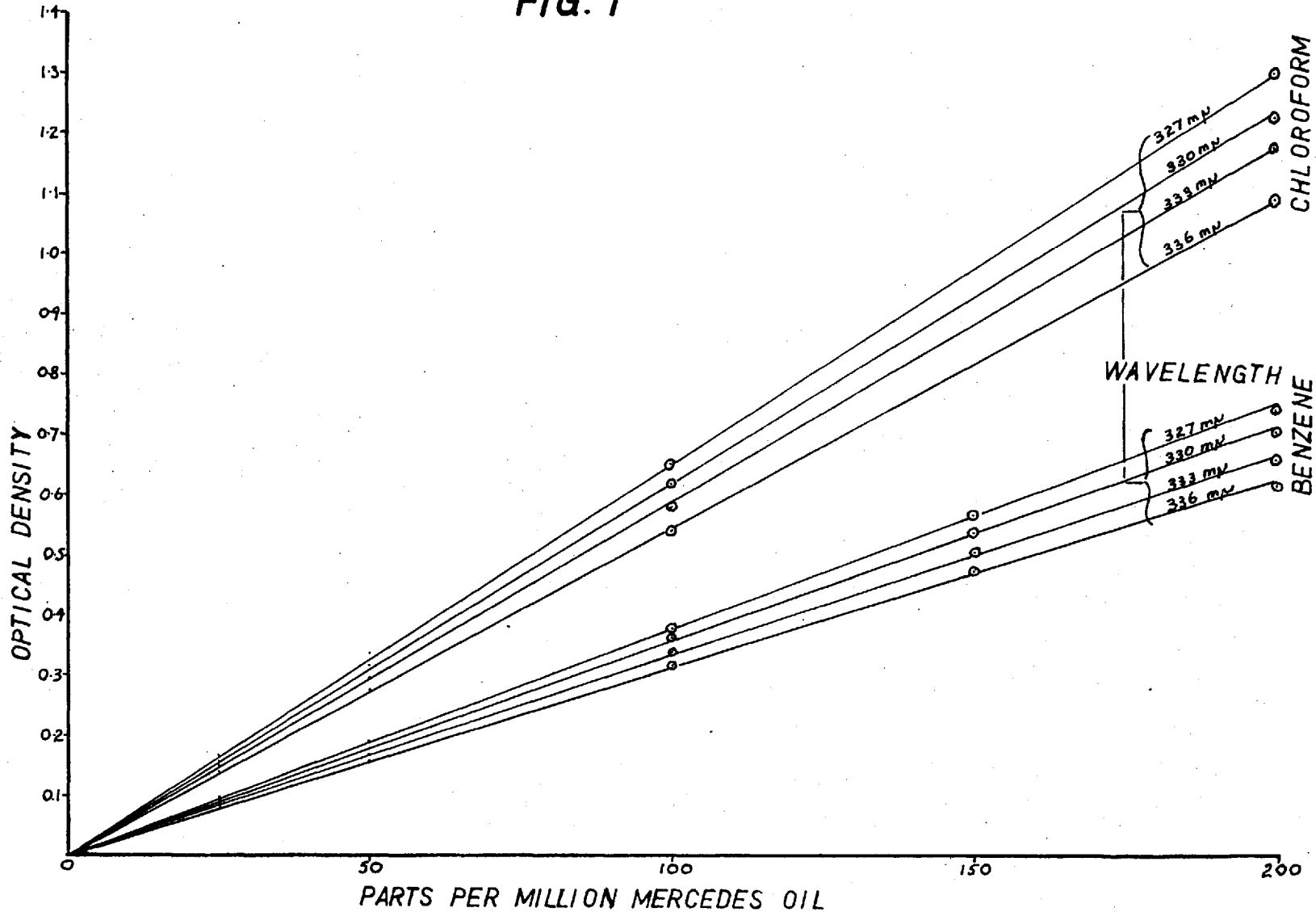
Field	% of original crude by wt.	Specific gravity	Asphaltene content, % residue	Sulphur content, % residue	Ash content, % residue
Mercedes	64.2	0.9103	7.2	0.88	0.026
Ancon	66.5	0.9122	0.09	0.101	0.004

Development of Experimental Procedures.

In the first experiments mechanical stirring was used in attempts to incorporate the oil in a slurry of water and clay. This method was, however, found to be somewhat ineffective, because there was not sufficient breakdown of the oil into small globules. As a result there was poor distribution of the oil in the slurry.

Following this a method was developed in which a fine dispersion of oil was obtained by shearing a mixture of oil and distilled water. This was accomplished in a simple type of colloid mill such as is used in making artifical cream, the suspension being recycled two or three times to ensure a thorough breakdown of the oil into small globules.

FIG. 1


OPTICAL DENSITY
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
50
100
150
200
PARTS PER MILLION MERCEDES OIL
CHLOROFORM
327 mμ
330 mμ
333 mμ
336 mμ
WAVELENGTH
BENZENE
327 mμ
330 mμ
333 mμ
336 mμ

The suspension was not a stable emulsion, and coalescence of the droplets, followed by gravity separation, commonly termed "creaming", took place. After preparation the original suspension was allowed to stand for sixty minutes in order to allow the excess oil in suspension to cream, leaving a reasonably fine stable suspension. Bramley (1959) has shown that the rate of separation decreases logarithmically with time. The relatively stable suspension could be handled and mixed with a clay slurry with comparative ease.

The concentration of oil in such a suspension was obtained by treating a known volume of suspension with a solvent, normally benzene or chloroform, and finding the amount of oil in the solvent, either spectrophotometrically, or gravimetrically after evaporation of the solvent. The spectrophotometric proceedure, based on Beer's law, requires measurements of the optical density of the solution with light of given wavelength, and comparison of the result with a set of standard plots, of optical density against concentration for the particular oil and solvent. The calibration curves are straight lines passing through the origin, and were determined at a room temperature of 70°F. (see Fig. 1).

The suspensions prepared by the above method were mixed with the clay-water slurries, either by shaking or by allowing the slurry to settle through them, thus obtaining, as far

as possible, an even distribution of oil and clay in water. A flocculated clay after shaking with or settling through an oil-in-water dispersion, always carried down all the oil present (of the order of 0.1 gm./gm. of dry clay) leaving the supernatant water clear. At no time was any oil observed to have separated at the surface by buoyancy, this being in agreement with the work of Poirier and Thiel (1941), who found that for a variety of fine-grained sediments in sea water, one gram could carry down, on average, from 0.6 to 1.21 cc. of 0.865 specific gravity oil. They also showed that the volume of oil sedimented was generally inversely proportional to the size of the mineral grains, and that the oil was carried down by the weight of mineral grains adhering to the globules. These high oil-to-clay ratios were never approached in the present experiments, so the absence of free oil at the surface after sedimentation was complete, is not surprising.

The present experiments, together with the results obtained by Poirier and Thiel, indicate that some mechanism of "trapping" is operative. Poirier and Thiel favoured a physical mechanism involving weak forces, the effects of which are most prominent in fine-grained, large-specific-area materials, aided by neutralization of the double layer around the individual particles of clay and oil due to the presence of electrolyte lowering the zeta potential, thereby

allowing them to come into contact. Murray (1926) in earlier experiments, had suggested a purely mechanical means of deposition by the mud particles.

With regard to the mechanisms that might account for the observed "trapping" of oil by wet clay, the following possibilities must be considered:-

a) There is no "surface" interaction of any kind, other than purely mechanical sweeping out by an excess of clay particles, as suggested by Murray, i.e. the oil is absorbed or occluded by the clay.

b) Non-specific or physical adsorption occurs, as put forward in brief by Poirier and Thiel.

c) Specific or chemical adsorption takes place.

Since crude oil is a complex mixture of hydrocarbons and non-hydrocarbons, it is possible to have a combination of any or all of these mechanisms, or in an extreme case one of them could apply to the oil as a whole.

If the first alone applied one would expect dilution, followed by deflocculation and dispersion of the clay, to release the oil and allow it to separate and "cream", due to the reduction in the "blanketing" effect of the excess clay. This was not found to be the case. Microscopical examination showed the presence of a number of spherical droplets in the interstices of the flocculated clay, but as well as these there were fibrous filament-like structures formed by very

fine oil films in contact with the clays. Poirier and Thiel noted similar features. They are apparently the result of fine clay particles adhering to the oil droplets, causing a reduction in the interfacial tension between the oil and water, and allowing the oil to spread out rather than to stay as compact masses. They lack surface uniformity, and remain as stable, flaky, stringy aggregates. Similar results were obtained when an oil suspension was shaken with initially deflocculated clay, suggesting that the interaction is not primarily dependent on the double layer of the clay particles having been neutralized by electrolyte.

Having obtained intimate mixing of the oil and clay in water, the next step was to try to find if a detectable change had taken place in the oil. The method employed for separating the oil from prepared samples was solvent extraction, similar to the procedure used in determining the oil concentration of the oil-in-water dispersion. Pure hydrocarbon solvents (principally benzene) were used in the majority of cases, because of their non-polar character and the unlikelihood of their influencing the system by being adsorbed themselves, although chloroform was also used on a number of occasions, i.e. the extraction solvent was similar to that used for determining oil-in-water dispersion concentration. They are not, however, entirely satisfactory since extensive emulsion formation took place when they were

shaken violently with the samples. This is partially the result of the solid clay particles acting as an emulsion stabilizer as described by Pickering (1907), and possibly of stabilization caused by sorption of oil components at the oil-water-solid interface. Large solvent-to-sample volume ratios were, therefore, found to be necessary during extraction, in order to obtain even small volumes of clear supernatant solvent for quantitative determinations. This unfortunately reduced the accuracy of the determinations, owing to the small concentration of oil in the extracting solvent, and the small quantity of this solution which is available for quantitative determinations. Successive extractions with equal volumes of solvent were used in an attempt to ensure maximum possible recovery.

As well as emulsion formation, which increased with an increase in the clay content of the sample, another problem was that of solubility of the oil in the solvent used. In the case of the Mercedes oil asphaltene precipitation took place when n-heptane was used. Benzene, although it removed the precipitation problem, is somewhat more polar than the straight-chain aliphatic paraffin. Both these difficulties might have been avoided by the use of some solvent such as cyclohexane, which is intermediate in behaviour between the n-heptane and benzene. The problems of asphaltene precipitation and emulsion stability are in fact complementary according

to Greenlee (1960). It is not, however, the precipitated asphaltenes that stabilize water-in-oil emulsions, but the conditions which promote an approach to bulk flocculation or precipitation which is involved, i.e. the alteration of the oil by the addition of an aliphatic solvent tends to induce the flocculation of asphaltenes which are then more susceptible to adsorption and film formation at an interface prior to their actual precipitation in the bulk of the liquid.

A further source of uncertainty in the solvent extraction of the clay-water-oil complexes became apparent when an attempt was made to repeat some of the results. It was found that the length of time spent in shaking the solvent with the clay-water-oil complex in order to release the entrapped oil is quite important. Gentle mechanical shaking by a rocking motion failed to release the oil to any noticeable extent, again substantiating the observations regarding the unlikelihood of simple oil release. Violent manual shaking was found necessary, and as stated above, this resulted in the formation of quite stable emulsions.

The question arose as to what should be the procedure for obtaining data which can be compared on a sound basis, e.g. should a complex of clay-to-oil ratio of two to one say, be shaken twice as long as one with a one to one ratio, or for the same period but with double the volume of solvent, or should the treatment be identical in the two cases?

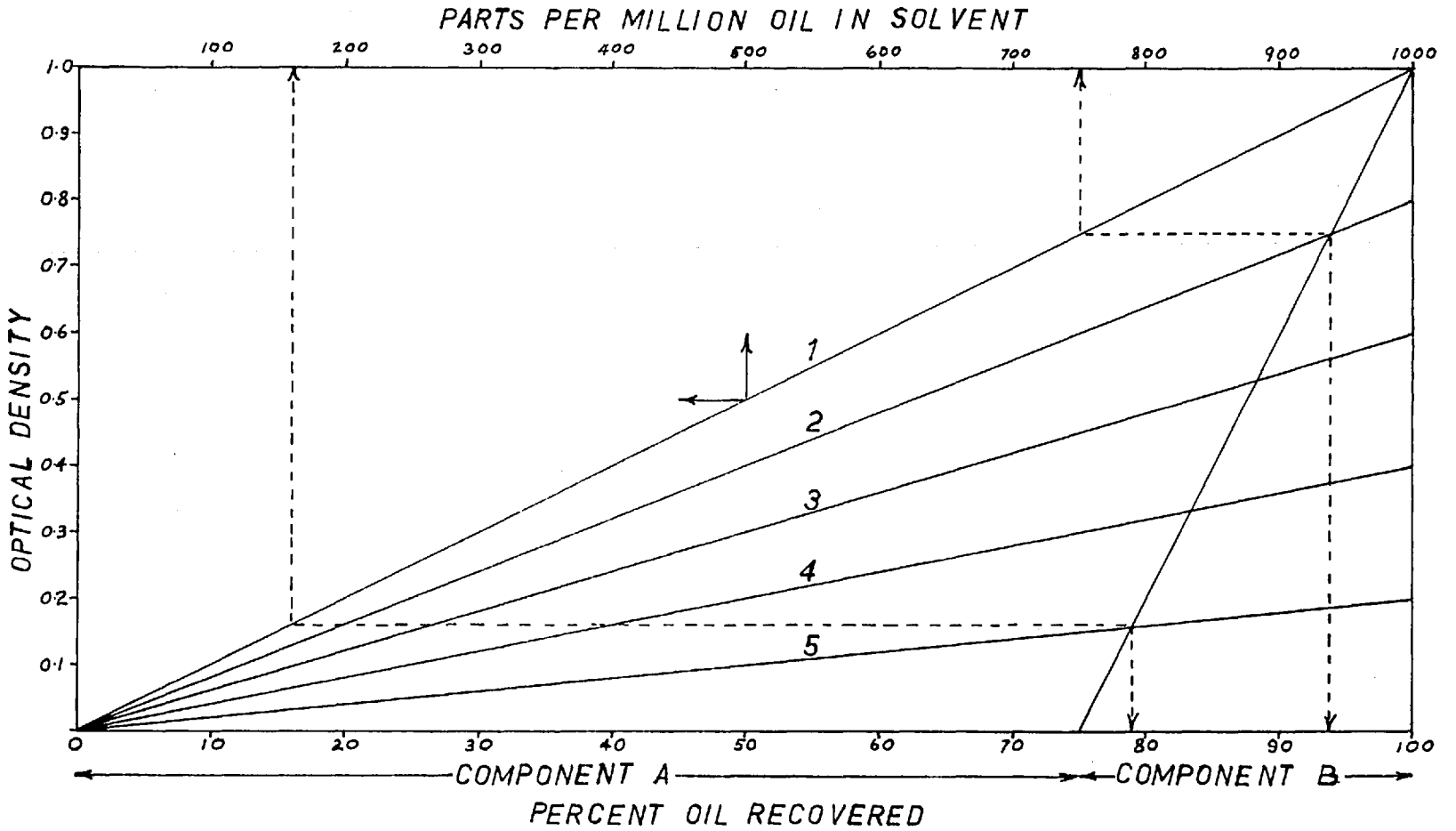
Attempts made to answer this question have thrown little light on the subject, since there is always the added unknown of the nature of the clay-water-oil interaction and the degree to which this affects the oil recovery in each case.

Having separated some of the oil from the complex by solvent extraction, determination of the weight of oil recovered raised other difficulties. Because small quantities were being used, very accurate weighing was necessary. This was done by the use of a Stanton automatic balance which reads to 0.0001 gm.

In some of the early experiments the solvent was removed in an oven at 110°C, but due to possible losses and alteration of the residue, this method was abandoned, and the solvent was removed in a stream of air at room temperature.

Determination of the weight of oil recovered by spectrophotometric means is not necessarily quantitatively accurate, because oil recovered by solvent extraction may differ in properties from that used to obtain the calibration curves. This will not be apparent from spectrophotometric measurements, unless complete spectra are determined on the oil before and after the experiments. Normally, however, the calibration curves are determined at certain wavelengths only, and therefore, they depend on a small portion of the constituents present. This is acceptable when the concentration of unaltered original oil in solution is to be

FIG. 2


PARTS PER MILLION OIL IN SOLVENT
100
200
300
400
500
600
700
800
900
1000
OPTICAL DENSITY
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
1
2
3
4
5
0
10
20
30
40
50
60
70
80
90
100
COMPONENT A
COMPONENT B
PERCENT OIL RECOVERED

measured, since dilution or concentration affects all the constituents equally.

This point may be clarified by reference to Fig. 2, which relates to a hypothetical two-component oil.

Let A be that component of the oil which does not absorb light at the wavelength at which the calibration curve was determined; it amounts ot 75% by weight. Let B be that component which absorbs light at the given wavelength; this is 25% by weight.

Curve (1) is the calibration curve for the original oil in a given solvent at different dilutions.

If the oil is recovered unaltered or components A and B are adsorbed in the same proportion as they occur in the original oil, then the calibration curve will give the weight of oil recovered, provided that the same solvent is used. If, on the other hand, one component is adsorbed preferentially to the other, then the calibration curve is no longer a guide to the amount of oil recovered.

Assuming that component A is adsorbed preferentially to component B, then as component A does not absorb light at the given wavelength the weight of oil recovered, as deduced from the calibration curve, will be greater than that actually recovered, i.e. the calibration curve is based on the concentration of B in the solution and is independent or nearly so, of the concentration of A. On the other hand if B is

adsorbed preferentially to A the reverse is true, as is shown in Fig. 2, where an optical density reading of 0.75 suggests from the calibration curve that 750 p.p.m. of original oil are present, whereas actually 937 p.p.m. are present. Similarly, a reading of 0.16 suggests 160 p.p.m. are present, i.e. 840 p.p.m. adsorbed, whereas 790 p.p.m. are actually present, assuming that in both cases component A is not adsorbed, but remains in its original concentration. The above state of affairs is always a possibility in a solution of mixed composition.

In the simple case illustrated, true quantitative determination might be possible by making a calibration curve for each component at different wavelengths, provided that the absorption spectra of the two components are sufficiently different in form for each to be calibrated at separate wavelengths, for which their spectra do not mutually interfere to any great extent. Referring to their calibration wavelengths as their "key" wavelengths, L_A and L_B for components A and B, respectively, the following procedure could be adopted.

Since from Beer's law the optical density at any given wavelength is directly proportional to solution concentration, the ratio of the optical densities of a solution at two different wavelengths is constant regardless of its concentration. Thus, for a standard solution of component A,

determine its proportionality factor x, of optical density to solution concentration at key wavelength L_A, and similarly for a standard solution of component B determine its proportionality factor y, of optical density to solution concentration at key wavelength L_B. Furthermore, determine the ratios a and b, of the optical densities at the two key wavelengths L_A and L_B for each solution:-

i.e. for standard solution A

$$a = \frac{\text{optical density at } L_B}{\text{optical density at } L_A}$$) constant for component A regardless of solution concentration

and for standard solution B

$$b = \frac{\text{optical density at } L_A}{\text{optical density at } L_B}$$) constant for component B regardless of solution concentration

Then for any solution containing a mixture of components A and B the optical densities of the mixture determined at wavelengths L_A and L_B are:-

$$D_A = C_A x + C_B by \quad \text{at} \quad L_A$$

and $$D_B = C_B y + C_A ax \quad \text{at} \quad L_B$$

where C_A and C_B are the concentrations of components A and B respectively. Since x, ax, y and by have been determined from the standard solutions of A and B, and D_A and D_B can be measured from the solution of the mixture, C_A and C_B may be found by simple calculation.

The key wavelengths for each component are normally taken at some wavelength in their respective absorption spectra

where a characteristic prominent peak occurs, in order to obtain the maximum accuracy for calibration, i.e. large change in optical density for small change in concentration. The constants a, and b, are dependent only on the form of the absorption spectra of the individual components at the respective key wavelengths, and for maximum accuracy would have values which tend to zero, i.e. little or no mutual interference of the two spectra.

In the case of crude oil, however, there is a series of components which absorb light throughout the ultra-violet and visible wavelengths. Their properties overlap and hence make it difficult tofind key wavelengths for a suitable series of calibration curves. Furthermore, the solvent itself restricts the range of wavelengths within which a key wavelength may be found. This is particularly true in the case of crude oil which has to be dissolved in an organic solvent, thereby precluding measurements below the extinction wavelength of the solvent.

The solvents with the widest range of usable wavelengths are low-molecular-weight paraffins, cyclo-paraffins, and aliphatic alcohols, but these hydrocarbons are not always suitable in other respects. Some cause precipitation of asphaltenes from certain crudes; moreover, determination of the concentration of saturated hydrocarbons, i.e. paraffins and naphthenes, is difficult when their extinction wavelength is similar to that of the solvent.

A qualitative result may be obtained, however, in the case of oil for the removal by adsorption of aromatic, and non-hydrocarbon components from an oil solution. In this case a series of arbitrary key wavelengths are chosen throughout the spectrum of the oil, and the relative change in optical density at these wavelengths compared graphically. This procedure indicates the type of component being most strongly adsorbed, based upon a comparison of its characteristic spectrum with the relative changes of optical density at the key wavelengths, particularly at those wavelengths at which only that type of component is known to absorb light.

This brief discussion of some aspects of spectrophotometric calibrations has been inserted to draw attention to the limitation of some of the quantitative data, and to facilitate appreciation of the development of later methods.

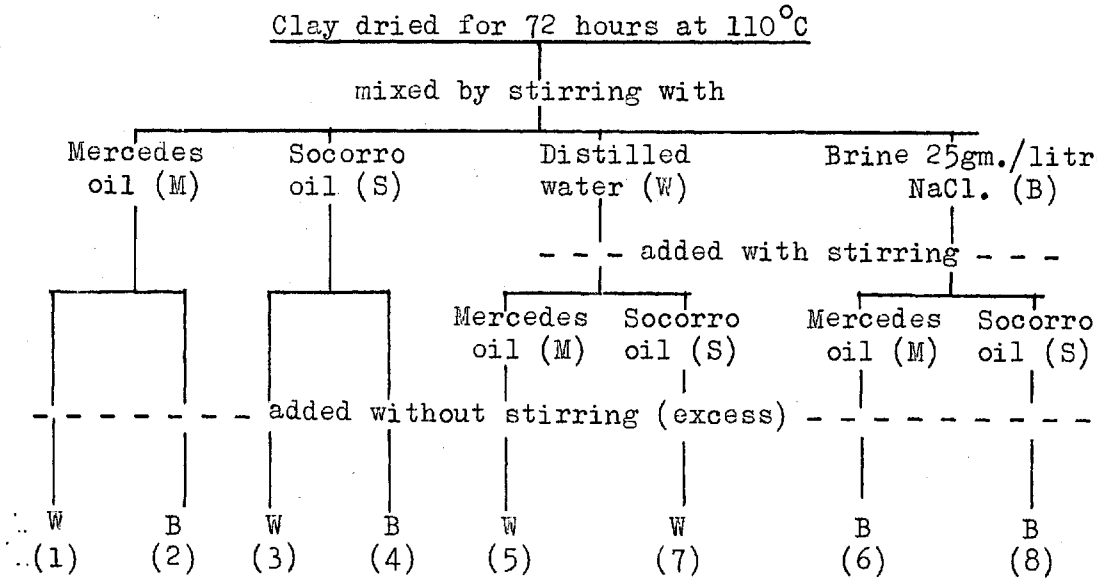
Although the weights of oil recovered could be found gravimetrically, the effectiveness and reproducibility of solvent extraction of the wet-clay-oil complexes was still open to question.

The results indicated that the greater the clay-to-oil ratio the smaller was the absolute recovery of oil, and also that the more polar the extraction solvent the greater the recovery for a given volume of solvent. Nevertheless, it seems that in some tests full recovery from these complexes

may have been obtained, although this cannot be proved conclusively.

Qualitative Investigation into the Relationship of Crude Oil and Fine-grained Mineral Matter.

At this point a series of qualitative experiments were performed in order to obtain some idea of the nature of the oil-clay-water relationship. These involved the water-wetting of the clay before adding oil, as well as mixing dry clay and oil prior to adding water. All the clay samples were dried in an oven at 110°C, before mixing either with oil, or water. The procedure was as outlined in the following flow diagram:



Eight samples were made up as shown in the above diagram for each of the four clays: Aquagel, Fuller's Earth, Gault and China Clay. The samples were mixed in 25 cc. flat-bottomed, cylindrical sample tubes, and left to stand for a week before

being agitated in any way. Only in the case of Aquagel samples was any spontaneous oil release observed; tapping or vigorous shaking was required to release some oil from the other clays, as is shown in Table VI. Even though spherical globules of oil were released from the Aquagel, some fine clay particles were seen to be adhering to their surfaces, some of which fell off when the globules reached the water-air interface.

Some further tests on Gault clay and China clay indicated that water could not be imbibed by, and oil displaced from them, even when the uhdried clays, i.e. in equilibrium with atmospheric humidity conditions, were initially wet with oil.

The rather distinctive behaviour of Aquagel in these tests corroborates to some extent the findings of Poirier and Thiel, who found Wyoming bentonite to be a rather poor material for the sedimentation of oil in sea water, whilst kaolinite in contrast was the best. Similar experiments carried out by Hodgson and Hitchon (1959) using a 3% saline system and clay concentrations varying from 1 to 8% by weight of the total system, resulted in the deposition 1.3, 1.0, and 0.25 millilitres of the purified hydrocarbon Nujol per gram of illite, kaolinite, and montmorillonite, respectively. It is interesting to note that they extracted their clay-water-Nujol system with

Table VI

M - Mercedes oil, S - Socorro oil, W - Distilled Water,
B - Brine, Capital letters - Initial wetting phase;
Subscript lower case letters - Added phase.

AQUAGEL.

STATE	NO.	BRIEF DESCRIPTION OF SAMPLES.
M_w	(1)	Clay dispersed and released oil globules, small globules being released by tapping tube.
M_b	(2)	Clay dispersed releasing most of oil as globules, some remaining in upper layers of clay.
S_w	(3)	Clay dispersed and released most of oil with some globules trapped by clay.
S_b	(4)	Clay completely dispersed with release of large globules, they did not coalesce at water surface.
W_m	(5)	Clay dispersed allowing oil to form globules which were released but did not coalesce.
B_m	(6)	Clay dispersed with release of oil as globules, some trapped in clay but released by tapping.
W_s	(7)	Clay dispersed with release of oil globules. As above they did not coalesce at the surface.
B_s	(8)	Clay dispersed and released oil as globules, with the smaller globules released by tapping; no coalescence.

Table VI (Continued)

M - Mercedes oil, S - Socorro oil, W - Distilled Water,
B - Brine, Capital letters - Initial wetting phase;
Subscript lower case letters - Added phase.

FULLER'S EARTH.

STATE	NO.	BRIEF DESCRIPTION OF SAMPLES.
M_w	(1)	Some clay near surface dispersed, but oil remained combined with the rest.
M_b	(2)	As for above sample, both of which formed oblate spheroidal masses at the bottom of the tubes.
S_w	(3)	Oil remained trapped in the clay, but excess rose to top of the clay due to buoyancy.
S_b	(4)	As for sample (3); lower part of clay was oil-stained in spite of segregation.
W_m	(5)	Oil held in clay as a fibrous mass, some released to the surface with no coalescence.
B_m	(6)	As for sample (5); the fibrous aggregates remained dispersed at water surface (no globules formed).
W_s	(7)	Oil held as fibrous, hair-like, finely dispersed aggregates, which were released by tapping.
B_s	(8)	As for sample (7) but oil released as fibrous non-coalescing aggregates only after hard shaking.

Table VI (Continued).

M - Mercedes oil, S - Socorro oil, W - Distilled water,

B - Brine, Capital letters - Initial wetting phase;

Subscript lower case letters - Added phase.

GAULT.

STATE	NO.	BRIEF DESCRIPTION OF SAMPLES.
M_w	(1)	Samples (1) and (2). No dispersion whatsoever, the whole clay-oil complex remaining as an oblate spheroidal globule at the bottom of the tube.
M_b	(2)	
S_w	(3)	Oil remained trapped in clay with some gravity segregation of oil taking place within clay-oil mass.
S_b	(4)	As for sample (3) both showed a lesser degree of oil segregation than the corresponding Fuller's Earth example.
W_m	(5)	Oil remained as fibrous aggregates with some aggregates rising to the surface, no coalescence.
B_m	(6)	As for sample (5), fibrous aggregates only released by shaking, with no coalescence.
W_s	(7)	Oil formed fibrous aggregates, fine and hair-like, released by tapping, no coalescence.
B_s	(8)	Aggregates even more finely dispersed than for (7), released aggregates did not coalesce.

Table VI (Continued).

M - Mercedes oil, S - Socorro oil, W - Distilled water,

B - Brine, Capital letters - Initial wetting phase;

Subscript lower case letters - Added phase.

CHINA CLAY.

STATE	NO.	BRIEF DESCRIPTION OF SAMPLES.
M_w	(1)	Samples (1) and (2). No dispersion whatsoever, the whole clay-oil complex remaining as an oblate spheroidal globule at the bottom of the tube as in corresponding Gault samples.
M_b	(2)	
S_w	(3)	Samples (3) and (4). Oil showed gravity segregation within the clay-oil complex but was not released. Oil staining remaining at the bottom even after the layered segregation.
S_b	(4)	
W_m	(5)	Samples (5) and (6). Oil formed very fine hair-like fibrous structures with very little being released even after severe shaking.
B_m	(6)	
W_s	(7)	Samples (7) and (8). Oil formed fibrous aggregates as in samples (5) and (6), very finely disseminated, with only slight release and no coalescence after severe shaking.
B_s	(8)	

diethyl-ether, and measured its concentration by means of spectrophotometric determinations at key wavelengths in the ultra-violet and infra-red ranges. They further noted that the slow gravity settling of the clay-water-Nujol complex deposited eight times as much Nujol as centrifugal deposition at 3,000 r.p.m. Oil-in-water emulsions stabilized by the clays by the preferential wetting of the clays by water rather than true adsorption is how they account for the phenomena

they observed, and since they used a purified paraffinic hydrocarbon to represent oil, this is probably the correct explanation. Nevertheless, one is again struck by the relative inefficiency of montmorillonite in carrying down oil as compared with illite and kaolinite. Poirier and Thiel relate the occurrence of irregular, flaky, and stringy aggregates of oil and wet clay, and the spreading of the oil as a film to the presence of organic matter in the clay resulting in a reduction of interfacial tension by higher members of the organic compounds associated with it, e.g. acids, although in their work they found that very little, if any, oil was sedimented by finely-ground oil shale, or humus soil, both of which were high in organic residues. The china clay in the above experiments (Table VI) is, to all intents and purposes, devoid of organic matter by reason of its mode of origin (weathered granite), and it would probably be difficult to find any material representative of a normal sedimentary environment with less; yet in spite of this, the most pronounced flaky aggregates were formed.

Gurwitsch (1926) refers to minute drops of oil of irregular shape, seen under the microscope, and caused by small adhering sand grains, the whole being suspended in water, presumably due to the preferential oil wetting of the sand grains accompanied by the spreading of oil as a film over their surfaces, and resulting in flotation of the sand grains

in the bulk of the water. According to Gurwitsch they form very stable emulsions which are not resolved by heating nor by the addition of naphthenic acids, as is found to be the case for certain water-in-oil emulsions, the oil being partially separated from them only by trituration with a small amount of coarser sand, which mechanically breaks down the stabilizing "sand" films. Gurwitsch classified these, together with certain other crude oil and water emulsions, as naphtha emulsions. The emulsion referred to above was found in certain Roumanian and Russian oil fields. The stability of the released irregular aggregates formed by mixing the water-wetted clays with oils was of the same order as in the cases described by Gurwitsch above. Heating them in a test tube on a water bath to 90°C had little or no effect, and the addition of methanol, followed by soap and a detergent to a few of the particles in water appeared to be equally unsuccessful in releasing oil.

During the preparation of the samples, another phenomenon was observed which occurred only with the initially water-wetted clays. On mixing the oils, by stirring, with the following distilled water and brine wetted clays, cracking of the base of the glass sample tubes was noticed. This is presumably due to some sudden release of heat, either heat of wetting, or heat of reaction with some component present in the oil.

Clay	and	Water	added	Oil.
Aquagel		Distilled		Mercedes
Fuller's Earth		Distilled		Mercedes
" "		Brine		Mercedes
" "		Distilled		Socorro
Gault		Distilled		Mercedes
"		Distilled		Socorro
"		Brine		Socorro

The final mixtures of the above samples were transferred to fresh sample tubes prior to adding excess water, which in all cases was the same as that used in preparing the original complex.

After six weeks of standing, all the samples originally prepared, i.e. thirty-two, were stirred and/or shaken, as no noticeable changes, other than those already described in Table VI, had taken place in the interim. After this treatment the sample tubes containing the following complexes developed cracks:-

Clay	and	Water	added	Oil.
Aquagel		Brine		Mercedes
"		Distilled		Socorro
"		Brine		Socorro
Fuller's Earth		Distilled		Socorro *
" "		Brine		Socorro
Gault		Distilled		Mercedes *
"		Distilled		Socorro *
"		Brine		Socorro *

* These samples had cracked previously.

Thus of the originally water-wetted clays, only those involving China clay and the Gault and Brine with added Mercedes oil did not exhibit this phenomenon.

The tenacity with which dry clays, other than Aquagel, held the oils, if initially wetted by them demonstrates the hydrophobic nature of the complex produced, water not being imbibed by the clay to displace the oil. When the clays were initially water-wetted, mixing with oil produced a three-component complex of clay, water and oil, and not the free oil that would be expected if no interaction had taken place. Furthermore, the ability of the clays to form complexes appears at leats in part to be some function of their degree of hydration, which in turn is a function of the clay mineral present, the specific surface area, the cation exchange capacity, and the cations present in the exchange positions.

This conclusion is reached from the fact that the Aquagel, basically a sodium montmorillonite, disperses quickly in water, even after complete initial contact with oil, whereas the Fuller's Earth, which is basically a calcium montmorillonite, does not disperse to anything like the same extent. Gault and China clay disperse even less readily, and as they are less highly hydrated than either Aquagel or Fuller's Earth, they permit the oil to wet their surface to some extent. The loss of weight when dried at 110^{o}C, expressed as a percentage

of their original weight under air dried conditions, is 0.5% and 2.8% for China clay and Gault, respectively, compared with 13.4% for Fuller's Earth and 8% for Aquagel. The apparent anomaly of the hydration characteristics of Fuller's Earth based on these figures is discussed below.

The qualitative results reported in Table VI, therefore, demonstrate a variation in the nature of the clay-water-oil interactions with different types of clay minerals, and also for clay minerals of similar type, but with different adsorbed cations.

The Relationship of the Properties of Clay Minerals to their Adsorption Characteristics.

According to Keeling (1958) there is a fairly good straight-line relationship between the water adsorption characteristics of an oven-dried clay placed in an atmosphere of constant relative humidity and its surface area as determined from its nitrogen adsorption isotherm at -183°C. White and Pichler (1959) concluded from their studies on the water-sorption characteristics of clay minerals that in montmorillonites the rate and amount of water sorption depends to some extent on the exchangeable cation, and that sodium montmorillonites will adsorb more water than will calcium montmorillonites, although the adsorption reaches equilibrium much more quickly for the calcium-base clay. The range of water adsorption values in per cent by weight at

equilibrium being 700 - 900 for sodium montmorillonites compared with 150 - 200 for the calcium clays. The ranges for kaolinites are 80 to 150 and for illites 70 to 160, for a muscovite sample 360, and a biotite sample 50; attapulgites have a similar range of values to calcium montmorillonites. These values are based on the adsorption of liquid water and not water vapour. Similarly, Grim (1953) states 'that Na montmorillonite, on drying at room temperature, tends to develop a single water layer between the silicate layers, and that Ca montmorillonite under the same conditions tends to develop two water layers, whereas at high relative humidities and in the presence of an abundance of water, Na montmorillionite sorbs by far the larger quantity of water".

Thus the apparent anomaly of the Fuller's Earth having greater hydration properties than Aquagel, so far as sorption of moisture from the atmosphere is concerned, is not unexpected. As a further test of this criterion, the surface areas of the clay samples used above were determined by the glycerol retention method of Kinter and Diamond (1958).

The method consists of preparing duplicate 1 to 3 gm. specimens of clay passing a 100 mesh B.S. sieve, drying at 110°C in aluminium foil dishes and weighing to 0.2 mg., adding 10 ml. of a 2% aqueous solution of glycerol and heating to constant weight at 110°C in a convection oven containing

a constant supply of glycerol vapour at a partial pressure just below saturation. The gain in weight represents the glycerol retained, and is expressed as a percentage of the 110°C oven-dry weight. This procedure was repeated for the samples after previously heating them to 600°C for four hours. The reason for heating the samples to this temperature was to cause the irreversible collapse of the expanding lattice minerals, so as to seal the internal surfaces against subsequent penetration by glycerol and to permit sorption only on the external surfaces. A modified pre-treatment of the clays by saturation with triethyl ammonium chloride, to block the penetration of glycerol into the interlayer spaces, has been proposed by Kinter and Diamond (1960), and although somewhat preferable, it was not attempted, because the very slight increase in the accuracy of the result possible, did not appear to justify the additional complications involved.

The area occupied by 1 gm. of glycerol orientated as a mono-layer is 1765 sq. metres. Thus a glycerol retention of 1% is equivalent to a mono-layer of 17.65 sq. metres/gm. However, since the mono-layer of glycerol is between two basal surfaces of the clay, the internal clay surface covered by the mono-layer is twice the area of the mono-layer itself, or 35.3 m^2/gm. Thus the internal surface area =

$$\left(\begin{array}{l}\text{\% glycerol retained}\\ \text{by untreated sample}\end{array} - \begin{array}{l}\text{\% glycerol retained}\\ \text{by heat-treated sample}\end{array}\right) \times 35.3$$

The results of these determinations are given below:-

Table VII

Surface area in sq. metres/gm.

	External:	Internal:	Total:
Aquagel	11	466	477
Fuller's Earth	42	575	617
Gault	51	35	86
China Clay	14	--	14

Kinter and Diamond (1958) demonstrated that the surface areas of a montmorillonite from a given source vary with the exchangeable cation, and that the sequence of increasing total surface areas, as determined by glycerol retention, was similar to that reported by Orchiston (1955) for water vapour sorption by a montmorillonite saturated with different cations. The results of Kinter and Diamond are reproduced below, see Table VIII.

The surface area of illite varies from 67 to 100 sq. metres/gm. for the minus 2-micron fraction, and from 7 to 30 sq. metres/gm. for the minus 2-micron fraction of various kaolinites.

The hydration characteristics of bentonites are dependent upon the exchangeable cation as discussed above. Hauser (1955) states that the wettability of oven-dried clay slips on unglazed ceramic tiles, is dependent on the exchangeable cation. Thus sodium montmorillonite adsorbs a drop of water immediately, the calcium-base adsorbs the water much more slowly and shows poor

wettability; and the lead-base clay is not wetted at all.

Table VIII

Surface area of Volclay Bentonite (<200 mesh) Saturated with various cations, as Calculated from Glycerol Retention.

(After Kinter and Diamond, 1958).

Cation.	Surface area $m^2/gm.$ External.	Internal.	Total.
Li (monovalent)	65	403	468
Na "	116	258	374
H "	74	364	438
NH_4 "	79	244	323
K "	44	265	309
Ca (divalent)	49	396	445
Mg "	35	508	543
Fe "	48	417	465
Fe (trivalent)	49	466	515
Al "	49	516	565

This behaviour he attributes to the effects which surface polarization exerts on the properties of siliceous matter. The degree of polarization increases from sodium to calcium to lead, and is caused by a shift of the electron distribution of the adsorbed cation in such a way as to make the ion act as if it were in a lower state of oxidation. This lowers the energy of the silica surface, tending to make it hydrophobic.

Although only qualitative the heating and cracking effects correspond with the type of clay minerals involved, since montmorillonites have been reported to have heats of wetting

of 22.1 cal./gram for Ca^{++} ion clay and 12.1 cal./gm. for Na^{+} ion clays, whereas kaolinites with these cations have heats of wetting of 1.45 and 1.30 cal./gram, respectively. Illite, which is represented by Gault, is intermediate between the two. The values for three natural clays, montmorillonite, illite, and kaolinite, were found to be 11.8, 4.0, and 1.9 cal./gram, respectively (Parmelee and Frechette, 1942). That the heat of wetting varies with the adsorbed cation, and is generally higher for divalent than for univalent ions, has been demonstrated by several workers. According to Grim (1953), the order is Ca> Mg > H >Na> K. An increase in heat of wetting with decrease in particle size has also been demonstrated. This is an expected relationship, since heat of wetting should increase as the surface area increases with decreasing particle size. Reference to Table VIII from Kinter and Diamond supports this concept in regard to the exchangeable cation relationship, with the exception of magnesium, which is higher in the series as regards surface area. Kinter and Diamond, however, pointed out that their value was considerably higher in the series than that determined by Orchiston and other workers. The heats of wetting determined by Siefert (1942), on montmorillonites with different exchangeable cations are compared with the surface areas as determined by Kinter and Diamond in order to demonstrate the relative order.

Table IX

Cation.	Heat of wetting cal./gm. (after Siefert, 1942)	Total surface area sq.m./gm. (after Kinter and Diamond, 1958)
Ca (divalent)	22.1	445
H (monovalent)	20.1	438
Na (monovalent)	12.1	374
K (monovalent)	9.1	309

A similar order of exchangeable cation and heat of wetting exists for kaolinite, but the values are 1.45, 1.40, 1.30, 1.22 cal./gm., respectively, and presumably reflect slight differences in surface area with change in the exchangeable cation.

The Relationship of Organic Material to the Wetting of Clays.

Heat of wetting of clays is not confined to water alone. Organic liquids also produce this phenomenon, and in some cases the heat of wetting may be higher than for water. The values in the case of organic liquids are generally higher for polar than for non-polar liquids; there does not, however, appear to be a direct correlation between polarity and heat of wetting, according to Janert (1934), i.e. polarity is not the sole determining factor. Furthermore, the heat of wetting of a clay decreases as the moisture content of the clay increases at the time of making the determination. This applies for both water and organic liquids.

The fact that organic liquids cause heat of wetting phenomena, even on moist clays, leads to the consideration of

clay-mineral-organic reactions. These reactions are of two types, the first of which will be mentioned only briefly, a more complete review being given by Grim (1953). The first type is mainly concerned with the montmorillonite type of clay which has high cationic exchange capacity, and involves the adsorption of ionic organic compounds to form salts with montmorillonite. Small ions are adsorbed only up to the exchange capacity of the clay and are held mainly by coulombic forces; the larger ions, however, are more strongly adsorbed, because of the greater Van der Waals forces and are difficult or impossible to replace with smaller ions; also they may be adsorbed in excess of the cation exchange capacity, the excess adsorbed molecules being undissociated and held by Van der Waals forces. The water-adsorbing properties of montmorillonite are gradually reduced as the basal surfaces of the mineral are coated with the organic ions. In general the larger the organic ion, the greater the reduction in the water-adsorbing capacity.

The second type of adsorption complex is concerned with polar molecules, both organic compounds and water, which as a result of the lack of symmetry of electron distribution within individual molecules act as dipoles. Clay-mineral structures are also polar, and the negative centres on the clay minerals attract the positive centres on polar substances in surrounding liquids, and positive centres on

clay minerals attract negative centres on surrounding polar particles. However, more than one polar group can be present in many molecules, and some quite stable associations occur with molecules which have no dipoles.

Bradley (1945) demonstrated that glycols, poly-glycols, and poly-glycol ethers were adsorbed on the basal plane surfaces of montmorillonite, displacing water from these surfaces. Similarly MacEwan (1948) showed that a large variety of polar organic molecules can be adsorbed on the basal surfaces of both montmorillonite and halloysite, the c-axis spacing of both minerals varying with the organic molecule adsorbed. The inorganic cations present on the surfaces of the clay minerals are not necessarily displaced by the adsorption of the organic molecules.

Both Bradley and MacEwan came to the conclusion that the polar molecules are held to the clay surface through a C-H...O (clay-mineral surface) bond. In general, the sorption energy for the organic dipolar molecules is greater than for water molecules, since montmorillonite dehydrated at 400° to 500°C will not rehydrate in water, but will take up glycol and expand. A somewhat similar, if not quite parallel, type of result was also found in the case of Aquagel used in the above experiments, which after heating for two hours at 400°C, allowing it to cool, then mixing with various crude oils, failed to disperse on the adition of water, and remained on

the bottom of the tube as in the case of Gault clay, and China clay (Table VI).

Bradley and MacEwan have shown that organic dipoles adsorbed by montmorillonite were capable of forming multiple molecular layers, whereas for halloysite a single molecular layer is the general rule. This was explained by MacEwan as being due to each of the surfaces of montmorillonite sheets being formed by a layer of oxygen ions and behaving like sheets with a uniform diffuse negative charge, thus collecting a layer of dipoles on both of its surfaces, so that between such sheets there will be two layers, e.g. glycerol. In the case of halloysite only one layer of oxygen ions is present, and as a result only single-layer adsorption takes place.

For non-polar molecules or groups only Van der Waals forces of attraction between them and montmorillonite sheets exist, and since this is non-directional only a single molecular layer is held in common by two neighbouring sheets. On occasions the presence of excess of a highly polar liquid causes the formation of more than two layers, and this is believed to be due to an increase of the molecular dipole moment with respect to the molecular size (parachor).

The recent work of Brindley and Rustom (1958), and Hoffman and Brindley (1960), has extended the understanding of the physical adsorption processes of neutral polar organic

compounds. Their studies have been confined to adsorption of water-soluble organic compounds on montmorillonite, and include x-ray examination of the clays before and after adsorption.

In the case of the adsorption of a non-ionic wetting agent (a polyethylene glycol ester of oleic acid)(1958), a Langmuir type of adsorption isotherm was obtained. As the concentration of the wetting agent was increased the clay adsorption complex increased from one layer to two layers of organic material between the basal layers of the clay lattice. Extensive water washing and soxhlet extraction reduced the amount to one layer, but the organic material could not be removed beyond this stage. Sodium, magnesium, and calcium base clays behaved in a similar manner.

The later work (1960) involved the adsorption of non-ionic neutral aliphatic molecules of different structural types (nitriles, ketones, esters, ethers and alcohols), on a calcium montmorillonite. One-, two-, and three-layer complexes were recorded, and differences in polar adsorption were attributed to the influence of the chain length and CH- activity, the effects of which were shown to operate independently. The polar adsorption was found to increase with increasing chain length, this being critical. Below five units (CH_3, or CH_2- is equivalent to one unit) adsorption is weak or absent, and above ten units, chain length does

not affect the adsorption appreciably, the adsorption behaviour being then determined mainly by the chemical character.

CH- activity refers to activated methylene groups, and it appears that adsorbed molecules are held by a kind of hydrogen bonding over the methylene groups of the aliphatic chain, thus forming a CH...O - Si interaction, as suggested by Bradley and MacEwan, rather than O - H ...O - Si or N - H...O - Si interaction of the normal type of hydrogen bond. Although CH- activity cannot be divorced from the polarity by which it is induced, it was shown that compounds of greater polarity, i.e. higher dipole moment, such as nitriles, were not adsorbed to as great an extent as similar chain length ketones with greater CH- activity.

An interesting point that arose during the experiments of Hoffman and Brindley (1960) was the difference of adsorption of the organic material from solution, and the adsorption characteristics of the clay after it had been dried. Washing treatments in this case tended to remove organic materials from the clay, and drying without washing also changed the organic content; the following extreme cases were noted. In the case of high-boiling point organic substances not adsorbed in the presence of water, the water evaporated preferentially forming an organic-clay complex of the type produced by the immersion of dry

montmorillonite in an organic liquid. If on the other hand, the organic substance evaporates with water, pure clay is left despite the high adsorption of the substance from aqueous solution. Therefore the dried complexes may have little in common with adsorption equilibria existing in solution. This severely limits the interpretation of x-ray measurements which are made in a dry atmosphere.

These observations support the view of MacEwan who concluded, on the basis of observed distances between successive clay-mineral sheets in the complexes, and computed values based on Van der Waals dimensions, that each layer of dipoles occupies its full clearance space in the c-axis direction, i.e. the space necessary to allow molecules to move freely over a plane parallel to the surface of the structural sheets. This suggests that the adsorbed layers are in a state of a two-dimensional liquid, firmly adhering to the clay surface, but able to move over it in a random manner, a conclusion which is supported by the extremely labile nature of the complexes, such that one may be changed to another by washing with excess of a second miscible liquid, and also by the absence of a simple integral number of molecules per unit cell, which would be expected for a crystalline arrangement of the adsorbed molecules on the clay surface.

The variation of basal spacing of clay-organic complexes

with the relative humidity at which the complex is formed has previously been observed by Glaeser (1949) in the case of acetone-montmorillonite complexes, and is a function of the hydration tendencies of the adsorbed cation at high relative humidities.

A different approach to clay mineral organic systems was made by Legate (1958), who used gas-solid chromatography to measure the activity coefficients and heat of adsorption of a series of organic compounds in contact with a standard A.P.I. (sample H-26) sodium-base montmorillonite. The measurement of the above thermodynamic constants offered a quantitative method of evaluating the following previously undetermined experimental variables:- Relative vapour pressure of the organic portion of the system, temperature of complex formation, and adsorbate-adsorbent molecular interactions. He measured the initial apparent retention volumes of n-hexane, cyclohexane, benzene, toluene, acetone, acetonitrile, 1-propanethiol, methanol, ethanol, n-propanol and water when passed through a column of montmorillonite as a vapour with helium saturated with water vapour as the carrier gas. From these measurements he derived the activity coefficients and heats of adsorption of the various compounds over the temperature ranges 40 - 90°C. The results obtained for heats of adsorption indicated that physical, rather than chemical, adsorption was the active process for the system

studied, the adsorptions being completely reversible. The values obtained for heats of adsorption were of the same order of magnitude as the calculated heats of vaporization of the respective compounds. The attraction between all the organic compounds and hydrated montmorillonites at higher temperatures (50 - 90°C) appeared to be partially due to solution of the various compounds in water, in this case hydration water, although both solubility and physical adsorption are governed chiefly by polarity and the tendency to form hydrogen bonds. Legate states that it must be assumed that solution, rather than hydrogen bonding, was an important factor in the attraction between all of the organic compounds and the hydrated montmorillonite, due to the lack of variation of bond energies indicated by the experimentally derived heats of adsorption.

MacEwan showed that pure saturated hydrocarbons (hexane and heptane) did not form complexes with montmorillonite (based on x-ray data), so the wetting constituents present in crude oil are presumably confined to the polar and unsaturated hydrocarbon fractions.

Chapter IV

AN EXAMINATION OF THE OILS USED WITH RESPECT TO THEIR ADSORPTION CHARACTERISTICS ON DRY ADSORBENTS.

Introduction.

Having obtained some indications regarding the part played by the different types of clays, it was thought necessary that an attempt should be made to determine the action of the oil in these relationships. At the same time it was hoped that some criteria might be developed which could be used quantitatively for comparing the relative wetting characteristics of the clays used.

Since the system being dealt with is one involving surface activity and surface forces, it was felt that chromatographic analysis of the oils would be reasonably rapid and at the same time would throw some light on the character of the adsorbable components present.

The Nature of the Separation Process.

Chromatography is primarily a process which is used for the separation of essentially molecular mixtures, as opposed to suspensions or colloidal mixtures; it is not a filtration process. The separations depend upon the redistribution of the molecules of a mixture between two or more phases, and thus they are comparable to liquid-liquid extractions, and distillation. The kind of distribution that occurs in chromatography is a distribution between a bulk phase and an interfacial phase or a thin film of liquid.

The definition of chromatography given by Cassidy (1957) is "a separation process applicable to essentially molecular mixtures which relies on distribution of the mixture between an essentially two-dimensional, or thin, phase and one or more bulk phases which are brought into contact in a differential counter current manner".

Adsorption chromatography or adsorption column analysis is used in the separation and analysis of crude oils, where the thin phase is an "immobile" interfacial film at the surface of a solid adsorbent. Its name was derived from the separations carried out by the Russian botanist Tswett (1903) on plant pigments, the separations being characterized by the colour of the various pigments. The separation occurs as a result of retardation of certain components of the mixture in the mobile fluid phase, by adsorption on a stationary interfacial phase, the more strongly adsorbed substances being more strongly retarded. The mobile liquid phase is applied to a column of adsorbent of suitable material and particle size, and allowed to flow through it. At times the mobile phase may be forced through the bed of adsorbent by applied pressure, or by centrifugal force, as well as by gravity.

Chromatography is essentially an empirical separation method, and according to Van Nes and Van Westen (1951), theory appears unlikely to further the development of practical procedures.

Its application to the analysis of petroleum has grown since it was used by Mair and White (1953). Prior to this, however, it had had much practical use in the decolorization of lubricating oils during refining. Gurwitsch (1926), states in his book that "A great service has been rendered by D. Day, who first showed that the filtration of petroleum through finely porous media not only brings about its decolorization, but also its separation into fractions of different specific gravities, boiling temperatures, viscosity, etc., this being known as Day's phenomenon". Day, who published his results in 1897, might well replace Tswett as the originator of adsorption analysis. Gurwitsch further discusses the mechanism involved in adsorption analysis, and describes the method of determining the eluting power of solvents by their relative heat of wetting when contacted by the adsorbent.

Individual compounds, however, were not separated from crude oil by chromatography until the work on A.P.I. project No. 6, by Rossini and his co-workers (1958), was undertaken, and so far these separations have been confined to the gasoline and kerosene ranges of distillates. Chromatography has been applied to crude oils as a whole and also to the higher boiling point fractions, but due to the multiplicity of components in each fraction increasing as its boiling point increases, the results have been restricted to

separation of the different classes of components present rather than to separation of individual members of each class.

The order in which classes of organic compounds are separated from a mixture is shown in the following rough classification given by Lederer (1957). The first members are most strongly adsorbed, the latter members the least strongly adsorbed: Acids and bases > alcohols, thiols > aldehydes, ketones > esters, halogen-containing substances > unsaturated hydrocarbons > saturated hydrocarbons. Thus, in general, the greater the polarity of a component the more strongly is it adsorbed on a polar adsorbent.

Consequently a separation of saturated and aromatic hydrocarbons from a crude oil may be achieved by introducing a small quantity of the organic mixture on to an adsorbent column, and washing the column with a series of solvents of increasing desorbing power, thereby giving a succession of fractions of increasing polarity. In the case of crude oil the asphaltic hydrocarbon complexes are most strongly adsorbed and require a very powerful desorbing solvent for their removal from the column.

The desorptive power of solvents varies considerably with the adsorbent used. Table X gives a series of eluents of increasing desorption power, as determined by different workers, for elution on silica gel.

Table X

Eluents of Increasing Desorption Power on Silica Gel.

E - Dielectric constant.

Q - Relative heat of wetting on silica gel as compared to heat of wetting by benzene for different samples of silica gel; i.e. ratio is constant regardless of adsorbent sample.

Strain, 1945.

Petroleum Ether	30 - 50
Petroleum Ether	50 - 70
Petroleum Ether	70 - 100
Carbon Tetrachloride	
Cyclohexane	
Carbon Disluphide	
Ether (absolute)	
Acetone (absolute)	
Benzene	
Toluene	
Esters of organic acids	
1, 2, - Dichloroethane, Chloroform, Dichloromethane	
Alcohols	
Water	
Pyridine	
Organic acids	
Mixtures of acids and Bases with Water, alcohol, or Pyridine.	

Jacques and Mathieu, 1946.

	E
Hexane	1.88
Benzene	2.29
Ether	4.47
Chloroform	5.2
Ethyl Acetate	6.11
Dichloroethane	10.4
Butanol-2	15.5
Acetone	21.5
Ethanol	26
Methanol	31.2

Bartell and Almy, 1932.

	Q
Hexane	0.56
Carbon Tetrachloride	0.69
Chloroform	0.82
Ethyl Benzene	0.85
Chlorobenzene	0.94
Benzene	1.00
Nitrobenzene	1.21
Water	1.51
Acetone	1.64

Table X (Continued)

Eluents of Increasing Desorption Power on Silica Gel.

Trappe, 1940.	Knight and Groennings, 1954.
Petroleum Ether	Heptane
Cyclohexane	Di-isobutylene
Carbon Tetrachloride	Benzene
Trichlorethylene	Isopropyl Chloride
Toluene	Di-isopropyl ether
Benzene	Ethyl Ether
Dichloroethylene	Ethyl Acetate
Chloroform	sec. - Butyl Alcohol
Ether	Water
Acetone	Acetone
n-Propyl Alcohol	Methyl Alcohol
Ethyl Alcohol	Pyruric Acid
Methyl Alcohol	
Water	

It is seen from Table X that the series of eluents are in agreement, with certain exceptions. Jacques and Mathieu (1946) have stated that the eluting power of a solvent is proportional to its dielectric constant E, and have verified that eluents function by being themselves adsorbed. In a mixture of two eluents, the solvent with the highest eluting power (having the higher value of E) is the most strongly adsorbed. In the series due to Strain (1945), the positions of ether and acetone do not seem to be justified, and these compounds should be placed after benzene and toluene.

Moseley et al. (1954) studied the eluting power of a

series of pure solvents on silica and calcium hydroxide. No correlation of dipole moment of the solvent with adsorption affinity of the adsorbate (material adsorbed), was found. Also the correlation of dielectric constant of the solvent with its eluting power was found to have exceptions, notably the eluting power of acetone was greater than that of nitrobenzene, whereas their dielectric constants are 20.7 and 34.8, respectively. This discrepancy was explained by the effect of hydrogen bonding. Acetone is capable of hydrogen bonding with the $-\mathrm{Si}<^{O}_{OH}$ of the silica and hydroxyls of calcium hydroxide, thus exerting a displacement effect on the adsorptive. This is in agreement with the series given by Bartell and Almy (1932), showing the relative heat of wetting, Q, of the pure solvents with respect to benzene on activated silica gels. As stated earlier, Gurwitsch also used this method for determining the adsorptive capacity of adsorbents, and Müller (1943), using a purified light petroleum, determined the state of activation (power of adsorption) of alumina as an adsorbent with various water contents by the same method. Again in this instance the exception of chloroform being higher in the series than benzene, is noted. These variations show that only general rules can be made for predicting the adsorption phenomena likely to take place in a given system, since slight differences of an adsorbent surface as a result of its method

of preparation can often alter substantially its adsorption characteristics. Cassidy (1957), has summarized some general rules for predicting the relative extent of adsorption as follows:-

1) Greater adsorption at a surface will occur from that system which produces the greater lowering of interfacial tension, i.e. a liquid which is highly adsorbed by a solid will show a low interfacial tension against the solid. This rule follows the Gibbs relation.

2) The extent of adsorption is usually greater from solvents in which the adsorbate is less soluble. Thus for a given adsorbate the better solvent will make the better eluent. This holds well in cases in which the solvents show similar interfacial tensions towards the adsorbent used.

3) The more polar the substance, the more extensive its adsorption at a polar surface, other things being equal. Hence a polar substance will be better adsorbed from a non-polar solvent than from a polar one. Similarly the less polar a substance the more extensive its adsorption at a non-polar surface, other things being equal.

4) The extent of adsorption changes in a regular manner in a homologous series. Thus since polarity decreases for the higher members of a homologous series, the extent of adsorption at non-polar surfaces should increase, and

for polar surfaces decrease, for the higher members. This is a restatement of the Traube relation.

It can be seen from these rules, that a number of factors influence the extent of adsorption of a particular substance by a given adsorbent, and in a mixture as complex as that found in the higher-boiling-point fractions of crude oil (high-molecular-weight components) distinct separation of classes of compounds is as much as can be expected, even in carefully controlled chromatograms.

Previous Work on the Chromatographic Fractionation of Crude Oils.

Fractionation of topped crude oils by the use of adsorbents had received a certain amount of attention, and interest in this kind of study has increased since hydrocarbon groups were separated from the organic extracts of recent and ancient fine-grained sediments. Allibone (1941), was one of the first to attempt to fractionate topped crude by this means. He used silica gel as adsorbent, the ratio of adsorbent to charge was 6:1 by weight, and the column had a length-to-diameter ratio of 15:1. The residue was introduced in solution in light petroleum ether and the column washed with the same solvent, a series of fractions being obtained. The silica gel was then extruded from the column and divided into convenient portions as dictated by variations in the colour of the gel. After being allowed to dry, each portion was extracted with methyl ethyl ketone in a Soxhlet apparatus.

He found that the following factors affected the efficiency of the method.

1) The proportion of adsorbent used.

2) The fractional sub-division of the filtrate.

3) The concentration of the charge in the petroleum diluent.

He experienced particular trouble with the asphaltic residues due to:

a) Substantial precipitation of hard asphalt in making up the primary solution in petroleum ether.

b) This precipitation being but a single equilibrium is imperfect.

c) The gel does not readily adsorb the asphaltic compounds left in solution, and quickly becomes exhausted when such solutions are filtered.

Lawrence and Barby (1949) attempted to separate residual oils into their main hydrocarbon types. They carried out chromatographic separations of four distillation cuts in the range 140°C - 340°C (53.6% by weight of the original oil) on the residuum (46.4%), and also on the original oil. The ratio of column length to diameter was 12:1. The charges were made up as 2% solutions in hexane, and sucked through alumina colums. The eluents consisted of cyclohexane, followed by chloroform, carbon disulphide, and finally pyridine. Consistent results were obtained, and the sum of

the eluent fractions of the various distillate cuts and residuum agreed well on the whole with the eluent fractions in the original oil. It was found that the hexane-insoluble material, which was not passed through the column, was greater for the residuum than for the original oil. This is accounted for to some extent by the presence of much black suspended matter in the carbon disulphide and pyridine fractions of the original oil and not by any polymerization effects due to distillation. Thus the separation of asphaltenes on a solubility basis is not specific, since their solubility characteristics in the original crude are different from those in the residuum. This is in agreement with Allibone's experience, and a recent investigation by Heithaus (1960) supports their findings. The precipitation of asphaltenes is dependent on a combination of factors including the polarity of the solvent, the degree of dilution by the solvent, and the ability of the maltenes associated with the asphaltenes to act as peptizing agents and keep the asphaltenes in colloidal suspension.

Furby (1950) also analyzed oil residua, but before chromatographic adsorption he removed the asphaltenes by precipitation with petroleum ether, i.e. he adopted a standard procedure for asphaltene removal which again was only of an arbitrary nature; the resins were removed by adsorption on Fuller's Earth, and the wax by precipitation with methyl ethyl ketone, in successive steps. Elution from silica

gel by n-pentane gave erratic results, particularly with high sulphur, high asphalt content residua. This unsatisfactory feature was avoided by using a catalytic cracking catalyst as the adsorbent. The catalyst was stated to have had a larger average pore size than the silica gel.

O'Donnell (1951), who analyzed asphalts, also precipitated the asphaltenes prior to molecular distillation and chromatography on silica gel. His adsorbent-to-charge ratio varied from 6 to 1 for low-molecular-weight fractions to 50 to 1 for those of high molecular weight. The column was wet by n-pentane and the eluents were successively n-pentane, benzene and alcohol. The n-pentane eluted the saturated hydrocarbons, and the benzene the aromatics, the change-over point being determined by the ultra-violet light absorption properties of the pentane effluent. The alcohols eluted the material not removed by benzene, and this was described as "the black resinous fraction" by O'Donnell. He found, by using alumina above the silica gel, that less silica was required. This was due, apparently, to the greater adsorption capacity of alumina for "resins", but it also altered the separation of aromatics and resins.

Karr, Weatherford and Capell (1954) fractionated entire crude oils chromatographically, using both simple columns and a continuous operation employing a distillation column to recycle the eluents and recover the low-boiling-point fractions.

They used alumina and bauxite as adsorbents wet by n-pentane to avoid heating effects during charge introduction. Their adsorbent-to-charge ratio was 6 to 1, e.g. 10 ml. of charge, on a 60 cm. x 12 mm. column, i.e. length to diameter ratio of 50 to 1. They used ten times the initial charge volume of n-pentane, benzene, and benzene-ethyl alcohol (3:1 by volume) as successive eluents. The solvent was removed from the fractions by a stream of air or nitrogen at room temperature in the case of fractions eluted from the simple column. They also used a photo-electric cell to monitor the n-pentane eluate to prevent the elution of excess sulphur in this fraction.

Kleinschmidt (1955) attempted fractionation of asphalts into distinctive groups of components by means of chromatography, using Fuller's Earth as adsorbent (less than 200-mesh and heated at 150°C for 18 hours prior to use). Like Furby and O'Donnell, he also precipitated the asphaltenes prior to chromatographic fractionation of the soluble (n-pentane) portion. The first fraction eluted by n-pentane he called "water white oils"; this was followed by the methylene chloride eluate which he termed "dark oils". Next methyl ethyl ketone eluted the "asphaltic resins". Final development of the column was carried out either by water-saturated methyl ethyl ketone, or an acetone-water (9:1 by volume) mixture followed by chloroform, this fraction being without a formal

name. The very small residue remaining after this treatment was found impossible to elute with organic solvents, and water just resulted in the clay swelling, thus obstructing flow and causing the column to burst when pressure was applied. The column used had a length-to-diameter ratio of 10 to 1, and he used an adsorbent-to-charge ratio of 15 to 1 by weight. The latter ratio was important, since varying the ratio from 10 to 1 to 25 to 1 decreased the percentage of "water white oil" whereas the percentage of "dark oil" and "asphaltic resins" increased correspondingly, showing the arbitrary definition of the fractions separated.

Schwartz and Brasseaux (1958) devloped a method for the chromatographic separation of petroleum residues which avoided the alteration of residues by asphaltene precipitation. They showed that the amount and nature of the asphaltenes and resins vary with the method of separation employed. Asphaltene precipitation, for example, co-precipitates other materials as well. For example, an "asphaltene" (8% of a residue) precipitated by pentane, was partially dissolved (5.4% of a residue) in cyclohexane and separated on silica gel into resins (3.0%), aromatics (1.6%) and saturates (0.8%), demonstrating the arbitrary nature of the original asphaltene separation. Similarly, the separation of resins and aromatics by Attapulgus clay was shown to be of an arbitrary nature as follows:-

Table XI

	Adsorbent as received (non-activated)		Adsorbent activated at 110°C.	
Oil residue Sample No.	Wt. % resins.	Wt. % aromatics.	Wt. % resins.	Wt. % aromatics.
1	24	27	37	15
2	10	23	23	14

Accordingly, the authors state "The effect of varying humidity upon Attapulgus is not known but from these results appears to be an important factor". Resins are lower-molecular-weight compounds than asphaltenes, and are generally considered to contain nitrogen, sulphur, and oxygen in aromatic-type ring systems.

In the method they developed silica gel was preferred for the separation of saturated from aromatic hydrocarbons, due to a stronger adsorption of the latter, although no rigorous explanation has been given for this fact. Alumina also gives a similar separation, but has a lower adsorption capacity than silica gel (Fink, Lewis and Weiss, 1950).

Schwartz and Brasseaux used a column of length-to-diameter ratio of 20 to 1, and an adsorbent-to-charge ratio of 50 to 1. The difference from O'Donnell's method, however, lay in the use of two different grades of silica gel in equal weights; the lower half of the column was packed with 912-grade (832 sq. metres/gram), followed by 70-grade (340 sq. metres/gram) above. The column was wet with cyclohexane and the charge

introduced, diluted in twenty-five volumes of cyclohexane, cyclohexane, benzene and methanol being used as successive eluents. The saturated fraction, eluted by cyclohexane, was monitored by means of ultra-violet absorption, and should contain less than 5% aromatics.

Schwartz et al. came to the conclusion, which is in agreement with the tentative suggestions of Furby and O'Donnell, that the larger pore size (140 Å diameter) of the 70-grade silica was much better able to adsorb the asphaltenes and resins than the 912-grade (22 Å diameter). Comparable results were obtained when a grade of alumina having a similar pore diameter was used in place of the 70-grade silica, but according to the authors this might introduce catalytic effects, so they recommend two grades of silica as being the preferable arrangement.

A recent paper by Ferguson (1960) on "analytical problems in determing hydrocarbons in sediments", has substantiated these results for the separation of organic extracts from sediments. The adsorbent-to-charge ratio of silica gel having 32 Å diameter pores was restricted to 1000 to 1, whilst a layer of 170 Å gel above 32 Å gel increased the adsorbent capacity of a given column so that a 50 to 1 adsorbent-to-charge ratio could be satisfactorily fractionated.

Chromatographic Fractionation of Mercedes and Socorro Crude Oil Residues.

In an attempt to fractionate the Mercedes and Socorro crude oil residues the following method was developed.

1) Materials.

Adsorbent used: Silica gel supplied by Hopkins and Williams Limited; no grade size stated, but all the gel passes 100-mesh B.S. sieve and is retained on a 200-mesh B.S. sieve. The gel is prepared especially for chromatography.

Solvents used:

i) n-heptane, I.P.T. specification supplied by Hopkins and Williams.

ii) Benzene "Analar" grade, 95% boiling between 79.5 and 80.5°C, supplied by Hopkins and Williams.

iii) Methanol "Analar" grade, 95% boiling between 64.5 and 65.5°C, supplied by Hopkins and Williams.

iv) Acetone "Analar" grade, 95% boils between 55.5 and 56.5°C, supplied by Hopkins and Williams.

Columns: The chromatographic columns used were of two sizes.

i) 10 cm. x 1 cm. diameter columns fitted with a ground-glass stop-cock, above which is

a sintered glass disc for the support of the adsorbent.

ii) 35 cm. x 8 mm. diameter columns of similar construction.

2) Preparation of Adsorbent and Purification of the Solvents.

To ensure the efficiency and reproducible activation of the silica gel it was heated at 300°C for two hours in a furnace, as proposed by Bartell and Almy (1932), and stored in a desiccator until required.

The solvents were purified by distillation in a three-foot fractionating column filled with fine glass rings, and fitted with a still head that allowed atmospheric moisture to be excluded from the column and receiver. Ground-glass joints on the column were left dry because the solvents attack silicone grease. The fractional distillation of the solvents ensured their dryness, because only that portion of the solvent boiling within 0.1°C of the boiling point of the pure compound was collected for use as an eluent.

3) Preparation of the Chromatographic column.

In all separations the adsorbent was wet by n-heptane in order to reduce the heating effects caused by direct contact of the gel and the oil.

To obtain even packing of the column the silica gel was sedimented into the column through n-heptane, although to do this satisfactorily required practice.

An electrical stirrer clamped to the same retort stand as the column being packed, was used as a vibrator to aid in the even packing of the column. To ensure that air is not trapped in the adsorbent during this operation the column must be completely filled with solvent prior to packing. This included filling the air gap between the sintered glass disc and ground glass stop-cock by filling the column above the glass disc and continuously tapping the top of the column with a rubber bung on a glass rod. Although this removed the bulk of the air by solvent displacement, the final bubble had to be removed by the following procedure: the reservoir, fitted with a complementary ground-glass joint and stop-cock, was fitted to the top of the column, and the air gap between the reservoir and the top of the column filled with solvent by tapping as before. The reservoir was closed so that no air could enter the column, and then holding the reservoir and column together they were inverted. Any bubbles trapped below the glass disc rose to the stop-cock of the inverted column and by opening the tap they entered the tap which was then closed. The column and reservoir were restored to the normal position and the stop-cock on the reservoir opened. This was followed by opening the stop-cock at the bottom of the column, whereon the air bubble was immediately displaced. The solvent was allowed to drain down in the column to some convenient height

above the sintered glass disc and the reservoir removed.

Following the removal of the reservoir, two filter paper discs, cut to the correct size by a cork borer, were introduced into the column and tamped, one after the other, into place on top of the sintered glass disc; this prevents any adsorbent from moving through the glass disc.

Packing by sedimentation then proceeds, using the reservoir as the source of solvent-wetted adsorbent by placing it on top of the column. The stop-cock on the reservoir was opened and sedimentation occurred with the vibration of the stirrer. As much air as possible was removed from the adsorbent by swirling it together with the solvent in the reservoir prior to sedimentation. The stop-cock at the bottom of the column must be kept closed, since attempts to obtain a better packing by allowing flow of solvent through the column at the same time as vibration, resulted in air entering the gap between the tap and the sintered disc, followed by air entering the adsorbent itself from the bottom.

4) The Procedure of Chromatographic separation.

The oil sample to be separated was weighed into a small beaker or weighing bottle of known weight and then transferred in the minimum amount of pre-wetting solvent to the top of the column, the beaker being rinsed two or three times to ensure maximum transfer. After evaporation of any solvent

remaining in the beaker it was reweighed to determine exactly, by difference, the amount transferred.

Having introduced the charge to the column, the stop-cock on the column was opened and the charge allowed to percolate through, displacing the wetting solvent as it did so. The reservoir was then placed on top of the column and the column washed with the same solvent as that used for pre-wetting the column and for transfer of the sample. 50 ml. of n-heptane was used as an average wash, increased at times to 100 ml. in some trial experiments, the exact amount required for a perfect separation of the saturated components from the aromatics being difficult to determine because of overlapping of structural types between the paraffins, naphthenes, and lower members of the aromatics (single-ring, long side-chain). Having washed the column with n-heptane, approximately 25 ml. of benzene was dripped into the column, followed by 25 ml. of methanol.

During its development the column was viewed by ultra-violet light and the fluorescent zones observed as each eluent was introduced. Washing the column with n-heptane caused the column to fluoresce a light royal blue, this being replaced by a yellow zone on eluting with benzene. After the benzene zone had passed down the column, the fluorescence remaining behind it was grey-blue in colour. Methanol in its turn displaced this, leaving the column with a faint light blue fluorescence.

Each fraction was collected separately in previously weighed weighing bottles, the change-over point being taken just prior to the elution of the following zone from the bottom of the column. This helped to reduce the losses due to tailing of the zones.

After collection the solvent was evaporated off in a stream of air at atmospheric temperature. The weighing bottles were then reweighed, all weighings being done on a Stanton automatic balance which could be read to 0.0001 gm.

5) Results and Modifications of Technique for Mercedes Oil Fractionation.

Being unaware of the work of Schwartz and Brasseaux (1958) at the start of these experiments, much time was spent in an endeavour to obtain reproducible separations with the asphaltic Mercedes residue. Both the choice of n-heptane as the initial solvent, causing asphaltene precipitation on the top of the column, and the use of only one grade of silica gel, it is now realized, precluded any likelihood of good reproducibility.

The following are typical of the variations obtained using the 10 cm. 1 cm. column and 5 gm. of silica gel.

Table XII

Sample No.	Weight of sample gm	Adsorbent / charge ratio	Fractions (% by Wt. corrected to 100%) Heptane.	Benzene.	Methanol.
1	0.1004	49.8	74.5	15.3	10.2
2	0.1463	34.2	71.6	20.8	7.6
3	0.0591	84.6	66.2	25.5	8.3
	Using a 35 cm. x 0.8 cm. column and 10 gm. of silica gel gave:-				
4	0.2752	36.4	65.0	29.6	5.4

It was realized that the precipitation of the asphaltenes by n-heptane was obviously one of the sources of error, so an attempt was made to overcome this by a two-chromatogram technique.

Initially the column was prepared as before, but benzene was used in place of n-heptane as the pre-wetting solvent. Since the Mercedes residue is completely soluble in benzene this overcame the problem of asphaltene precipitation. Having introduced the charge on to the column, it was then washed with a further 50 ml. of benzene and the eluent collected in a previously weighed weighing bottle. Methanol was used to develop the column and the methanol-eluted fraction collected separately. By this means it was hoped to adsorb all the true asphaltenes (i.e. the highly polar, high-molecular-weight aromatic compounds) from the oil and thus make easier the separation of the saturated and aromatic hydrocarbons. The benzene-eluted fraction was evaporated down and all traces of solvent removed by air blowing at atmospheric temperature.

A second column was prepared in the normal way with n-heptane as the pre-wetting solvent and the benzene fraction of the first separation was introduced on to the second column in n-heptane in which it now appeared to be completely soluble. Elution by n-heptane followed by benzene was carried out in the normal way. In spite of the original charge being eluted from the first column by benzene, it was found that even after the second column had been eluted by benzene, adsorbed material still remained on the column. This remaining adsorbed material was eluted in the usual way by methanol and included with the benzene fraction of the second column.

After evaporation of solvent from the eluates of the second column (2) the recovered material was weighed before it was diluted in n-heptane and stored in a dark cupboard.

It was noticed after some time that the benzene eluate, now dissolved in n-heptane, showed some slight precipitation of asphaltenes, indicating that not all the asphaltenes had been adsorbed on the first column (1) and that those asphaltenes were probably the methanol-desorbed material from the second column (2). Consequently the benzene eluate was again separated on a third column (3) as shown in Table XIII.

Table XIII

Column.	Weight of sample gm.	Adsorbent / charge ratio.	Fractions (% by Wt. corrected to 100%) Heptane.	Benzene.	Methanol.
(1)	0.2555	39.2	--	92.5	7.5
(2)	0.2362	42.4	60.8	31.7	--
(3)	0.0809	123.6	0.3	28.9	2.5
			61.1	28.9	10.0

All the above separations were made using 35 cm. x 0.8 cm. columns, each containing 10 grams of silica gel.

This series type of separations was undoubtedly the most accurate of those carried out, although how it compares with a separation of the kind proposed by Schwartz and Brasseaux (1958) is not known because this procedure has not been tried. It may be noted that a method for the commercial refining of lubricating oil by chromatography using a two-stage principle similar to that employed in the above separation has recently been developed by Nyul and Vamos (1960).

The separated Mercedes oil fractions showed the following appearance in normal reflected light, and characteristic fluorescence under ultra-violet light, after evaporation of the eluting solvents.

Table XIV

Fraction eluted by	Appearance in Normal Reflected Light.	Fluorescence in Ultra-violet Light.
n-heptane	Colourless viscous liquid.	Royal blue.
Benzene	Dark brown viscous liquid.	Orange-greem
Methanol	Black semi-solid	Brick red for small initial cut. Opaque for large final cut.

6) Results of Chromatographic Fractionation of Socorro Oil.

Although the improved two-stage procedure for the fractionation of the Mercedes oil showed promise as a method for obtaining reproducible results, the extra time required for analysis and the cumulative errors which are inherent in a two- or three-stage separation precluded further investigation of this oil.

It was decided, therefore, to continue the investigation with the Socorro oil, which, being less viscous and completely soluble in n-heptane, appeared to lend itself to the more rapid single-stage separation technique with the likelihood of more reproducible results. This in fact was found to be the case as shown by the following:-

Table XV

Chromatogram	A	B	C
Weight of oil fractionated (gm.)	0.1645	0.1743	0.7064
Heptane eluted fraction % by weight	75.2	74.1	77.2
Benzene " " " " "	17.6	18.1	16.9
Methanol " " " " "	6.2	7.0	5.0
Unrecovered	1.0	0.8	0.9
Adsorbent-charge ratio	61	58	14

Column 35 cm. x 0.8 cm. Weight of silica gel adsorbent, 10 gm.

The separated Socorro oil fractions showed the following appearance in normal reflected light and characteristic fluorescence under ultra-violet light after evaporation of the eluting solvents.

Table XVI

Fraction eluted by	Normal Reflected Light	Fluorescence in Ultra-violet light.
n-heptane	Colourless liquid	Royal blue
Benzene	Red-brown liquid	Salmon pink
Methanol	Very viscous black liquid	Brick red.

Correlation of the Ultra-violet Absorption Spectrum of the Socorro Oil with the Fractions Separated by Chromatography.

In an earlier section it was noted that spectrophotometry could only be used to make exact quantitative determinations on the amount of oil sorbed by wet clays if the spectrum of each individual component of the oil were known in detail. Even if these spectra were available, the multiplicity of

components would make a calculation of the type suggested extremely difficult, apart from the practical problems involved. However, a simpler approach to this problem was found which, it was felt, might lead to qualitative and possibly semi-quantitative results when applied to clay-water-oil systems. The method involves the determination of the ultra-violet absorption spectrum of the Socorro oil, followed by its chromatographic fractionation and the determination of the ultra-violet absorption spectra of the separated fractions. Thus, instead of determining the absorption spectra of all the individual components, the absorption spectra of the separated fractions could be correlated with the various component groups present in the oil. The following fractions were obtained during the course of two separate chromatographic fractionations:-

Table XVII

Fractionation (1)		Eluent	Cumulative % Recovery.
Weight of oil fractionated 0.0438 gm.			
First fraction % by weight of oil	84.7	Heptane	84.7
Second " " " " " "	10.9	Benzene	95.6
Fractionation (2)			
Weight of oil fractionated 0.0447 gm.			
First fraction % by weight of oil	72.8	Heptane	72.8
Second " " " " " "	7.9	Heptane	80.7
Third " " " " " "	11.8	Benzene	92.5

No attempt was made to obtain complete recovery in the above fractionations, since previous results had shown that the removal of the highly polar material retained on the silica gel after n-heptane and benzene elution, was only partially successful.

The spectra of the individual fractions are shown in Figs. 3 and 4 and the spectrum of the unrecovered portions of the oil (obtained by difference) are shown in Fig. 16, spectra 1 and 2. By the successive addition of the spectra of each fractionation, spectra were derived for the cumulative percentage recovery of the oil, and these are compared with the absorption spectra of the un-fractionated oil in Fig. 5.

The spectra, both determined and derived, are strictly comparable as they were determined in solvent solutions whose concentrations were equivalent to the concentration of the fractions in the solution used for the determination of the spectrum of unfractionated oil. A UNICAM SP 500 spectrophotometer which is manually operated, was used for measuring the spectra, n-heptane serving as the carrier solvent for the oil and its separated fractions. The concentration of the Socorro oil in n-heptane was kept at 1,000 p.p.m. and the optical cells used were of quartz with a 2 mm. light path.

A summary of the component types present in the fractions recovered in the two fractionations, based on an

FIG. 3

ULTRA-VIOLET ABSORPTION SPECTRA

FRACTIONATION 1 OF SOCORRO OIL

Fraction 1 = Spectrum 1 847ppm, 84·7% of oil

Fraction 2 = Spectrum 2 109ppm, 10·9% of oil

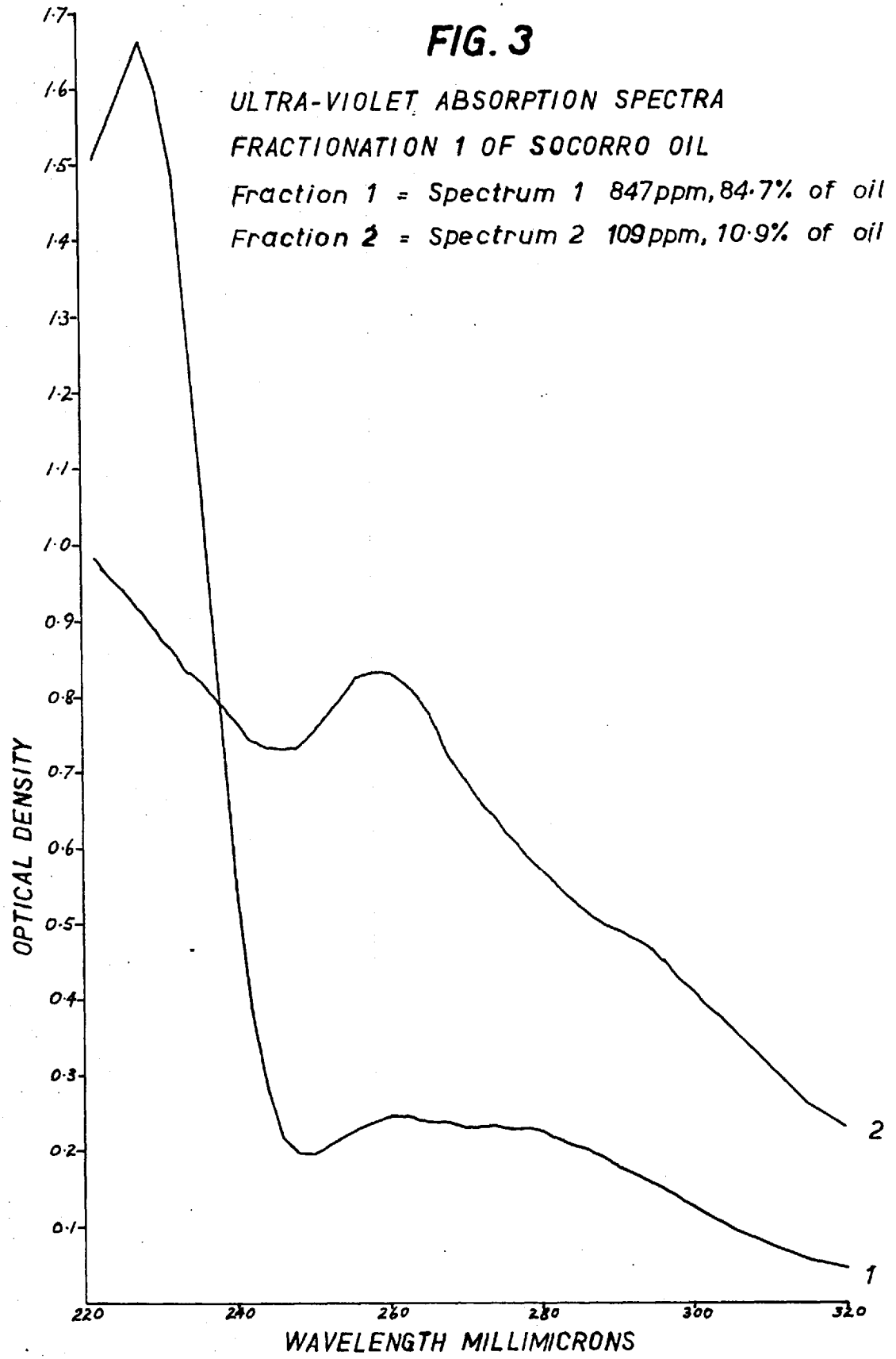


FIG. 4

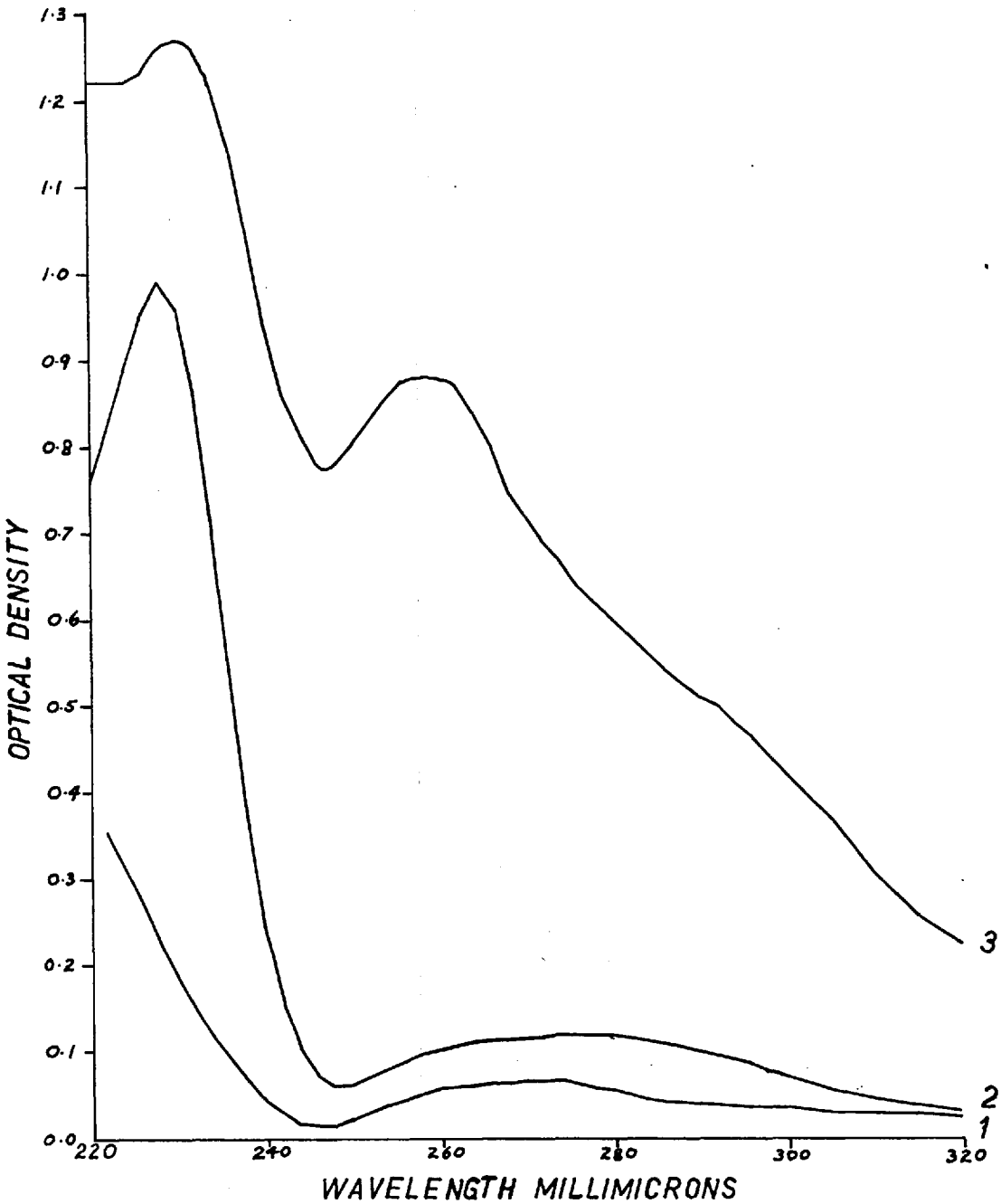
ULTRA-VIOLET ABSORPTION SPECTRA

FRACTIONATION 2 OF SOCORRO OIL

Fraction 1 = Spectrum 1 728ppm, 72·8% of oil

Fraction 2 = Spectrum 2 79ppm, 7·9% of oil

Fraction 3 = Spectrum 3 118ppm, 11·8% of oil



interpretation of their respective ultra-violet absorption spectra are shown in Tables XVIII and XIX.

Table XVIII

Fractionation 1.

Fraction	% weight	Fig.	Spectrum	Principal Component Types.
1	84.7	3	1	Paraffins-naphthenes; benzenes, naphthalenes and some phenanthrenes (i.e. 1-, 2-, and 3-ring aromatics).
2	10.9	3	2	4- and 5-ring aromatics, and aromatic-type non-hydrocarbon "resins".

Table XIX

Fractionation 2.

Fraction	% weight	Fig.	Spectrum	Principal Component Types.
1	72.8	4	1	Paraffins-naphthenes; trace of benzenes.
2	7.9	4	2	Benzenes and naphthalenes.
3	11.8	4	3	Some phenanthrenes (3-ring), mainly 4- and 5-ring aromatics, and aromatic-type non-hydrocarbon "resins".

The unrecovered 3.1% and 4.4% do not contribute greatly to the overall form of the Socorro oil spectrum, other than causing a small but gradual increase in the optical density values with decreasing wavelength (Fig. 16 spectra 1 and 2).

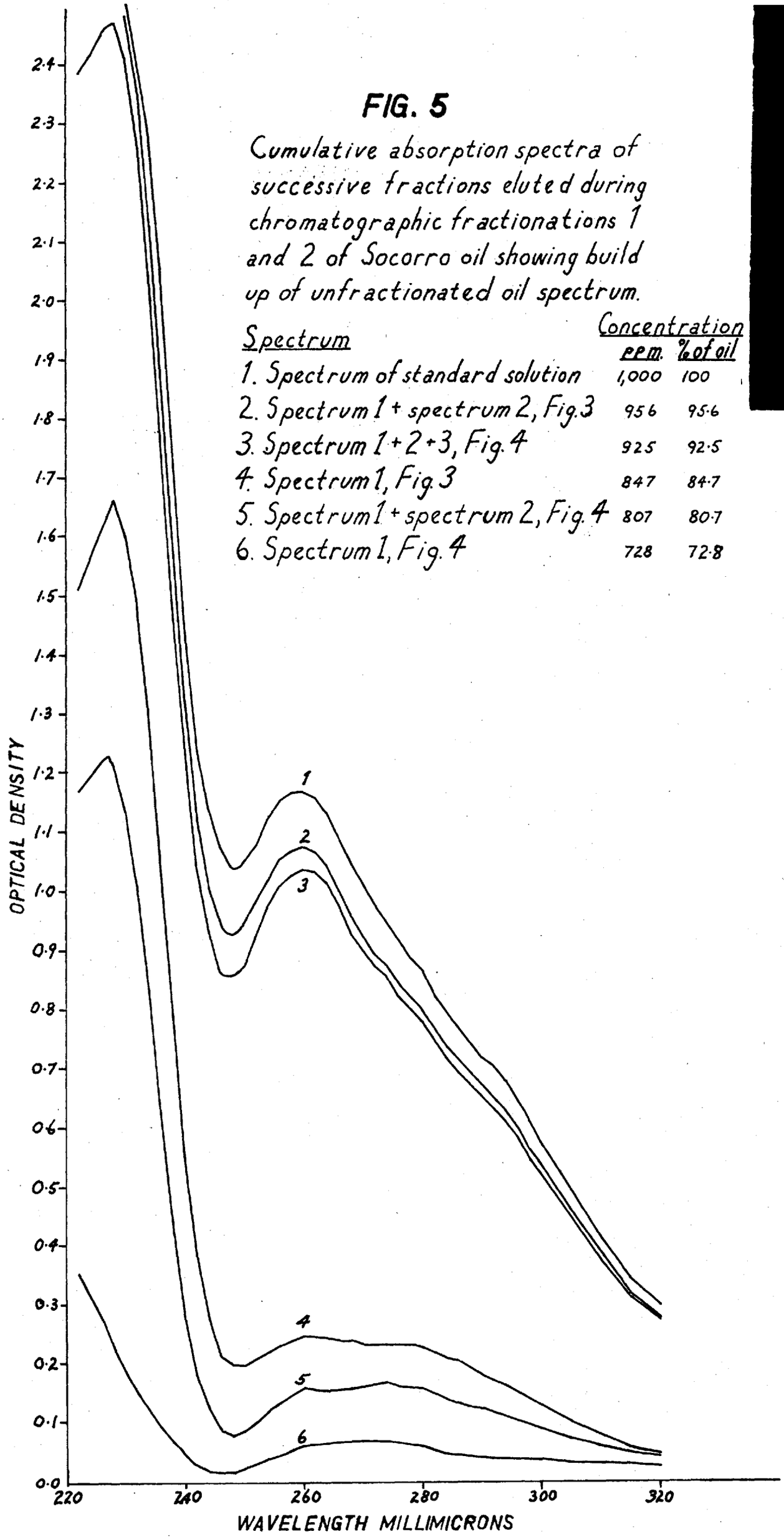
Summarising, the various groups of compounds present in crude oils have characteristic ultra-violet absorption spectra as follows:-

(1) The saturates, paraffin and naphthenic hydrocarbons,

FIG. 5

Cumulative absorption spectra of successive fractions eluted during chromatographic fractionations 1 and 2 of Socorro oil showing build up of unfractionated oil spectrum.

Spectrum	Concentration ppm.	Concentration % of oil
1. Spectrum of standard solution	1,000	100
2. Spectrum 1 + spectrum 2, Fig. 3	956	95.6
3. Spectrum 1 + 2 + 3, Fig. 4	925	92.5
4. Spectrum 1, Fig. 3	847	84.7
5. Spectrum 1 + spectrum 2, Fig. 4	807	80.7
6. Spectrum 1, Fig. 4	728	72.8



show little or no characteristic absorption bands in the wavelength range studied, thus accounting for the very small contribution of 72.8% of the oil to its overall ultra-violet absorption spectrum.

(ii) The aromatics have a complex of absorption bands in the region 290 to 250 mμ, followed by a minimum between 250 and 240 mμ, with weak absorption bands above 320 mμ. These characteristics are evident in 19.7% of the oil, i.e. between 72.8 and 92.5% of the eluted components, reaching maximum in 7.8% of the oil (from 84.7% to 92.5% of the eluted oil fractions). (see Fig. 5).

(iii) The non-hydrocarbon constituents, including material such as organic bases, ketones, sulphur compounds and asphaltic material, give a smooth curve which rises slowly above the base-line with decrease in wavelength over the region studied. They provide a background to the aromatic hydrocarbons in the 84.7 to 92.5% fraction, and also the characteristic spectrum of the unrecovered portion of the oil (Fig. 16).

From the above spectral analysis it is noted that the material eluted by benzene in the chromatographic fractionation of Socorro oil is not confined to aromatic hydrocarbons alone, i.e. it also includes a certain proportion of the less polar non-hydrocarbon material present in the oil. The benzene-eluted fraction may therefore be said to consist of the bulk

of the aromatic hydrocarbons, together with "resinous" non-hydrocarbon components, whilst the methanol-eluted fraction and the unrecovered material remaining adsorbed on the silica gel are the more highly polar "asphaltic" constituents present in the oil. The distinction between the "resinous" and "asphaltic" material is strictly arbitrary, since both contain nitrogen, sulphur and oxygen in aromatic-type ring systems, and on the basis of chromatography, the division between the two is dependent on their respective degrees of polarity as compared with the polarity of the eluents.

The Correlation of Ultra-violet Absorption Spectra with Oil Adsorption by Dry Adsorbents.

The chromatographic fractionation of Socorro oil into component groups, followed by an analysis of their respective ultra-violet absorption spectra, proved useful as a means of identifying the principal types of compound present. The addition of the various ultra-violet spectra further indicated the contribution which the different component groups make to the ultra-violet spectrum of the unfractionated oil. Unfortunately the percolation of oil, or oil solutions, through water-saturated clays is not a practical proposition, and the batch mixing of wet clay and oil solutions appeared to be the only reasonable method of investigating any interactions which might take place. Early experiences had

shown, however, that there are also practical difficulties involved in attempting to separate oil, or its component parts, from complexes formed with wet clays. Furthermore, the changes taking place in the oil composition as a result of wet-clay-oil interactions appeared to be quite small, and did not lend themselves to investigation by purely gravimetric methods. It was therefore decided that an attempt should be made to apply spectrophotometric measurements, previously correlated with oil concentration in solution, as a method for the evaluation of the extent and type of wet-clay-oil interactions. This technique would involve the spectrophotometric measurements of standard oil solutions before and after contact with wet clays and interpreting any differences found.

Attention was drawn in an earlier section to the difficulties involved in determining the concentration of a solution containing a number of solutes after differential removal of the solutes had taken place. Such would probably be the case for oil solutions, since the fractionation of Socorro oil demonstrated that its light-absorption characteristics were confined to approximately 30% of the total components present, and any spectrophotometric correlation based on these alone would certainly be in serious error if applied to total oil concentration.

Fortunately it appeared likely that any changes taking place in oil composition after contact with wet clays would be primarily concerned with this 30%, i.e. the non-hydrocarbons and aromatic hydrocarbons, rather than the non-polar saturated hydrocarbons which constitute the bulk (70%) of the oil. As a first approximation and as a standard for future comparison with oil solutions in contact with wet clays, the ultra-violet absorption spectrum of a standard oil solution was determined before and after contact with dry adsorbents. The validity of such comparisons was based on the supposition that the presence of water only reduced the adsorption capacity, or activity, of an adsorbent, i.e. the degree of adsorption, rather than altering the form of adsorption which takes place. This supposition was found to be only partially correct, nevertheless, the results obtained with dry adsorbents proved very useful in the interpretation of the results obtained with wet clays, as well as providing a quick, semi-quantitative method of finding residual solution concentrations.

Batch-type adsorptions of Socorro oil in n-heptane solution by different adsorbents dried at 110°C were performed, and the ultra-violet spectra of the equilibrium solutions measured. The adsorbents used were Fuller's Earth and Gault clay dried at 110°C, and activated silica gel (activated as for chromatography). The solvent

FIG. 6

Ultra-violet absorption spectra of 50 c.c. samples of standard Socorro oil in n-heptane solution (1,000 ppm) after contact with various weights of Fuller's Earth dried at 110°C.

Spectrum number	Concentration of oil in solution	Weight of Fuller's Earth
1	1,000 ppm	—
2	984 ppm	0·1520 gm
3	983 ppm	0·2183 gm.
4	930 ppm	0·3736 gm
5	852·5 ppm	0·9231 gm
6	770 ppm	2·5414 gm
7	707 ppm	4·1479 gm

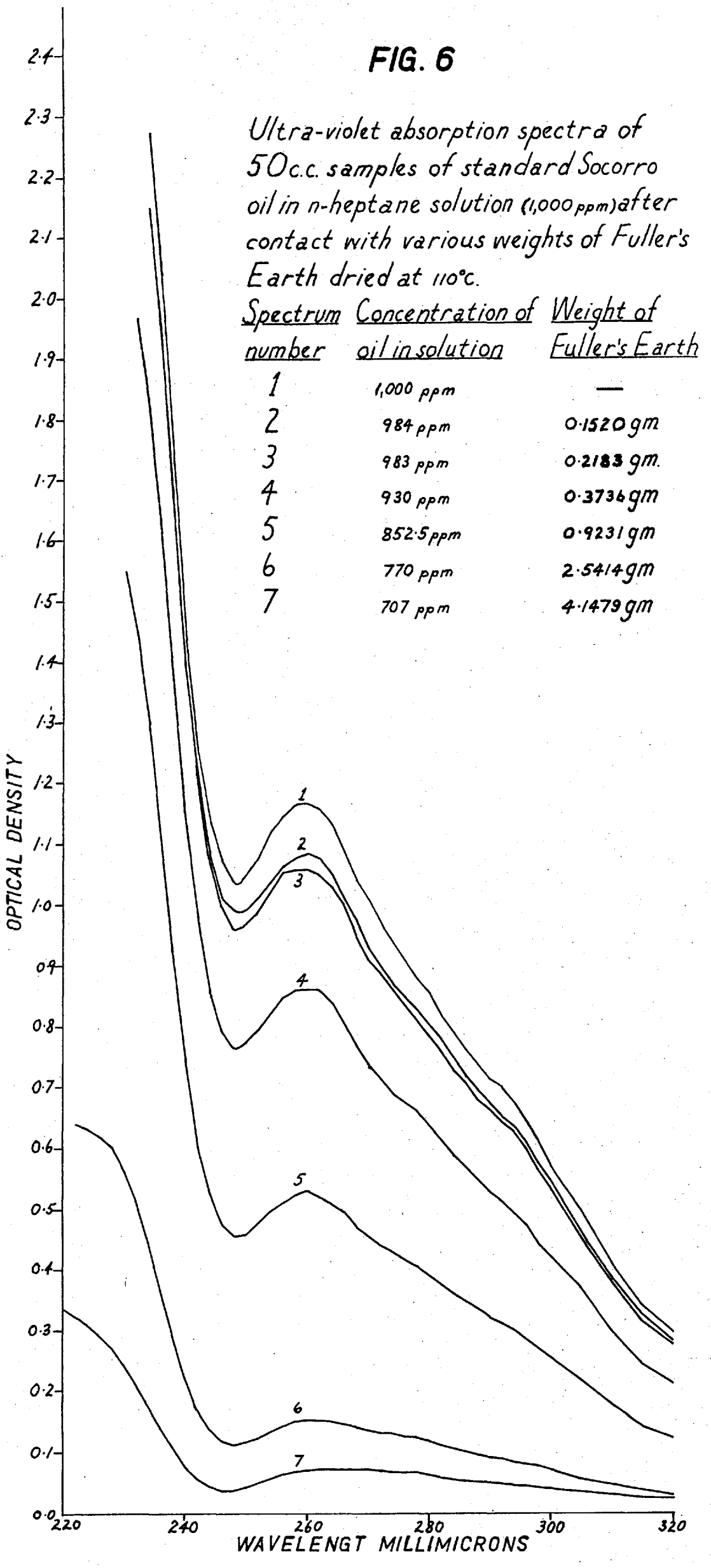


FIG. 7

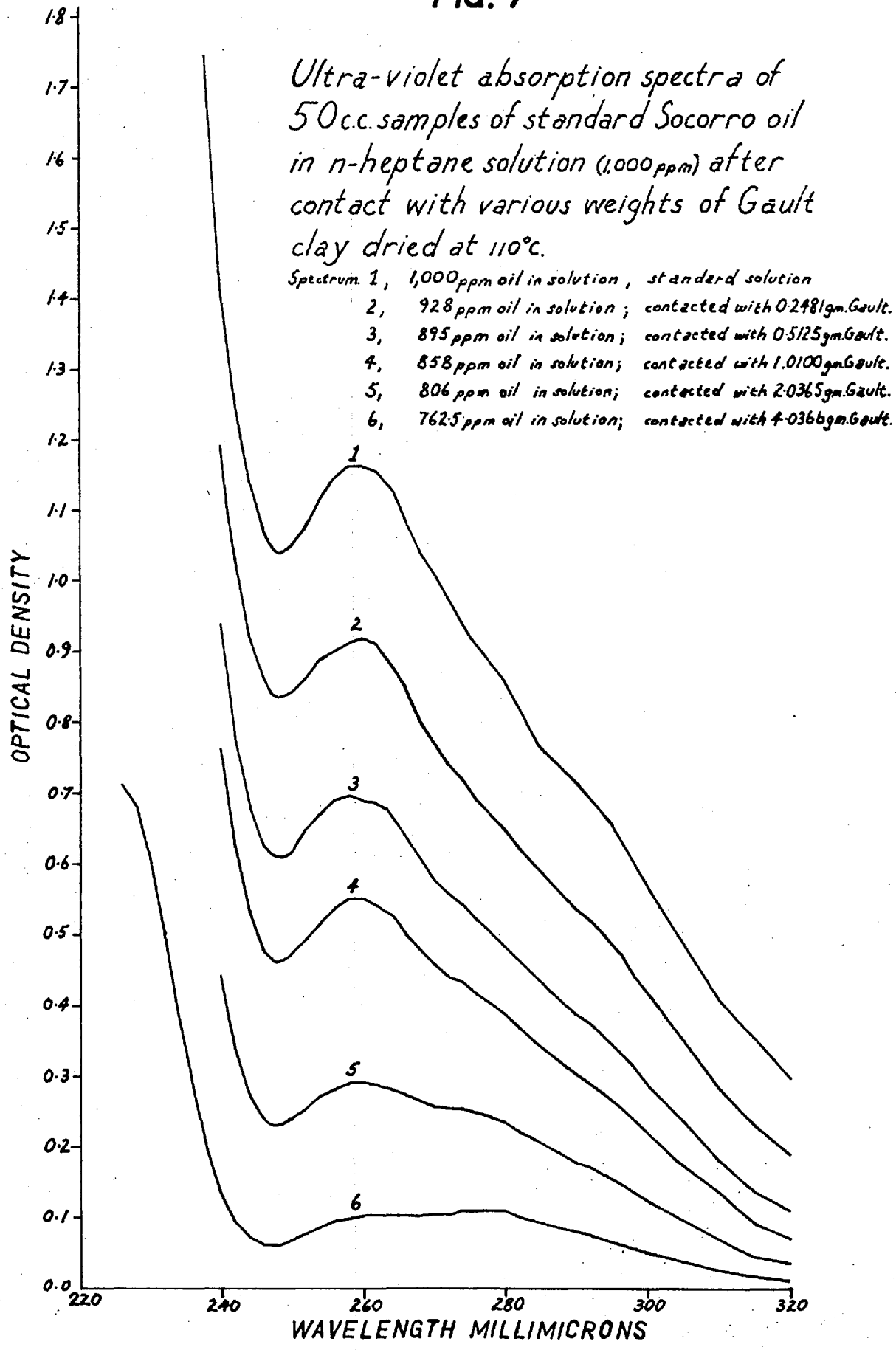

Ultra-violet absorption spectra of 50 c.c. samples of standard Socorro oil in n-heptane solution (1,000 ppm) after contact with various weights of Gault clay dried at 110°C.
Spectrum 1, 1,000 ppm oil in solution, standard solution
2, 928 ppm oil in solution; contacted with 0·2481 gm. Gault.
3, 895 ppm oil in solution; contacted with 0·5125 gm. Gault.
4, 858 ppm oil in solution; contacted with 1·0100 gm. Gault.
5, 806 ppm oil in solution; contacted with 2·0365 gm. Gault.
6, 762·5 ppm oil in solution; contacted with 4·0366 gm. Gault.
OPTICAL DENSITY
1·8
1·7
1·6
1·5
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0·0
220
240
260
280
300
320
WAVELENGTH MILLIMICRONS
1
2
3
4
5
6

FIG. 8

Ultra-violet absorption spectra of 50 c.c. samples of standard Socorro oil in n-heptane solution (1,000 ppm) after contact with various weights of activated silica gel.

Spectrum number	Concentration of oil in solution.	Weight of silica gel.
1	1,000 ppm.	
2	942 ppm.	0·0931 gm.
3	900 ppm.	0·1907 gm.
4	878 ppm.	0·4127 gm.
5	869 ppm.	0·7919 gm.
6	818 ppm.	1·7960 gm.
7	785 ppm.	2·8858 gm.
8	753 ppm.	6·2045 gm.

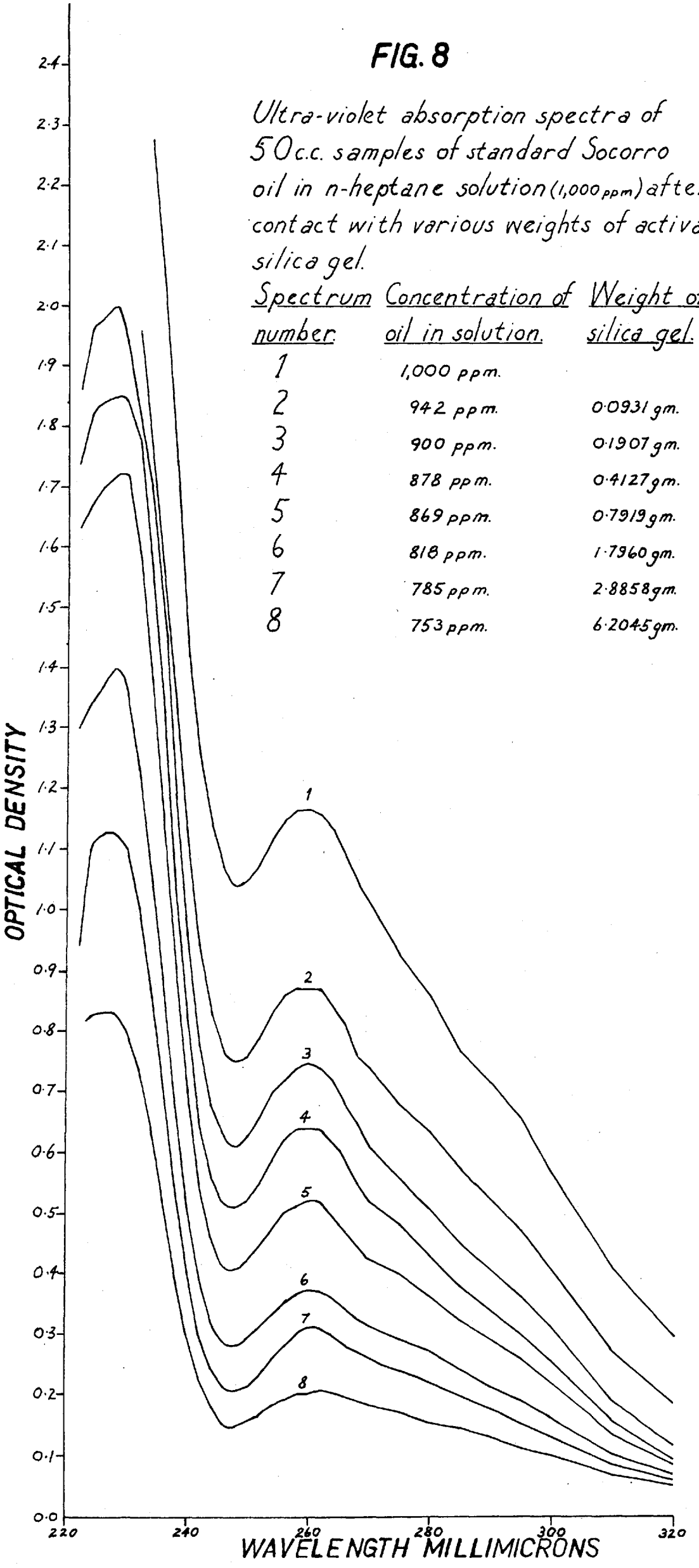


FIG. 9

Ultra-violet absorption spectra of a 50 c.c. sample of Socorro oil in n-heptane solution (1,000 ppm) after contact with 1·0188 gm. of Fuller's Earth dried at 110°c.

Spectrum number.

1. Socorro oil in n-heptane solution (1,000 ppm)
2. Solution 45 min. after initial contact.
3. Solution 72 hours after initial contact.
4. Solution after distilled water had been added and stirred with the clay-oil solution complex (96 hours after initial contact).

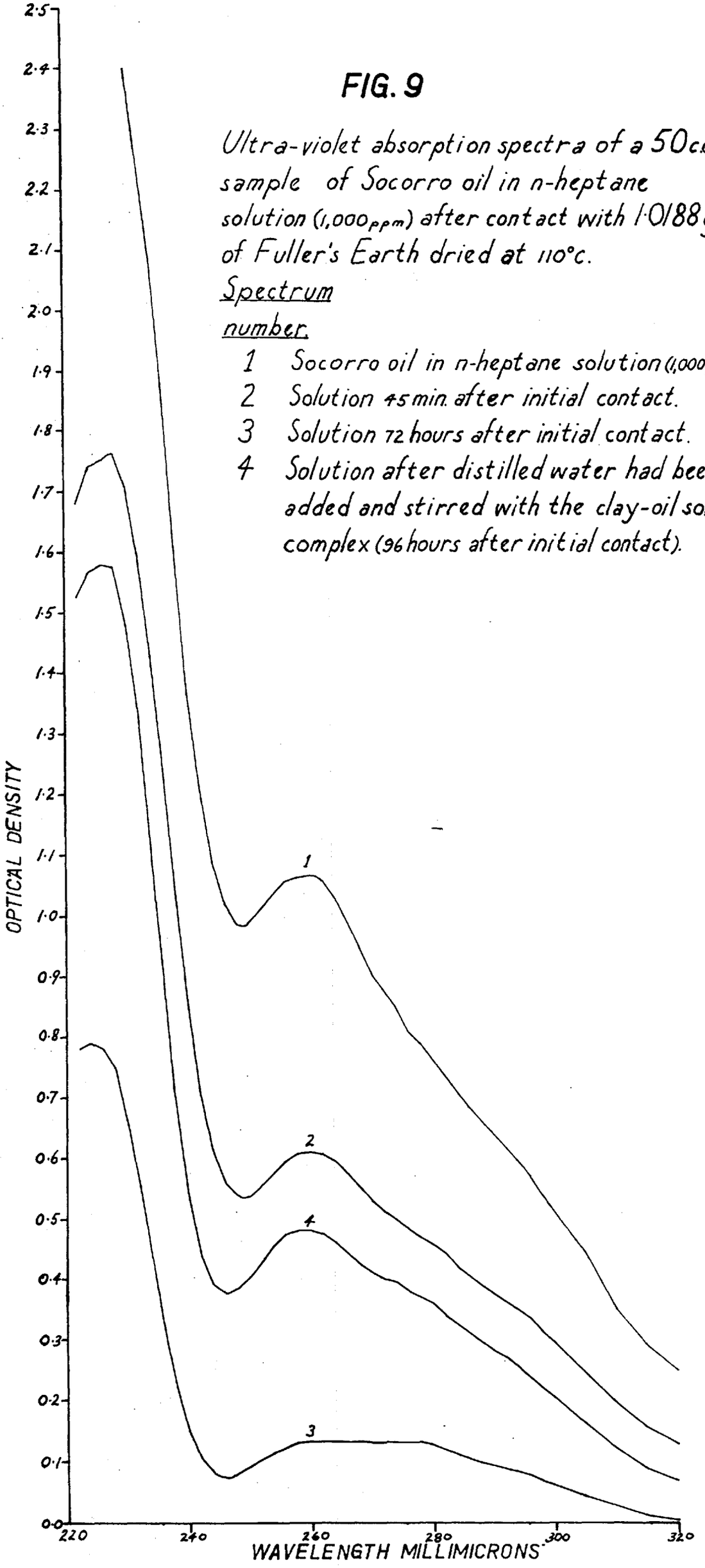
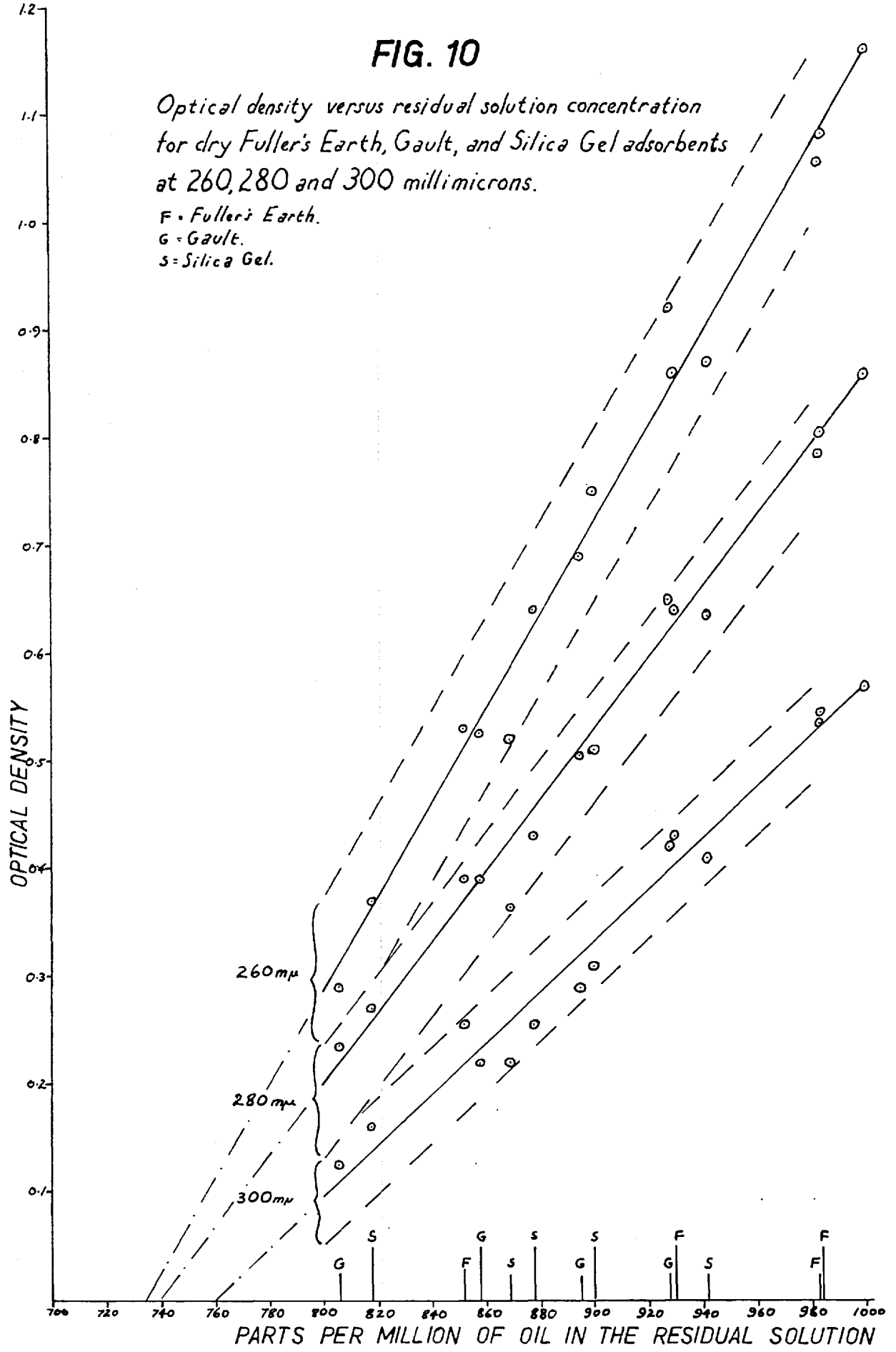


FIG. 10

Optical density versus residual solution concentration for dry Fuller's Earth, Gault, and Silica Gel adsorbents at 260, 280 and 300 millimicrons.

F = Fuller's Earth.
G = Gault.
S = Silica Gel.



carrier for the oil being n-heptane precluded the adsorption of the saturated oil components. The ultra-violet spectra of the residual oil solutions after contact with the adsorbents for a period of several hours compared with the spectrum of the standard solution, are shown in Figs. 6, 7 and 8, for Fuller's Earth, Gault and silica gel, respectively. The solutions in contact with Gault and silica gel quickly reached equilibrium (within one hour), but the solutions in contact with Fuller's Earth required up to 72 hours to reach final equilibrium (Fig. 9 spectrum 2 and spectrum 3). This does not invalidate the results shown in Fig. 6, since the quantity of oil in the residual solutions was gravimetrically determined after evaporation of the solution used for spectral determination, the solution having first been removed from contact with the clay. Since the main purpose was to correlate the quantity of oil adsorption with the absorption spectrum of the residual solution, the correlation shown remains unaffected.

A reasonably good linear relationship was found between optical density and residual solution concentration from 1,000 p.p.m. to 800 p.p.m. at the wavelengths 260, 280 and 300 millmicrons (Fig. 10). The limited range of the correlation is to be expected because the n-heptane solvent prevented the adsorption of at least 700 p.p.m. (70%) of the oil in solution. Extrapolarion of the linear relationships,

FIG. 11

Weight of dry Fuller's Earth versus optical density of residual solutions at 240, 260, 280 and 300 millimicrons.

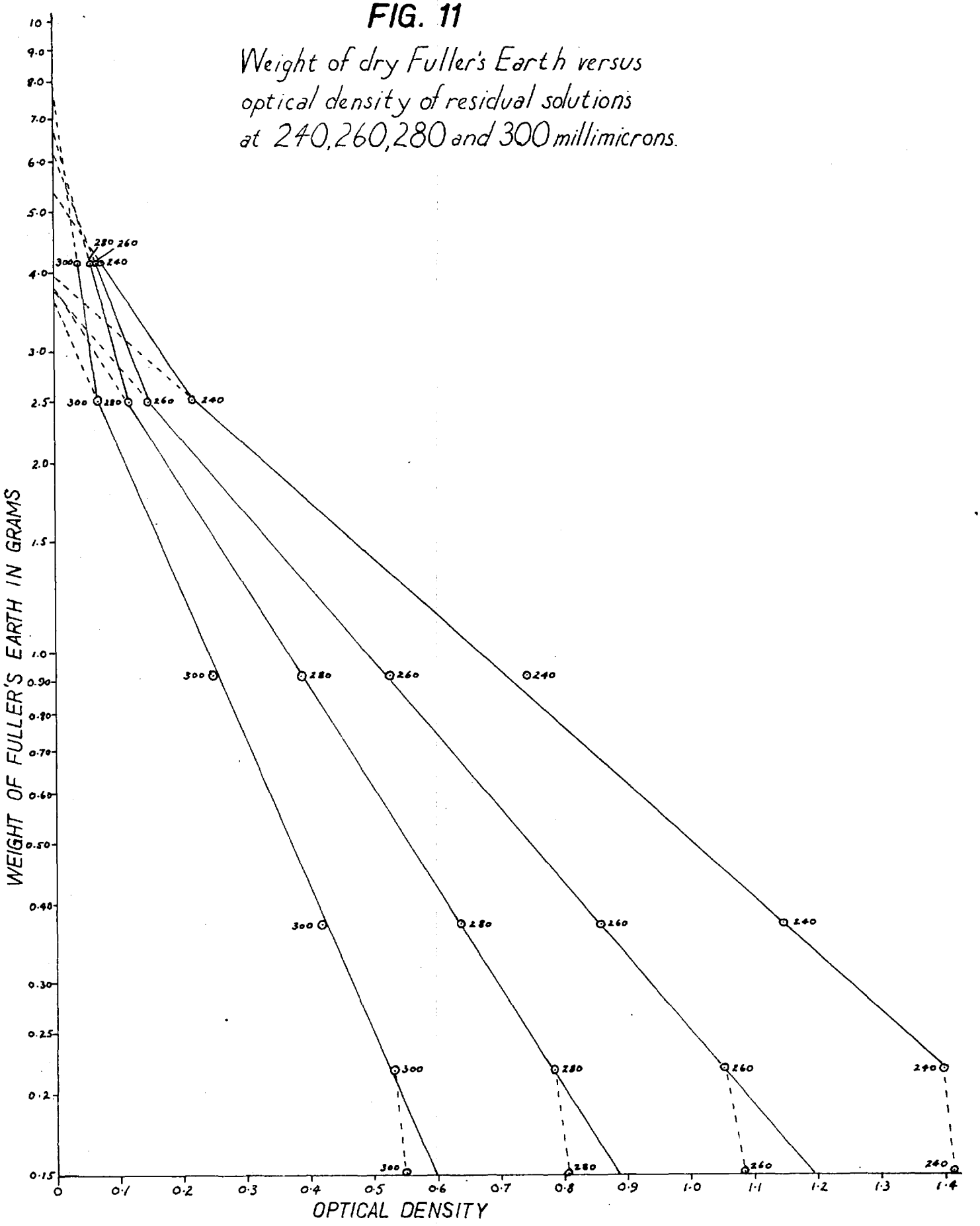


FIG. 12

Weight of dry Gault clay versus optical density of residual solutions at 240, 260, 280 and 300 millimicrons.

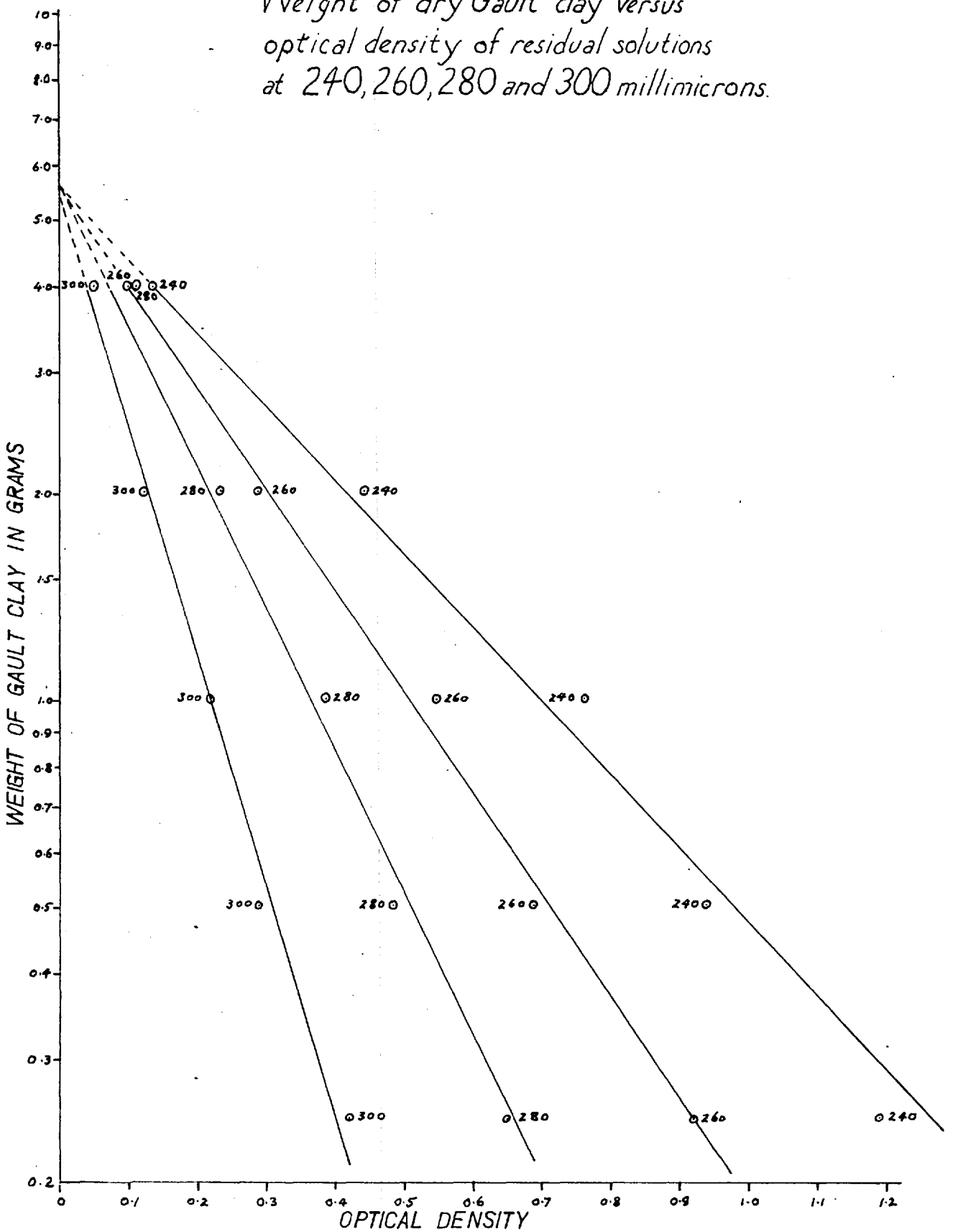
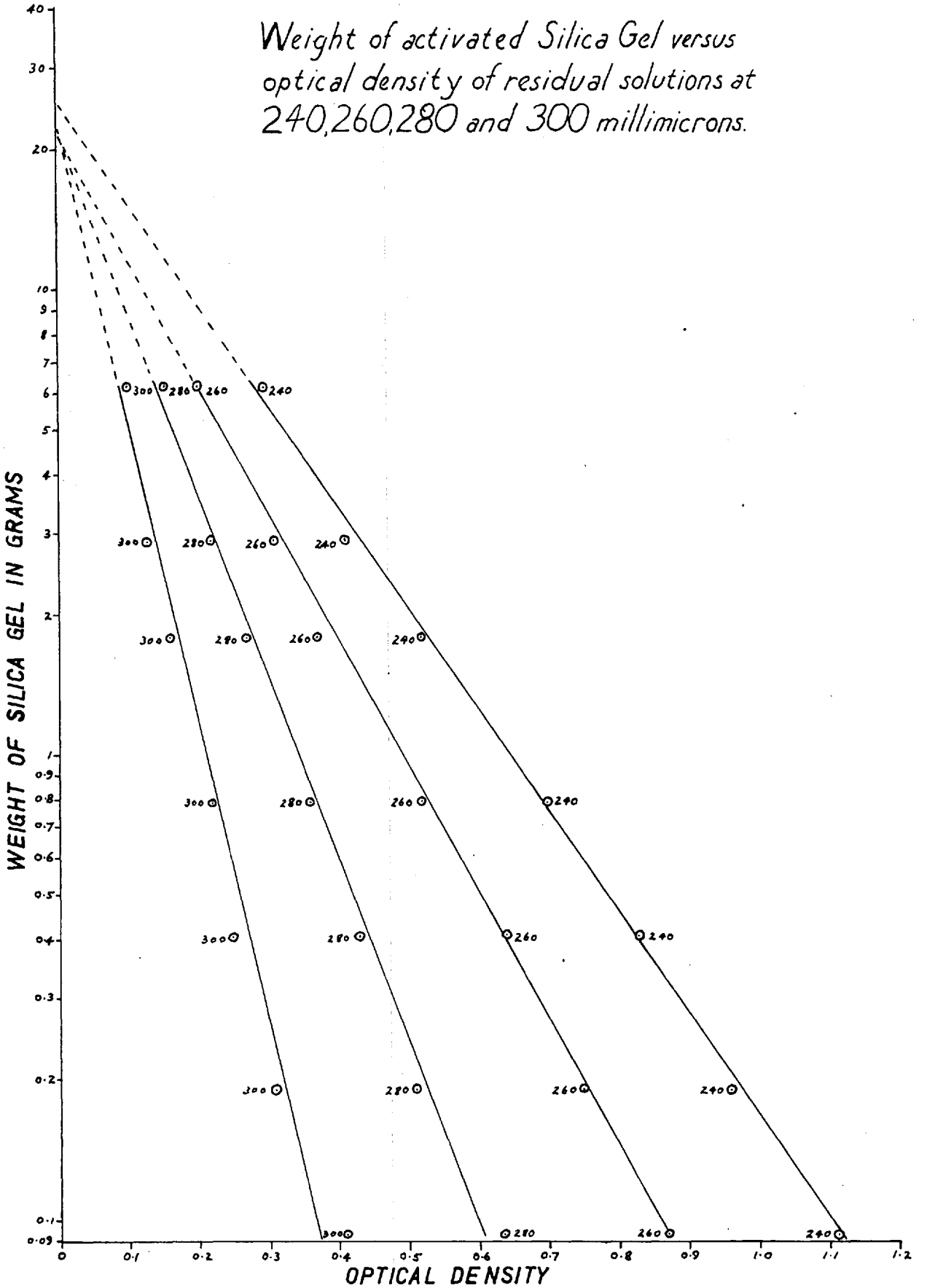


FIG. 13


Weight of activated Silica Gel versus optical density of residual solutions at 240, 260, 280 and 300 millimicrons.
WEIGHT OF SILICA GEL IN GRAMS
OPTICAL DENSITY
40
30
20
10
9
8
7
6
5
4
3
2
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.09
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
300
280
260
240

at the three wavelengths, does not, however, give a common intercept on the concentration axis as would be expected if the material adsorbed accounted for all the light absorption at these three wavelengths. Thus the lack of a linear correlation between optical density and solution concentration below 800 p.p.m. for all the adsorbents shows that there are other components absorbing light in this spectral range which do not obey the same relationship, i.e. they are not so extensively adsorbed. These components are presumably the least polar of the aromatic hydrocarbons and account for the other 10% (100 p.p.m.) of the oil, which is in general agreement with the results of the Socorro oil fractionations, (Fig. 4 spectra 1 and 2) i.e. the lower aromatics were associated with the saturates eluted by n-heptane.

In spite of the fact that the Fuller's Earth samples had not reached a final equilibrium at the time their residual solutions were examined, the relationship between the weight of adsorbent and optical density of the residual solutions at the four wavelengths 240, 260, 280 and 300 millimicrons (Fig. 11) was consistent in form with those of Gault (Fig. 12) and silica gel (Fig. 13). The weight of adsorbent plotted on a logarithmic scale bears a linear relationship with optical density plotted on a linear scale for optical density values down to 0.15 at 240 mμ,

0.1 at 260 mμ, 0.075 at 280 mμ and 0.05 at 300 mμ for the standard solution used. Thus, down to these optical density values the relationship may be expressed by the empirical equation $y = 10^{a+bx}$ for all three adsorbents, where y is the weight of adsorbent in grams, x is the optical density at a given wavelength and a, and b are constants. Taking logs, $\log y = bx + a$, and since for each adsorbent the extrapolation of the relationship at different wavelengths all intercept the ordinate axis at approximately the same point, a is constant for a given adsorbent, whilst the gradient b accounts for the variations between the different wavelengths. From the values of the intercepts on the ordinate axis, it is seen that the adsorbent capacity per gram of dry adsorbent, i.e. the specific adsorption capacity, is greatest for Fuller's Earth, even though final equilibrium had not been reached, followed by Gault, whilst silica gel is the least effective in adsorbing the oil components from solution.

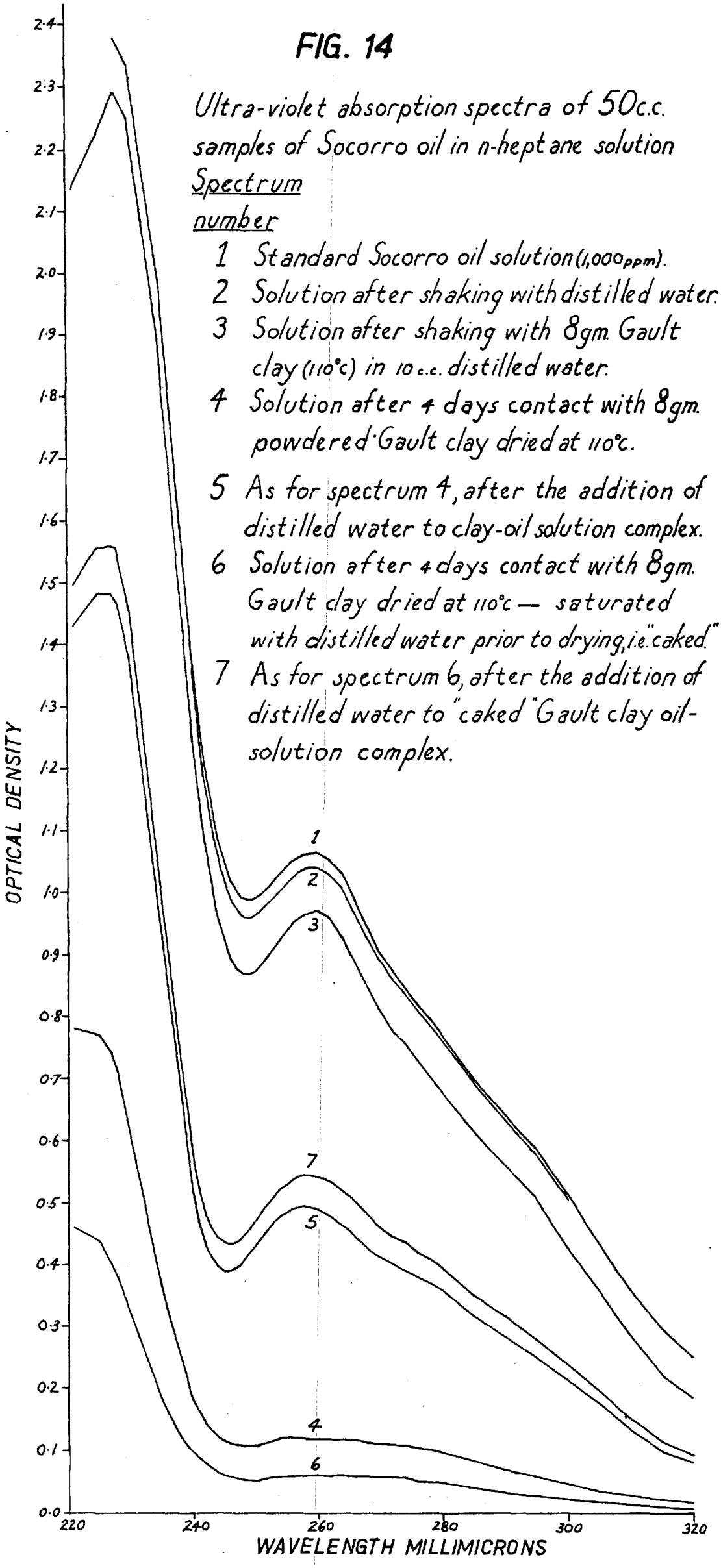
During the course of these experiments an interesting discovery was made concerning the adsorption properties of oven-dried clays. If two clay samples of equal weight were initially powdered (passing 100 mesh B.S. sieve) and one of them was thoroughly mixed with an excess of water, then after both had been oven-dried at 110°C for four days, it was found that the dry clay "cake" resulting from the

FIG. 14

Ultra-violet absorption spectra of 50c.c. samples of Socorro oil in n-heptane solution

Spectrum number

1 Standard Socorro oil solution (1,000 ppm).
2 Solution after shaking with distilled water.
3 Solution after shaking with 8gm. Gault clay (110°c) in 10 c.c. distilled water.
4 Solution after 4 days contact with 8gm. powdered Gault clay dried at 110°c.
5 As for spectrum 4, after the addition of distilled water to clay-oil solution complex.
6 Solution after 4 days contact with 8gm. Gault clay dried at 110°c — saturated with distilled water prior to drying, i.e. "caked."
7 As for spectrum 6, after the addition of distilled water to "caked" Gault clay oil-solution complex.



initially water saturated clay was capable of adsorbing a greater quantity of oil from solution than the oven-dried powdered sample. The time taken for equilibrium to be reached was, however, much greater for the clay cake than for the oven-dried powdered sample. The results of such an experiment using 8-gm. samples of Gault clay are shown in Fig. 14, spectrum 4 and spectrum 6. Thus it appears that the fairly rapid removal of excess water from a saturated clay sample activates the final dried clay to a greater degree than similar oven drying of an air-dry powdered clay, even though the rate of adsorption is higher for the latter sample.

Chapter V.

THE INFLUENCE OF WATER ON THE ADSORPTION OF OIL BY CLAYS.

The Effects of Water on Dried Clay-oil Adsorption Complexes.

Water being a highly polar compound could naturally be expected to have a marked effect on the adsorption by oven-dried clays of the non-polar hydrocarbons and also possibly on the less polar non-hydrocarbons present in the Socorro oil. The effect of water on the dried clay-oil complexes would also determine a limiting condition for the adsorption of oil components by water-wetted clays, since only those components whose affinity for the clay is greater than water could be expected to displace water from a wetted clay, i.e. the components would be preferentially adsorbed, thus causing water displacement.

The oven-dried clay-oil complexes used in these experiments consisted of:-

i) The 1 gm. Fuller's Earth sample in contact with 50 cc. of standard oil-in-heptane solution (1,000 p.p.m.) used for determing the effect of time on adsorption from oil solution (Fig. 9, spectrum 3).

ii) The "caked" Gault sample referred to in the last section, (Fig. 14, spectrum 6), consisting of 8 gm. of oven-dried clay in contact with 50 cc. of the standard solution.

iii) The powdered Gault sample (8 gm.) used as a control

for the adsorption by "caked" Gault (Fig. 14, spectrum 4).

It was indicated from a study of their respective absorption spectra, that each of the sample complexes approached a maximum in the amount of oil adsorbed, i.e. they had adsorbed most of the component types present in the oil other than the saturates, and lower aromatics.

The original oil solutions from which these samples had adsorbed components remained in contact with the clays at all times, and the small volume of residual solution necessary for spectral examination was always returned to the bulk of this solution on completion of the measurements.

Distilled water was added to the weighing bottles containing the clay-oil complexes in contact with their residual supernatant solutions, and after standing and stirring, the ultra-violet absorption spectra of the residual solutions were re-determined. These are shown in Fig. 9 , spectrum 4, and Fig. 14, spectra 5 and 7, for the Fuller's Earth, powdered, and caked Gault samples, respectively.

The most notable point regarding the three "water desorption" spectra is their similarity both in form and value. This is particularly noticeable when the differences of adsorbent type, adsorbent weight, and the variable extent of primary adsorption are taken into account. The primary adsorption varied from 23 to 30% of the oil in solution as

interpolated from Figs. 6, 7 and 8, whereas the amount remaining after desorption remains approximately constant between 13 and 15% based on similar interpolations. This similarity of final desorption suggests that there is a constant transition point of the components adsorbed from oil solution with respect to the presence of water, and that this transition point is a function of the type of oil component rather than the nature of the clay adsorbent. The majority of the components desorbed appear to be aromatic hydrocarbons, although there is a strong suggestion, as a result of the increase in optical density values at 320 mμ, that some non-hydrocarbons may also have been desorbed.

An interesting point that concerns the two Gault clay samples, is the slightly greater desorption of adsorbed components from the caked sample (Fig. 14, spectra 5 and 7). No explanation can be given to account for this observation other than the possibility of more efficient extraction of the desorbed components by the residual solution as a result of the break up of the clay cake during hydration.

In order to verify the "transition point" interpretation of the above experiments, a water "wetted" clay was prepared. A sample of powdered Gault clay was oven-dried at 110°C for four days and then placed in an air-tight dessicator over a saturated solution of sodium chloride. The saturated sodium chloride solution ensured that an atmosphere of 75%

FIG. 15

Ultra-violet absorption spectra of a 50c.c. sample of standard Socorro oil in n-heptane solution (1,000 ppm) after contact with 8 gm. of "mildly wetted" Gault clay (i.e. initially dried at 110°c, then exposed to a controlled atmosphere of 75% relative humidity).

Spectrum number

1 Socorro oil in n-heptane solution (1,000 ppm)

2 Standard solution after initial contact.

3 Residual solution after the addition of excess water (distilled) to the mildly wetted Gault clay in contact with standard Socorro oil in n-heptane solution

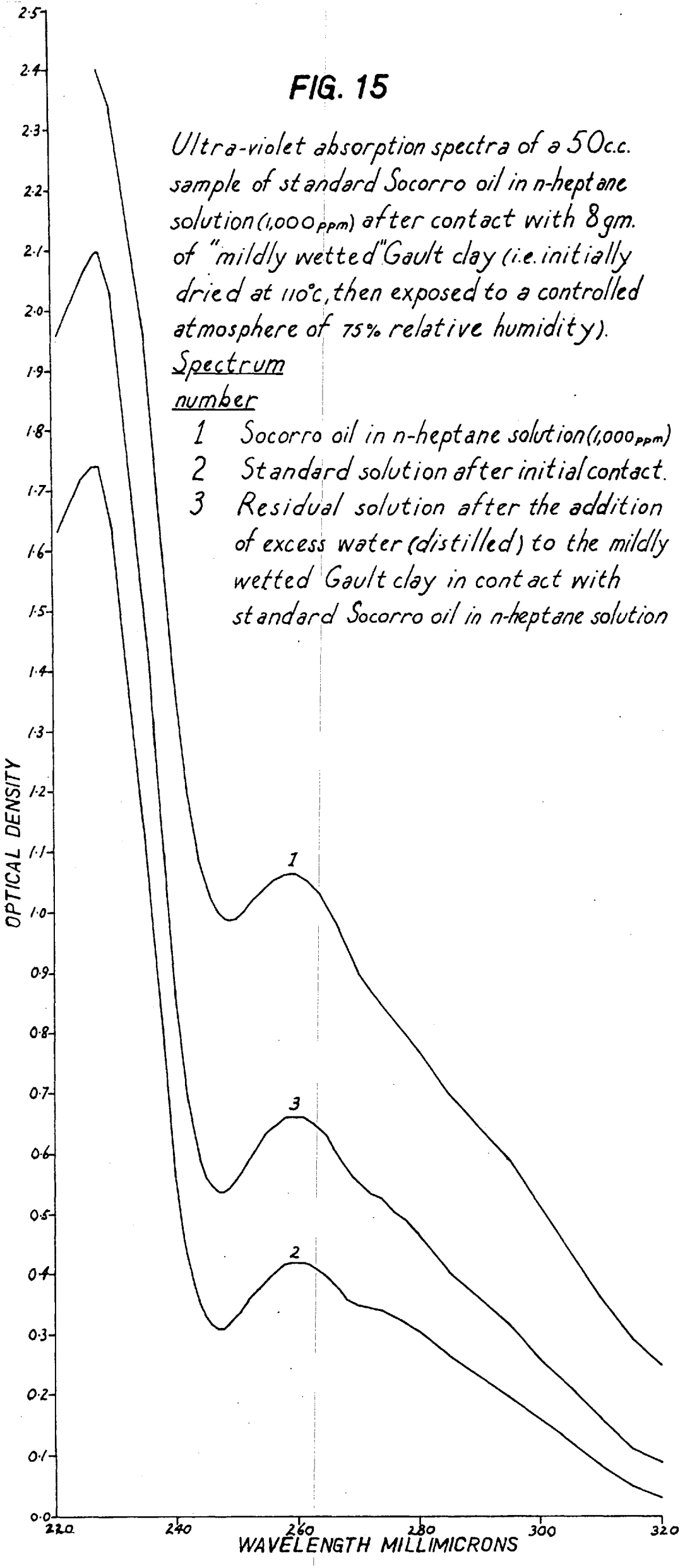
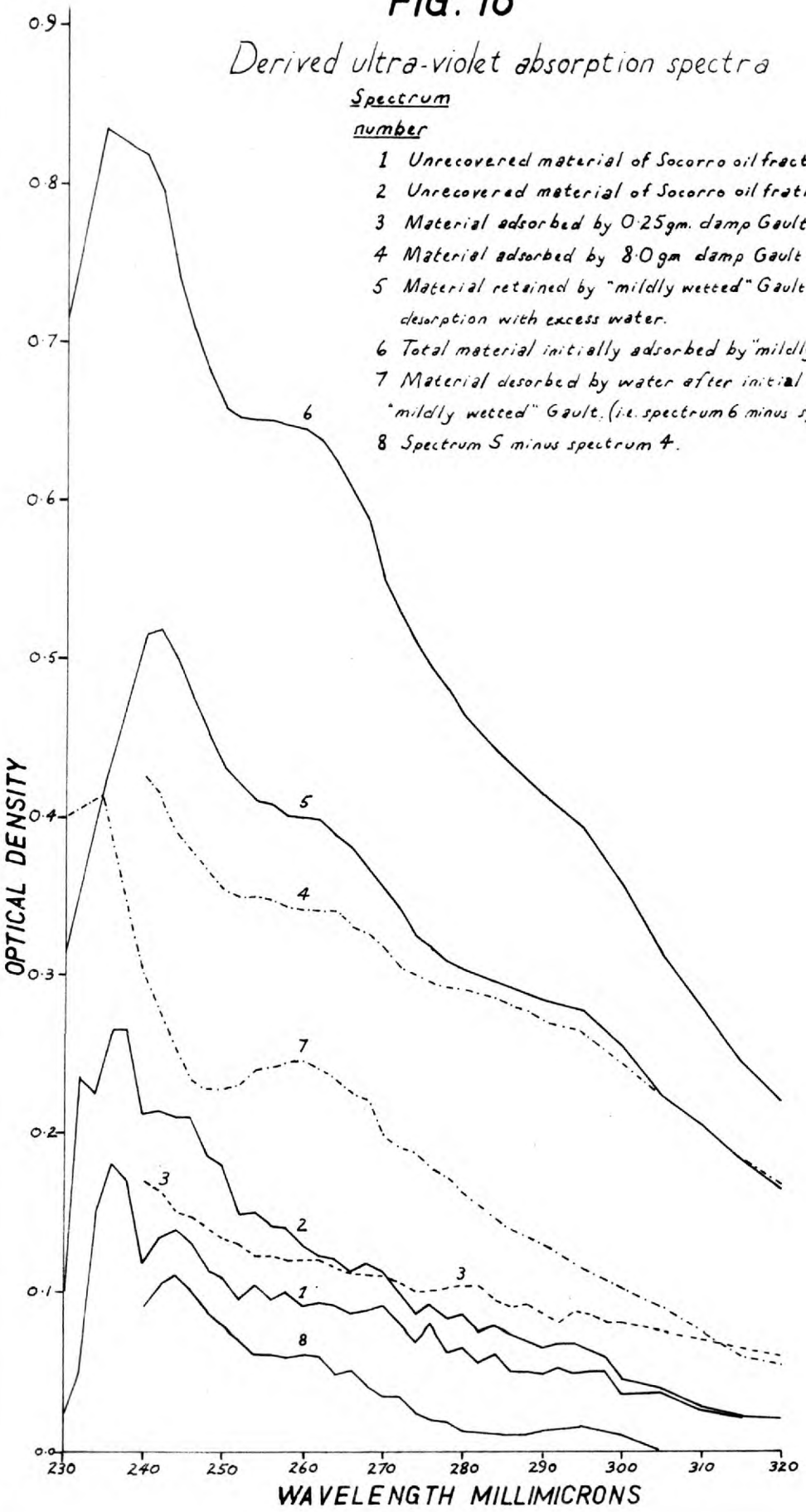


FIG. 16

Derived ultra-violet absorption spectra



relative humidity was maintained around the clay and allowed a water layer of molecular dimensions to be adsorbed onto its surface. The wetted clay was then shaken with a standard oil-in-heptane solution and the absorption spectrum of the residual solution measured (Fig. 15, spectrum 2); the derived spectrum of the material adsorbed is shown in Fig. 16, spectrum 6.

Certain small but noticeable differences were found to exist between this spectrum and the spectra obtained after the water desorption of dried clay-oil complexes. (Fig. 9, spectrum 4 and Fig. 14 spectra 5 and 7).

a) The absorption peak at 228 mμ is greater (1.74) than for the water desorption spectra (1.48 to 1.58).

b) The absorption peak between 258 and 260 mμ is lower (0.42) than for the corresponding peak in the water desorption spectra (0.48 to 0.55).

c) The optical density at 320 mμ is lower (0.03) compared with the values for the water desorption spectra (0.07 to 0.09).

The only spectrum which in any way resembles the spectrum obtained from this residual solution is shown in Fig. 3, spectrum 1, and this represents the bulk of the "pure" hydrocarbon fraction (saturate and aromatic) present in the oil (84.7%). On this basis it would appear that the residual oil solution spectrum shown in Fig. 15, spectrum 2, also

represents a slightly greater quantity of "pure" hydrocarbons than in Fig. 3, spectrum 1. This implies that all the non-hydrocarbons, and possibly some aromatic hydrocarbons, have been adsorbed by the "wetted" clay leaving only hydrocarbons in solution. This conclusion was reached from an examination of the derived spectrum of the material desorbed by water (Fig. 16, spectrum 7), and suggests from its general form that aromatic hydrocarbons, as well as non-hydrocarbons, are present in the material initially adsorbed by mildly wetted Gault clay. It also appears possible that some hydrocarbons may be retained in association with the non-hydrocarbons which constitute the bulk of the material not desorbed by the addition of water. (Fig. 16, spectrum 5). The desorption of some of the non-hydrocarbon components by an excess of water shows that the volume of water and/or the degree of orientation of water at the surface of or surrounding an adsorbent is important. Even in the presence of an excess of water, however, complete desorption is not achieved and between 10 and 12% of the components in the original oil solution still remains adsorbed.

These experiments appear to indicate that "wetted" clays are not able to adsorb the hydrocarbon components present in crude oils directly. The adsorption of the non-hydrocarbons by wetted clays may, however, act as intermediary amphipathic

substances which change the state of the clay from a hydrophilic to a hydrophobic material, thus permitting the sorption of the non-polar hydrocarbons.

Investigation of Crude Oil Sorption by Water-Saturated Clays.

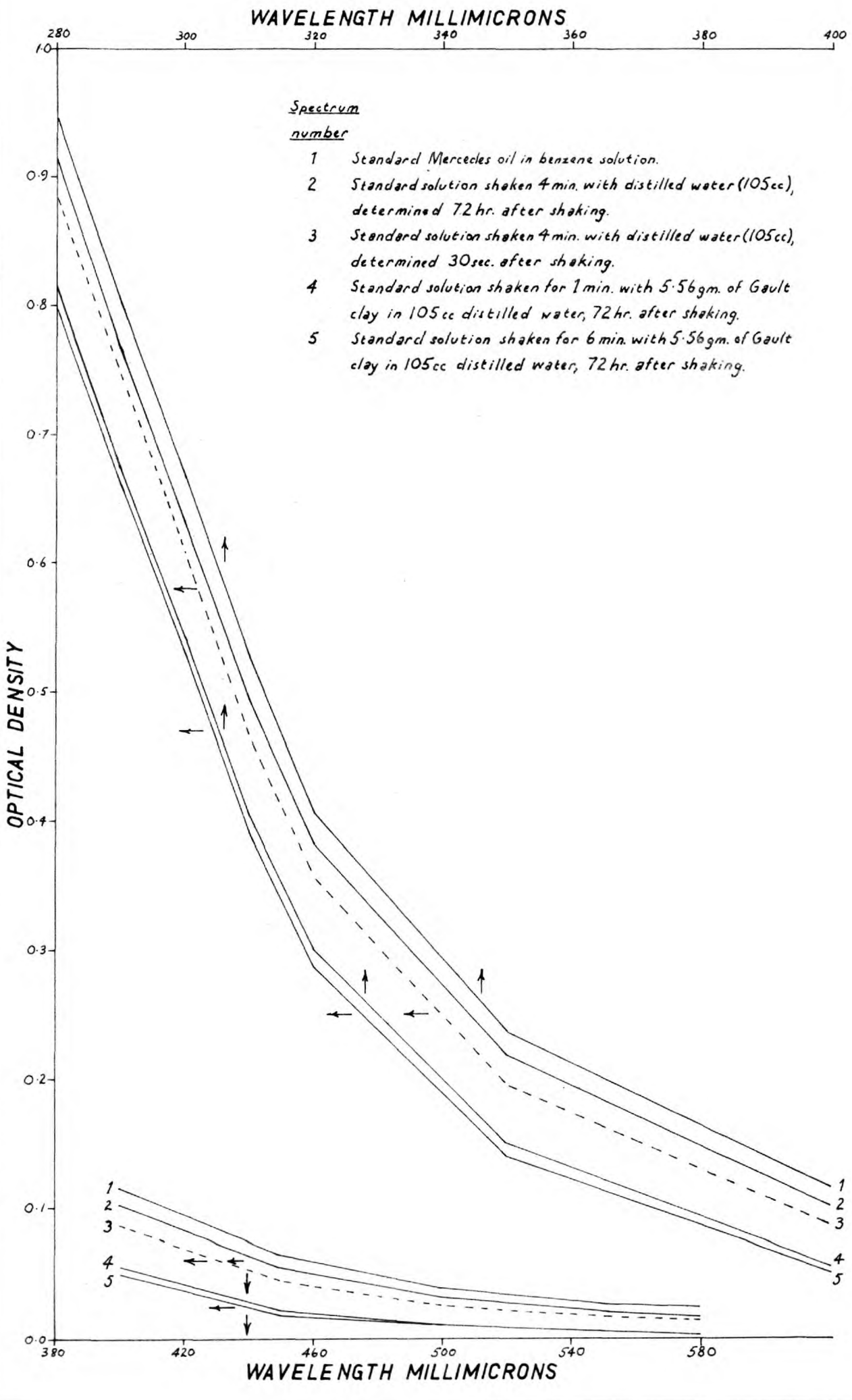
Having demonstrated that water is not capable of completely desorbing adsorbed crude oil components from dry and "mildly wetted" clays, the next step was to determine the effects of the presence of an excess of water on the adsorption of oil from the n-heptane solution using wet and damp clays. This is in effect a reverse of the method attempted earlier.

The reason for choosing n-heptane was its low polarity, its comparatively low volatility, and its low water solubility. The low polarity allows the full effect of adsorption to be felt (Cassidy's Rule 3), and the low volatility allows spectral determinations to be made without the likelihood of concentration due to evaporation of the solvent.

Initially a pilot experiment was carried out using a solution of Mercedes oil in benzene and distilled water saturated with benzene in order to avoid the solubility effects of the solvent. The object of the experiment was to investigate the possibility of adsorption by wet-clays from oil solution, and the variation of the absorption spectrum of the residual solution with the length of time the solution was shaken with a clay suspension.

FIG. 17

Ultra-violet absorption spectra of 25c.c. samples of standard Mercedes oil in benzene solution(463ppm) after shaking with distilled water, and Gault clay-distilled water slurries.



A suspension of Gault clay in distilled water (saturated with benzene) was prepared, and five 105cc. volumes of suspension were transferred to measuring cylinders, with ground-glass stoppers in order to avoid evaporation. To a sixth measuring cylinder was added 105 cc. of the benzene-saturated distilled water used in the preparation of the clay suspension. A 25cc. volume of a solution of the Mercedes oil in benzene was then added to each of the six measuring cylinders. The five oil-solution clay-suspension samples were then shaken very vigorously by hand for periods varying from one to six minutes, and the oil-solution distilled-water control samples shaken for four minutes. The results of this experiment are shown in Table XX.

From this Table and Fig. 17 the following points are noted.

1) There are slight differences between the spectrum of the original solution and that of the same solution after shaking with distilled water. This is presumably due to oil components being dissolved in the water and/or adsorbed at the water-solution interface.

2) There is an overall reduction in the values of the absorption spectrum when the solution is shaken with the Gault clay suspension, the greatest overall reduction occuring at the lower wavelengths.

3) There is a slight increase of adsorption with the time the samples were shaken, reaching apparent equilibrium after a minimum of four minutes.

FIG. 18

Comparison of optical density of 25cc standard Mercedes oil in benzene solution samples at various wavelengths throughout ultra-violet absorption spectrum, before and after shaking with benzene saturated distilled water, and a Gault clay slurry (5·56gm. in 105 c.c. benzene saturated distilled water), expressed as percentage of standard solution absorption.

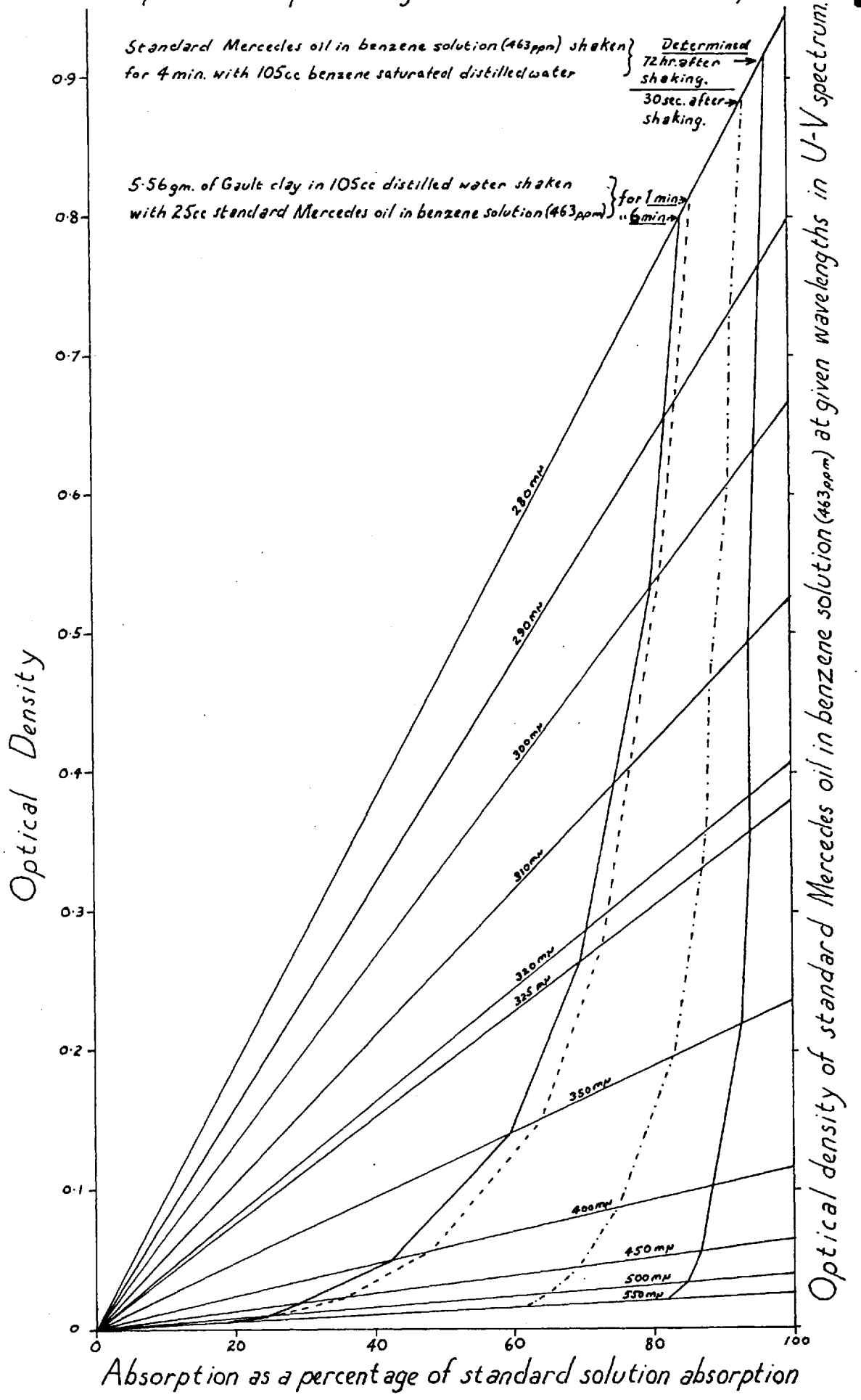


Table XX

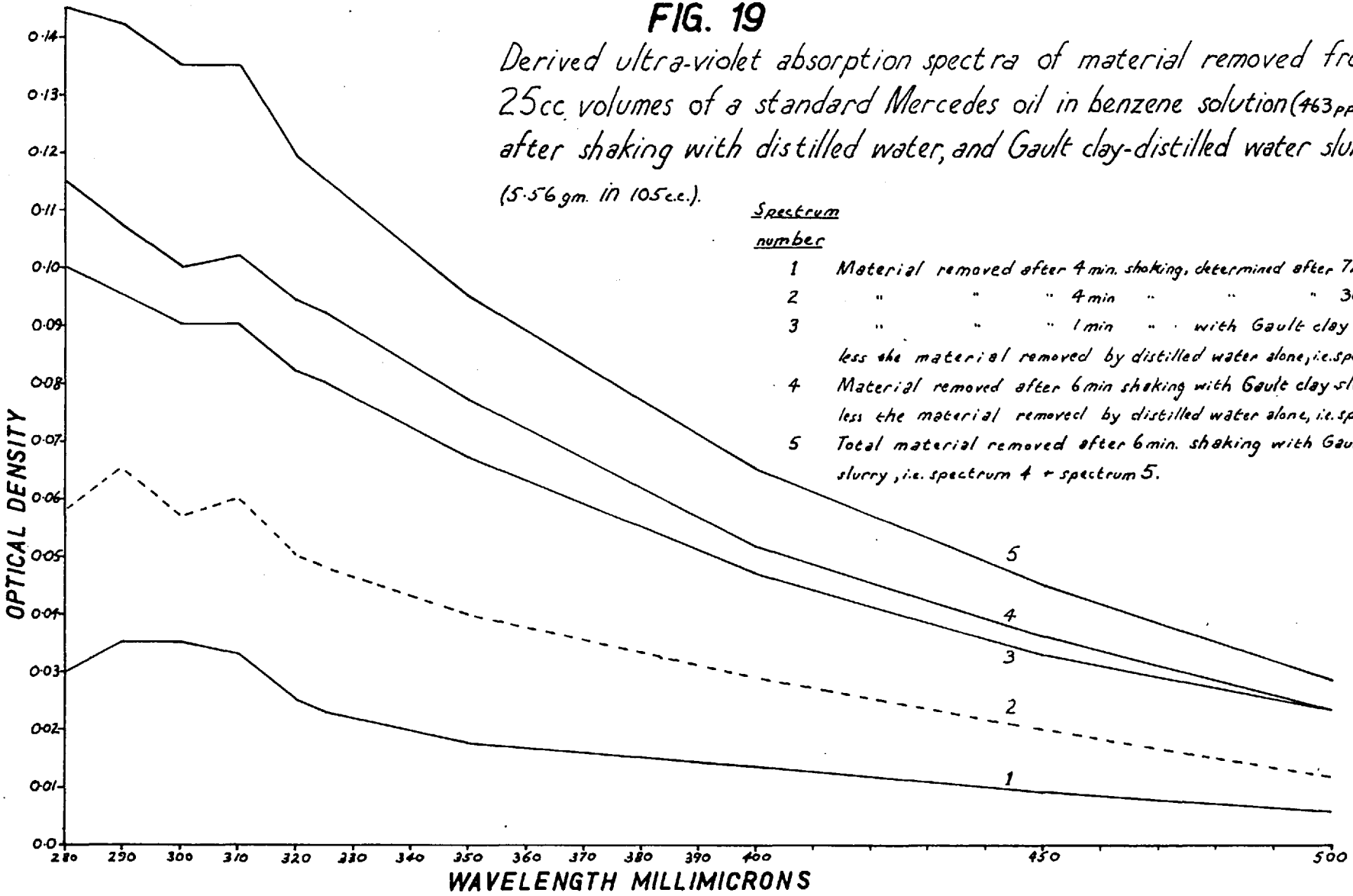
Optical density.

Wave-Length mμ.	Original Solution 463 p.p.m. Mercedes oil in benzene saturated with water.	Control 25 cc. of solution shaken with 105 cc. benzene-saturated distilled water. stood for 72 hours	Control 25 cc. of solution shaken with 105 cc. benzene-saturated distilled water. sampled 30 secs. after shaking stopped	25 cc. of soltn. shaken with 5.56 gm. of Gault clay in 105 cc. of benzene-saturated distilled water; allowed to stand for 72 hours. Time for which each sample was shaken. 1 1 min.	2 2 min.	3 3 min.	4 4 min.	5 6 min.
280	0.945	0.915	0.887	0.815	0.815	0.805	0.800	0.800
290	0.800	0.765	0.735	0.670	0.667	0.660	0.657	0.658
300	0.665	0.630	0.608	0.540	0.540	0.533	0.530	0.530
310	0.525	0.492	0.465	0.402	0.400	0.392	0.390	0.390
320	0.405	0.380	0.355	0.298	0.294	0.288	0.286	0.286
325	0.378	0.355	0.330	0.275	0.270	0.264	0.263	0.263
350	0.235	0.217	0.195	0.150	0.145	0.140	0.140	0.140
400	0.115	0.102	0.086	0.055	0.053	0.050	0.050	0.050
450	0.064	0.055	0.044	0.023	0.020	0.019	0.019	0.019
500	0.039	0.033	0.025	0.010	0.010	0.010	0.010	0.010
550	0.026	0.021	0.016	0.005	0.005	0.005	0.005	0.005
580	0.022	0.016	0.013	0.003	0.003	0.003	0.003	0.003

Remembering from Beer's law that at a given wavelength the optical density of a solution is directly proportional to the concentration of components absorbing light at that wavelength. Fig. 18 shows that the percentage decrease of optical density is greater with increase in wavelength. This is particularly noticeable in the "key" wavelength range 325 to 550 mμ, indicating the removal by adsorption of those components whose

FIG. 19

Derived ultra-violet absorption spectra of material removed from 25cc. volumes of a standard Mercedes oil in benzene solution (463 ppm) after shaking with distilled water, and Gault clay-distilled water slurries (5·56 gm. in 105 c.c.).



Spectrum number

1 Material removed after 4 min. shaking, determined after 72. hr.

2 " " " 4 min " " " 30 sec.

3 " " " 1 min " " with Gault clay slurry, less the material removed by distilled water alone, i.e. spectrum 1.

4 Material removed after 6 min shaking with Gault clay slurry, less the material removed by distilled water alone, i.e. spectrum 1.

5 Total material removed after 6 min. shaking with Gault clay slurry, i.e. spectrum 4 + spectrum 5.

ultra-violet spectra extend over this region, since if all components were removed in proportion to their concentration in the original solution the optical densities at all the "key" wavelengths of the solution after shaking would show the same percentage decrease.

The gradual increase in optical density with decrease in wavelength of the derived spectrum of the adsorbed components Fig. 19 (found by difference between initial and residual solution spectra) is typical of the spectrum of the non-hydrocarbon asphaltic and resinous components of crude oil as described by Erdman (1961).

The shaking of these oil solutions with clay suspensions always resulted in the formation of very stable emulsions at the solution-suspension interface, reducing the volume of clear oil-solution very considerably, and making the withdrawal of a sample of the residual solution difficult. They appeared to be water-in-oil emulsions, in the solution changing to oil-in-water emulsions in the water phase with no distinguishable boundary between the two. This being the case, the formation of two opposing emulsion types might be explained as follows:-

a) The non-hydrocarbon resinous and asphaltic material adsorbed by the wet clays makes them hydrophobic and they are then capable, as stated by Bancroft's rule, of stabilizing a water-in-oil emulsion, i.e. clay particles are preferentially

oil-wet, hence oil solution is the continuous phase.

b) The adsorption from oil solution of these surface-active components depleted the solution, causing it to become progressively less polar, and allowing an oil-in-water emulsion of the residual oil in benzene to form, stabilized by the hydrophilic clay particles (as expected from Bancroft's rule), i.e. clay particles are preferentially water-wet, hence water is the continuous phase.

Some indications of the mechanism of the adsorption were obtained from the shaking of the oil solution with distilled water. Two similar samples of oil solution and distilled water were shaken violently by hand for four minutes and the optical densities of the oil solution of one sample determined as soon as sufficient supernatant solution had separated from the dispersions (30 sec.), the other being allowed to stand for seventy-two hours with the resulting complete separation of the two phases in contact over a continuous interface. (Table XX and Fig. 17, spectra 2 and 3).

It was found that the percentage decrease of optical density with increase in wavelength, (Fig. 18) together with the derived ultra-violet spectrum of the components removed from the oil solution (Fig. 19, spectra 1 and 2) showed similar trends to those occurring when a clay suspension was present, although the changes were smaller. Furthermore,

it was found that the sample taken immediately after dispersion showed a greater quantity of material removed than did the sample allowed to separate completely. Similar results were obtained for samples shaken for 2 minutes, one being allowed to stand and the other sampled after 1 minute.

The conclusions drawn from these observations are:-

1) That the difference between the absorption spectrum of the original solution and the same solution after shaking with water is not only due to the possible solution of oil components in the water, but that selective adsorption at the oil-solution-water interface is a significant contributory factor.

2) The selective adsorption which takes place at oil-solution-water interfaces is enhanced by the presence of the wet clay particles in a clay suspension as a result of the increase in the stabilized oil-solution-water interface which they promote.

That the asphaltic and resinous type of components are apparently preferentially adsorbed is not surprising, in view of their greater polarity when compared with the hydrocarbons present, as was pointed out in the last section.

The use of the highly asphaltic Mercedes oil with its 7.2% asphaltene content (Table V) might be thought of as an anomalous case. However, the use of the aromatic hydrocarbon benzene as solvent precludes the precipitation of asphaltenes from solution, since aromatics are known to peptize the

asphaltic material. Aromatic hydrocarbon solvents also reduce the tendency of asphaltic material to be precipitated (or flocculated) at an oil-water interface according to Greenlee (1960), which, in turn reduces the stability of water-in-oil emulsions. Thus the system is not one which would normally be expected to promote the occurrence of adsorption on its own account.

In order to satisfy any doubts regarding this question, it was decided that a similar type of experiment should be carried out using the paraffinic Socorro oil with n-heptane as solvent. Two main advantages arise from using the latter system. The first is the lack of precipitable asphaltenes in the crude, and the second is that for spectral investigations n-heptane has a much lower extinction wavelength than benzene, thus permitting a more thorough investigation of any adsorption taking place in the aromatic range of light absorption, namely 220 to 320 mμ.

Fuller's Earth was chosen as the clay for these experiments because its adsorption capacity in the dried state is much greater than that of Gault clay, and it was thought that this characteristic might also assist in promoting maximum adsorption for a given weight of clay. However, the latter reason for choosing Fuller's Earth should be further qualified, since by the very nature of its high adsorption capacity and its bentonitic hydration

properties it appears that orientated water molecules should surround the clay particles to a much greater depth than for Gault clay, thus suppressing the adsorption of oil components. It was therefore uncertain as to what would be the resultant effect of these conflicting characteristics on the adsorption of oil components from solution.

A solution of one thousand parts per million of Socorro oil in n-heptane was made up, and the following amounts of oven-dried (110°C) Fuller's Earth and distilled water shaken together in 250 cc. measuring cylinders fitted with ground-glass stoppers.

Table XXI

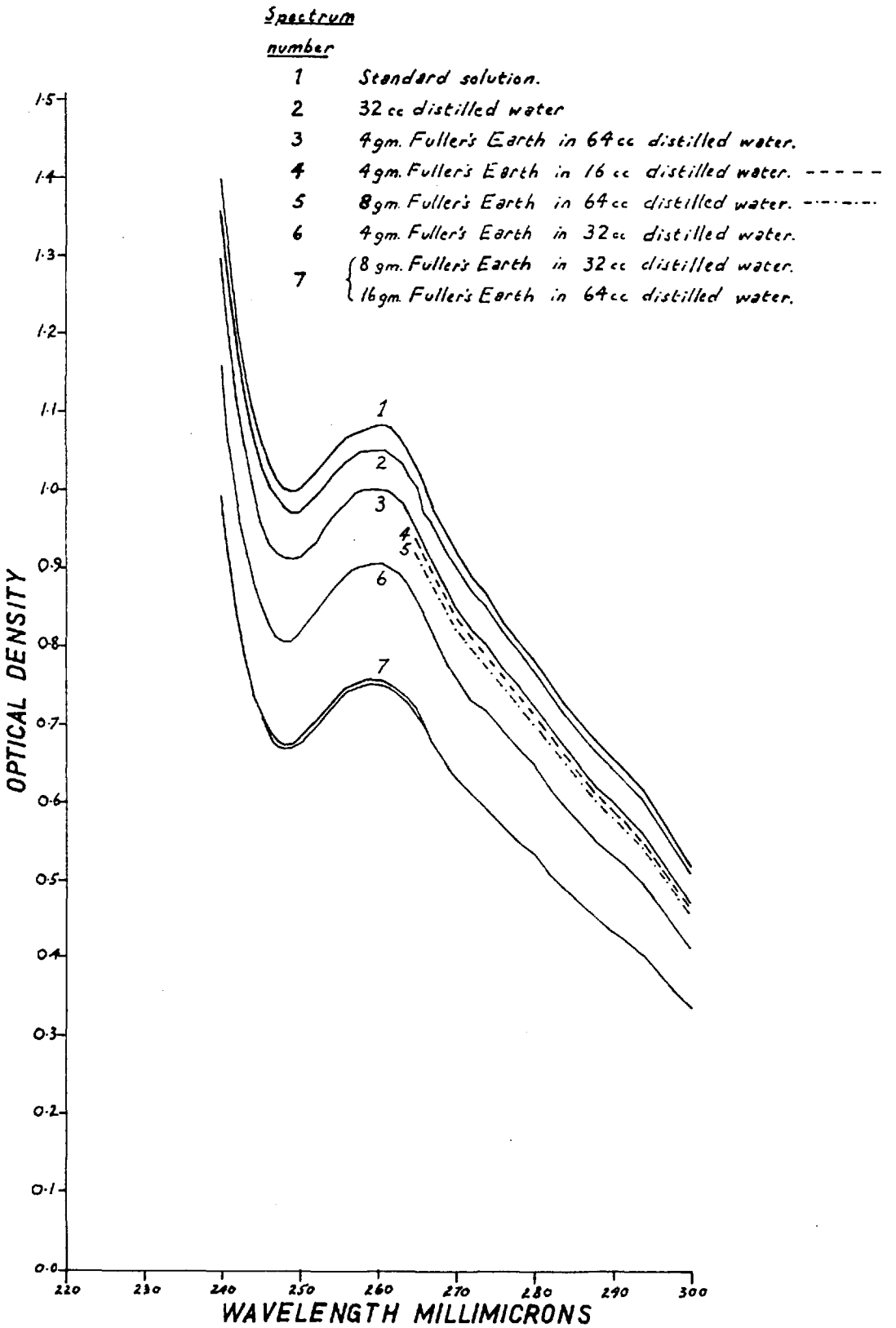
4.0830	gm.	of	dry	Fuller's	Earth	(110°C)	in	16 cc.	distilled water.
4.0232	gm.	"	"	"	"	"	"	32 cc.	" "
4.0378	gm.	"	"	"	"	"	"	64 cc.	" "
8.0100	gm.	"	"	"	"	"	"	32 cc.	" "
8.0804	gm.	"	"	"	"	"	"	64 cc.	" "
15.9982	gm.	"	"	"	"	"	"	64 cc.	" "

The above combinations of clay and distilled water were chosen in an attempt to investigate the influence of clay-water ratio on adsorption after a standard period of shaking.

25-cc. volumes of Socorro-heptane solution were added to each of the above samples, and similar amounts were added to 64-cc. and 32-cc. distilled water controls, also in glass-

FIG. 20

Ultra-violet absorption spectra of 25cc samples of standard Socorro oil in n-heptane solution (1,000 ppm) shaken for 2 min. with distilled water, and Fuller's Earth distilled water slurries.



stoppered measuring cylinders. The samples and the controls were each shaken violently by hand for two minutes. The reason for not shaking for four minutes, as was done in the previous experiment, was the very stable emulsion formed by the solution-clay suspension system which allowed only very small amounts of supernatant solution to be pipetted off for spectral determinations. The results of this experiment are shown graphically in Fig. 20.

With the exception of the 4 gm. in 16 cc. and the 8 gm. in 64 cc. samples, for which only partial spectra were determined, Fig. 20 shows a trend of increasing adsorption with increase in the clay-water ratio. The low adsorption value for the 4 gm. in 16 cc. sample may have resulted from the formation of a gel-like mass which prevented any free mixing, whilst the 8 gm. in 64 cc. sample may have resulted from an excess of water preventing its equilibrium reaching that of the 4 gm. in 32 cc. sample of similar clay-water ratio. However, the interpretation of increasing adsorption with increase in clay-water ratio may well be an over-simplification. A further factor which undoubtedly influences the interpretation and might be considered as an alternative explanation is that the degree of adsorption increases with the weight of clay present, the clay-water ratio possibly acting only as a dilution factor and reducing the chance of contact during shaking.

The character of the lowest residual oil-solution spectrum (Fig. 20, spectrum 7) parallels very closely the residual solution spectrum after the water desorption of mildly wetted Gault clay (Fig. 15, spectrum 3), and on this basis indicates an adsorption of about 80% of the available adsorbate by the 8 gm. in 32 cc. and 16 gm. in 64 cc. samples, i.e. about 10% by weight of the oil in the original solution. A comparison of the derived spectra of the material retained by the Fuller's Earth-in-water suspension (Fig. 24 (i), spectrum c), and the material retained by mildly wetted Gault clay after water desorption (Fig. 16, spectrum 5) further substantiates the similarity of the type of oil components adsorbed. From an inspection of the derived spectra of the material successively adsorbed by the Fuller's Earth-in-water suspensions (Fig. 24 (iii), spectrum 2) it is apparent that some hydrocarbons are also being retained, after the initial retention of non-hydrocarbons (Fig. 24 (i), spectrum A) has occurred. This is in agreement with the derived spectrum of the material desorbed by water from mildly wetted Gault clay (Fig. 16, spectrum 7) described earlier, and suggests that hydrocarbons are retained once the clay has adsorbed sufficient non-hydrocarbon to make its surface to some extent hydrophobic.

In terms of the actual weight of oil components adsorbed, however, the total amount of material adsorbed was only of

the order of 0.3 milligram per gram of wet clay, compared with 0.9 milligram per gram of mildly wetted clay, and 7 milligrams per gram of dried clay for similar types of oil components. This does not imply, however, that clay can only sorb these quantities of oil, but that they are, in effect, minimum quantities. The adsorption of these components, which causes the surface of the clay to become partially hydrophobic, also allows the "wetting" of the clay by additional oil. The quantity of any of the additional oil attached will thus be dependent on gravitational (buoyancy) and capillary forces acting on the system. This was clearly shown by the marked stability of the emulsions formed during the course of these experiments, which often hampered the recovery of even small samples of the residual solutions.

The Isolation and Investigation of the Nature of Oil Components Adsorbed by Wet and Damp Clays.

Introduction.

Isolation of the adsorbed components from clay-in-water suspensions is difficult to achieve, particularly as the emulsion stability results in the entrapment of residual solution and makes its separation from the clay-water-adsorbed-oil complex very difficult. Alternatively, the use of polar extraction solvents that might conceivably break down the emulsion would also alter the adsorption relationship of

the adsorbed components, causing their partial release and their return to the residual solution. Thus a method had to be developed that would allow the separation of adsorbed components as a fraction or fractions distinct from the bulk of the residual solution.

As mildly wetted clay had shown similar adsorption characteristics to the clay-in-water suspensions, it was decided that the contact of oil-solution with "damp" clay would provide an adsorption relationship analogous to the results obtained with water-saturated clays. If this proved to be correct, then the separation of the various components could be at least partially accomplished by placing the clays with their adsorbed components in a column and washing them successively with appropriate solvents.

Method.

The mildly wetted Gault clay used previously was prepared by placing an oven-dried clay in an atmosphere of controlled relative humidity of 75%. This procedure appears to have resulted in the adsorption of a mono-molecular layer of water similar to the mono-layer of water adsorbed on dried silica gel, obtained by placing it in a dessicator in which a controlled relative humidity of 58% maintained over 40 weight per cent aqueous sulphuric acid (Brooks, 1958). Adsorption from solution by the mildly wetted Gault, prior to water desorption (Fig. 15, spectrum 2), however resulted in a larger

percentage of component adsorption than that obtained by the Fuller's Earth-in-water suspension. Only after water desorption did the quantity and spectrum of the adsorbed components approach that of the clay suspension. It, therefore, appears that the pre-heating of the clay completely removed the excess of water normally adsorbed on clays under atmospheric conditions, and having reached this state of dryness, the controlled relative humidity restricted the quantity of water readsorbed (during the comparatively short time of exposure, 4 days) to mono-layer dimensions.

In order to avoid this large discrepancy in adsorption values, the Fuller's Earth and Gault clay used for the preparation of "damp" samples, were not oven dried prior to their exposure to the atmosphere of 75% controlled relative humidity. Thus the Fuller's Earth which contained 13.4% water (as a percentage of its weight under normal atmospheric conditions) increased in its water content by 4.43% to 17.83%. Similarly the water content of Gault clay was increased from 2.8 to 4.65%. This limited hydration of the clays avoided the complications of the excess of "free" water associated with water-saturated clays.

A series of samples were prepared using an exponential ratio for successive weights of clay (8, 4, 2, 1, 0.5, 0.25 gm., equivalent dry weight) and placed in contact by stirring with 50 cc. volumes of the standard Socorro oil in n-heptane solution.

FIG. 21

Ultra-violet absorption spectra of 50cc samples of standard Socorro oil in n-heptane solution (1,000 ppm) after contact with various weights of damp Fuller's Earth.

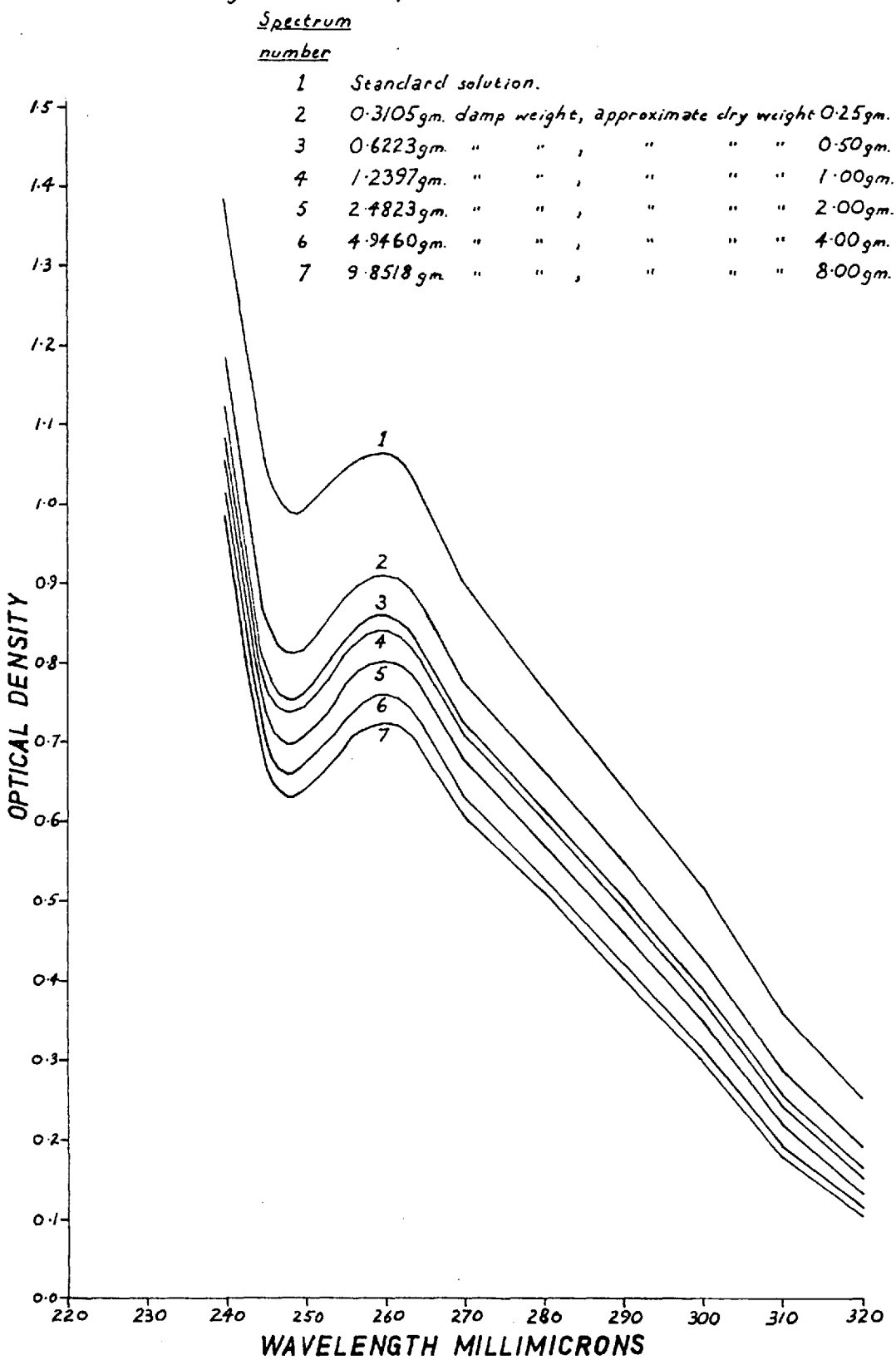


FIG. 22

Ultra-violet absorption spectra of 50cc samples of standard Socorro oil in n-heptane solution (1,000 ppm) after contact with various weights of damp Gault clay.

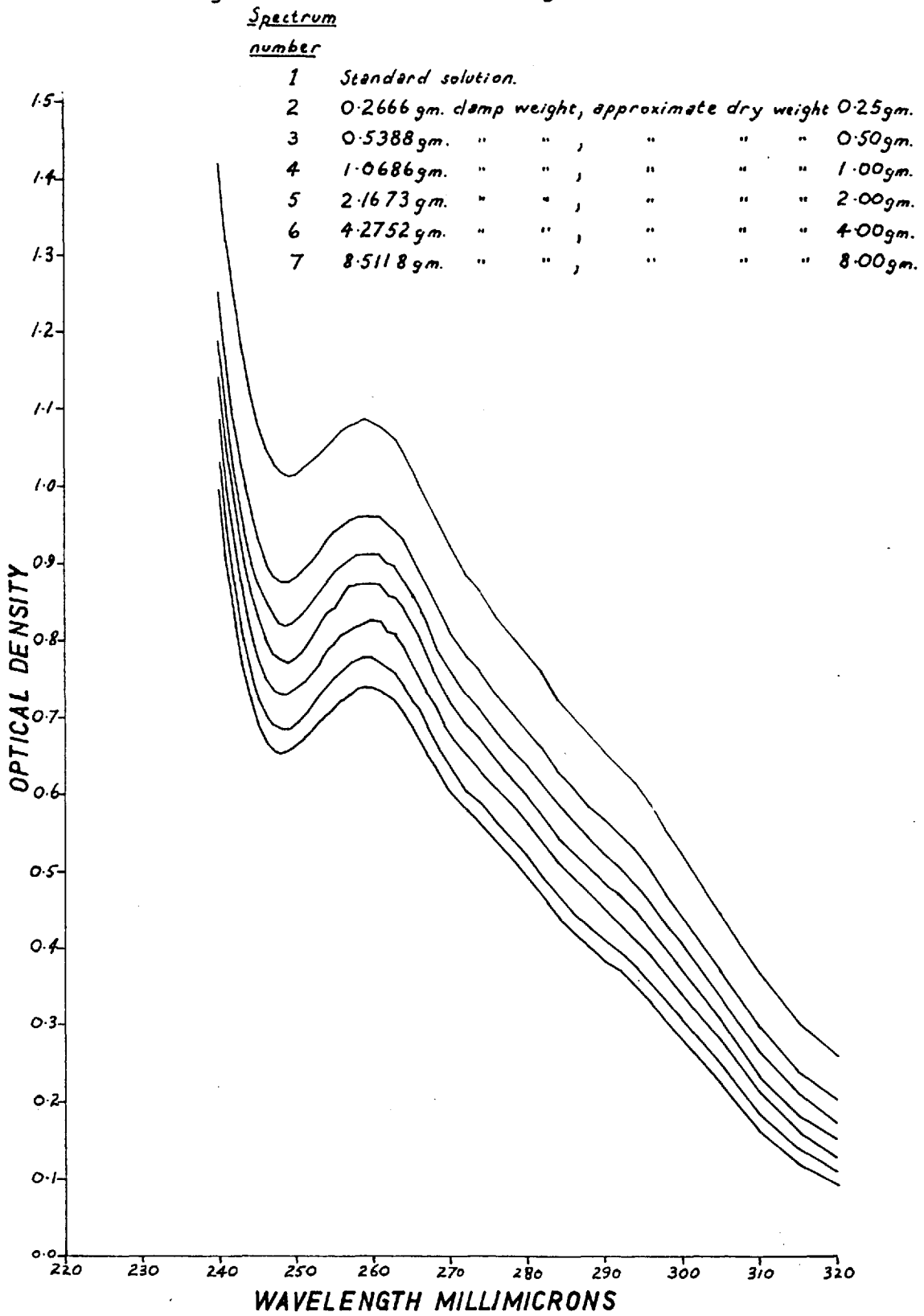
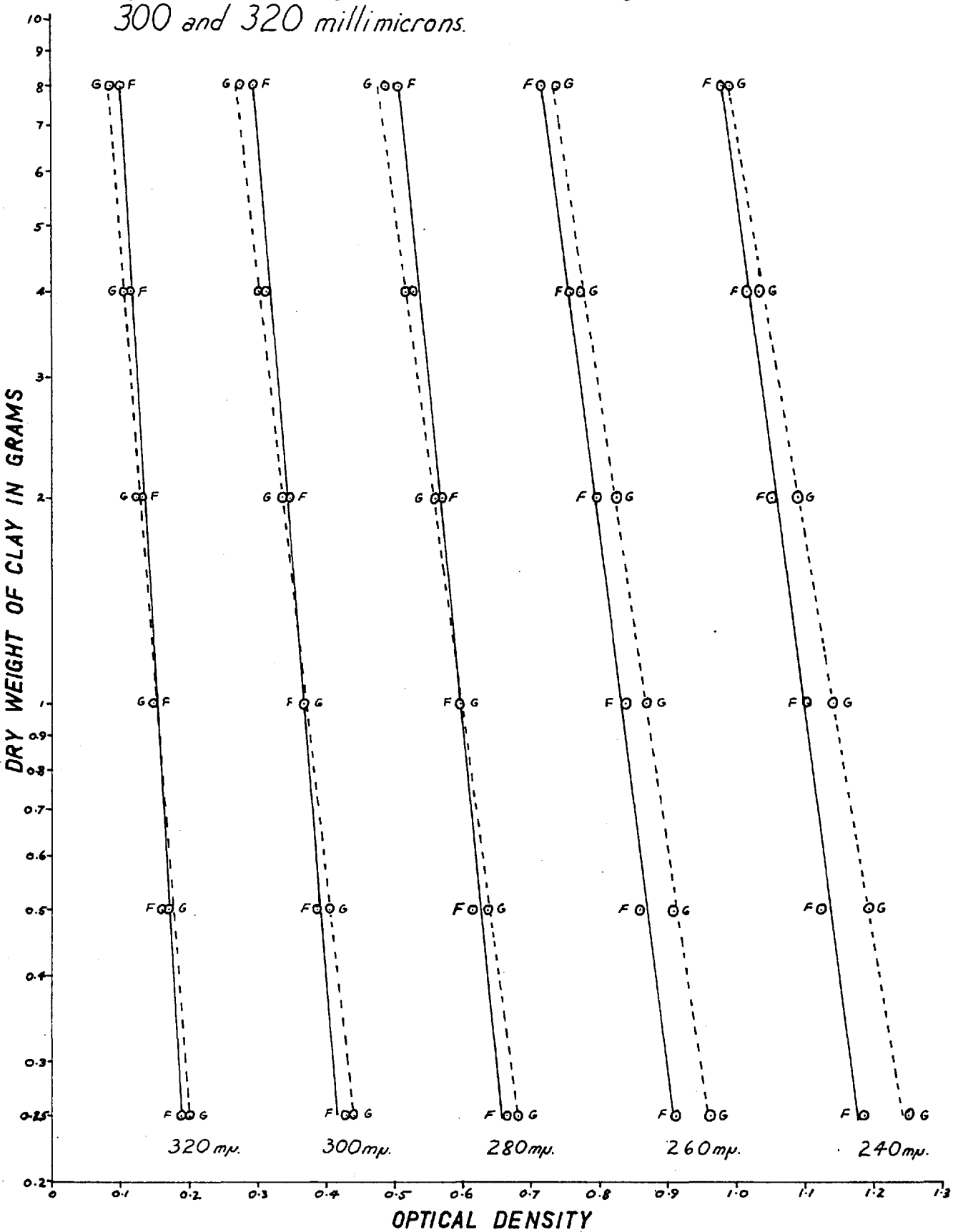


FIG. 23

Weight of damp Fuller's Earth and Gault clay, plotted as equivalent dry weight, versus optical density at 260, 240, 280, 300 and 320 millimicrons.



The spectra of the residual solutions, after standing in contact with the damp Fuller's Earth and Gault samples for four days, were then determined, (Fig. 21 and 22). A plot of adsorbent weight against optical density at 240, 260, 280, 300, 320 millimicrons was made for both the damp Gault and Fuller's Earth samples and is shown in Fig. 23. The relationship as before is of the form $y = 10^{a + bx}$, where y is adsorbent weight, and x is optical density, and a and b are constants. Unlike similar plots for dry adsorbents the various wavelength polts do not approach a common intercept on the ordinate axis. Furthermore, the high value of the intercepts implies that the quantity of damp adsorbent would have to be large in order to adsorb all the components absorbing light in this region of the spectrum, particularly at the lower wavelengths. What appears more likely is that the relationship shown, only applies to a proportion of the components present in the oil, i.e. the non-hydrocarbons, which absorb light in the ultra-violet region, and that adsorption ceases when they have been removed leaving the remainder of the ultra-violet light absorbing components (the aromatic hydrocarbons) permanently in the residual solution.

From a comparison of these spectra with the residual solution spectra of the Fuller's Earth-in-water adsorption complexes Fig. 20, it was observed:-

FIG. 24

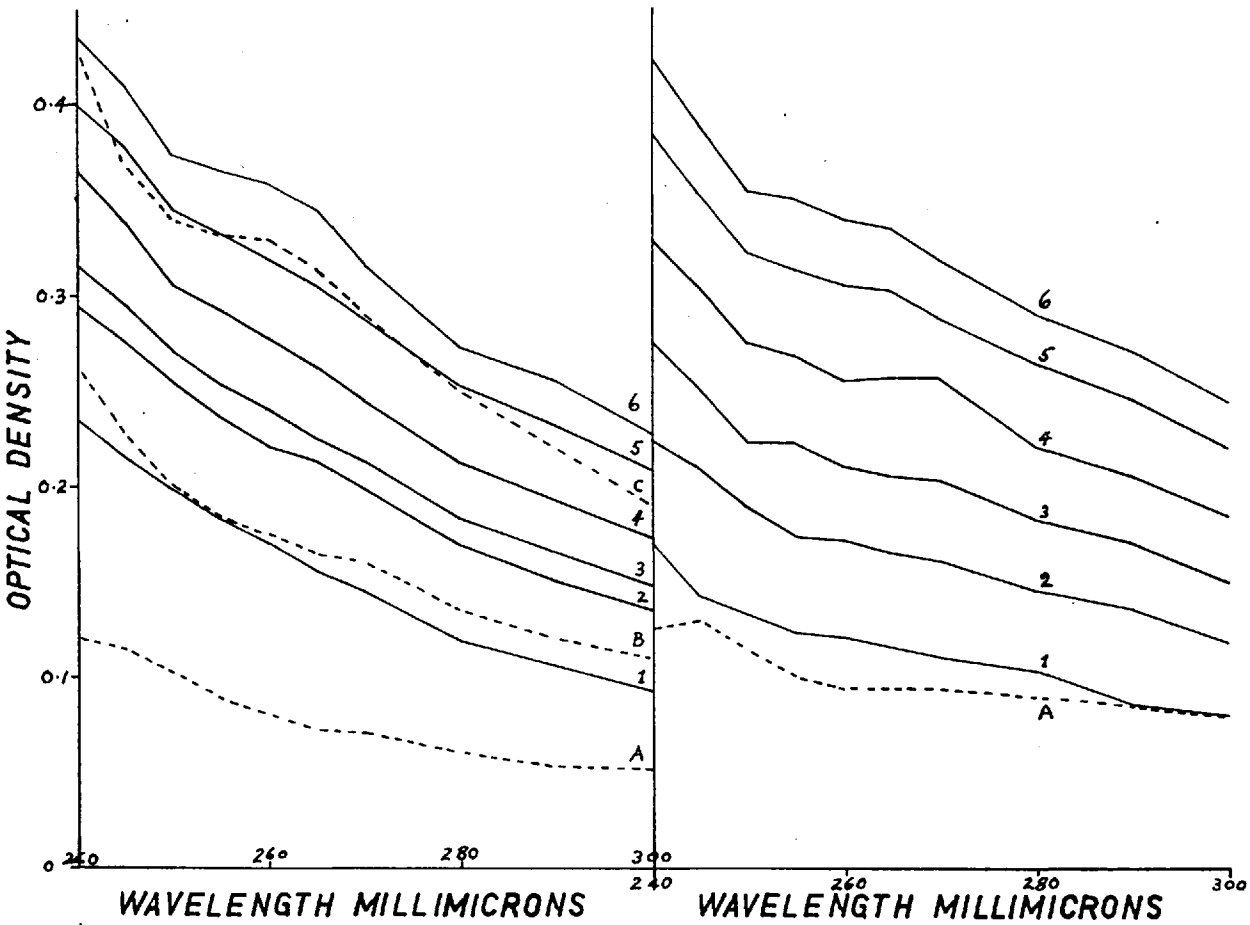
Derived ultra-violet spectra of components adsorbed from standard Socorro oil in heptane solution (1,000 ppm) by wet Fuller's Earth, and damp Fuller's Earth and Gault clay samples.

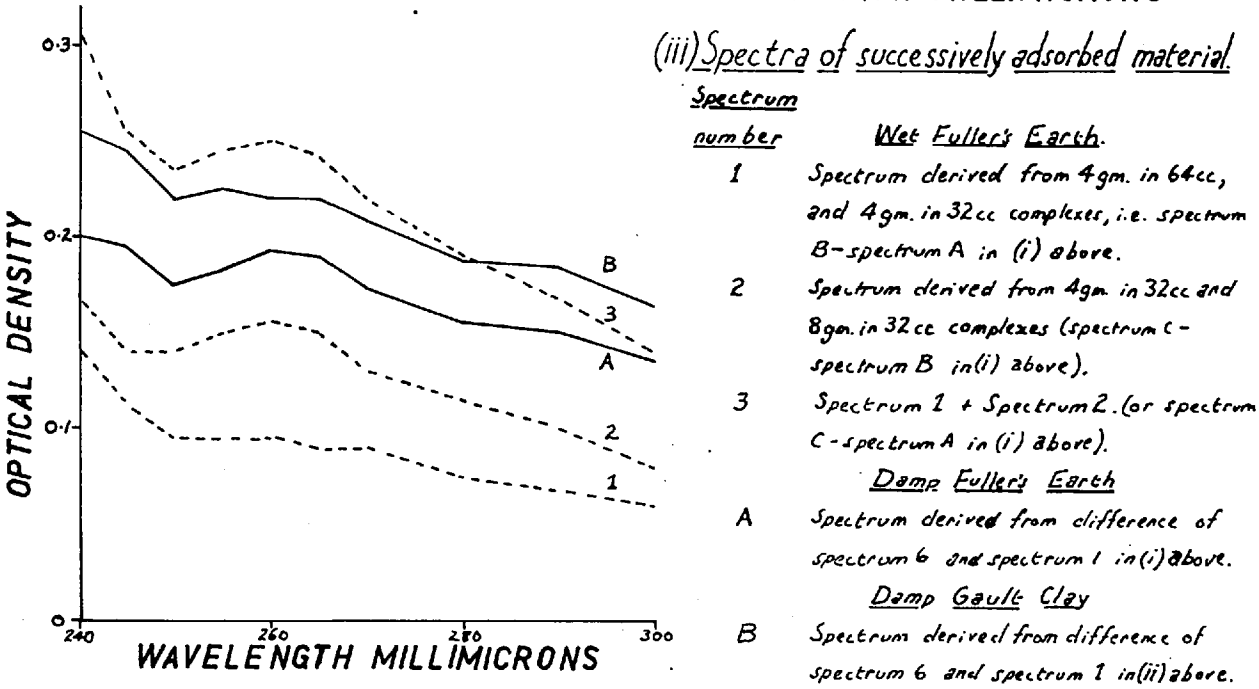
(i) Fuller's Earth

Spectrum number	Weight of Clay (gm.)	Volume of standard solution.
1	0·3105 (damp)	50 cc
2	0·6223 (")	50 cc
3	1·2397 (")	50 cc
4	2·4823 (")	50 cc
5	4·9460 (")	50 cc
6	9·8518 (")	50 cc
A	4·0378 (110°C) in 64cc water.	25cc
B	4·0232 (") + 32cc " .	25cc
C	8·0100 (") + 32cc " .	25cc

(ii) Gault clay

Spectrum number	Weight of Clay (gm.)	Volume of standard solution.
1	0·2666 (damp)	50 cc
2	0·5388 (")	50 cc
3	1·0686 (")	50 cc
4	2·1673 (")	50 cc
5	4·2752 (")	50 cc
6	8·5118 (")	50 cc
A	8·00 (110°C) in 10cc water.	50 cc





(iii) Spectra of successively adsorbed material

Spectrum number	Wet Fuller's Earth.
1	Spectrum derived from 4gm. in 64cc, and 4gm. in 32cc complexes, i.e. spectrum B − spectrum A in (i) above.
2	Spectrum derived from 4gm. in 32cc and 8gm. in 32cc complexes (spectrum C − spectrum B in (i) above).
3	Spectrum 1 + Spectrum 2. (or spectrum C − spectrum A in (i) above).
	Damp Fuller's Earth
A	Spectrum derived from difference of spectrum 6 and spectrum 1 in (i) above.
	Damp Gault Clay
B	Spectrum derived from difference of spectrum 6 and spectrum 1 in (ii) above.

i) The spectra of the residual solutions from damp clay and saturated clay-adsorption-complexes are identical in form, and hence reflect the adsorption of similar types of oil components, (Fig. 24, (i) and (ii)).

ii) The adsorption capacities, i.e. the weights of adsorbate adsorbed per gram of adsorbent, of damp Fuller's Earth and Gault clay are similar and are approximately twice the adsorption capacity of water-saturated Fuller's Earth.

iii) In spite of the difference in absolute adsorption capacity between the damp and wet clays, the spectrum of the residual solutions at maximum adsorption were practically identical, i.e. 50 cc. of standard oil-in-heptane solution was used in damp clay samples compared with 25 cc. for the water-saturated Fuller's Earth samples for equivalent residual solution spectra (Figs. 20, 21, and 22).

Although their absolute adsorption capacities may be different, the final adsorption of oil components from the original solution, as indicated from the lowest values of their respective residual solution spectra (Figs. 20, 21, 22, spectrum 7), and the derived spectra of the material adsorbed (Fig. 24 (i), spectrum C, and spectra 6 (i) and (ii)), were the same.

The last conclusion together with the plot of optical density against adsorbent weight, suggest that a maximum value is being approached for the percentage of oil components

available for adsorption in water-wet conditions. This final maximum value for wet and damp clay residual oil-solution spectra may be equivalent to the water desorption residual oil-solution spectrum of the mildly wetted Gault sample Fig. 15, spectrum 3, with which they correlate reasonably.

This is further shown from a comparison of the derived spectra of the material adsorbed by the 8 gm. sample of damp Gault Fig. 16, spectrum 4, and the material retained by the mildly wetted Gault clay after water desorption Fig. 16, spectrum 5. On the basis of the above conclusions, the assumption that oil components adsorbed by damp clays are identical with those adsorbed by fully hydrated clays appears to be valid.

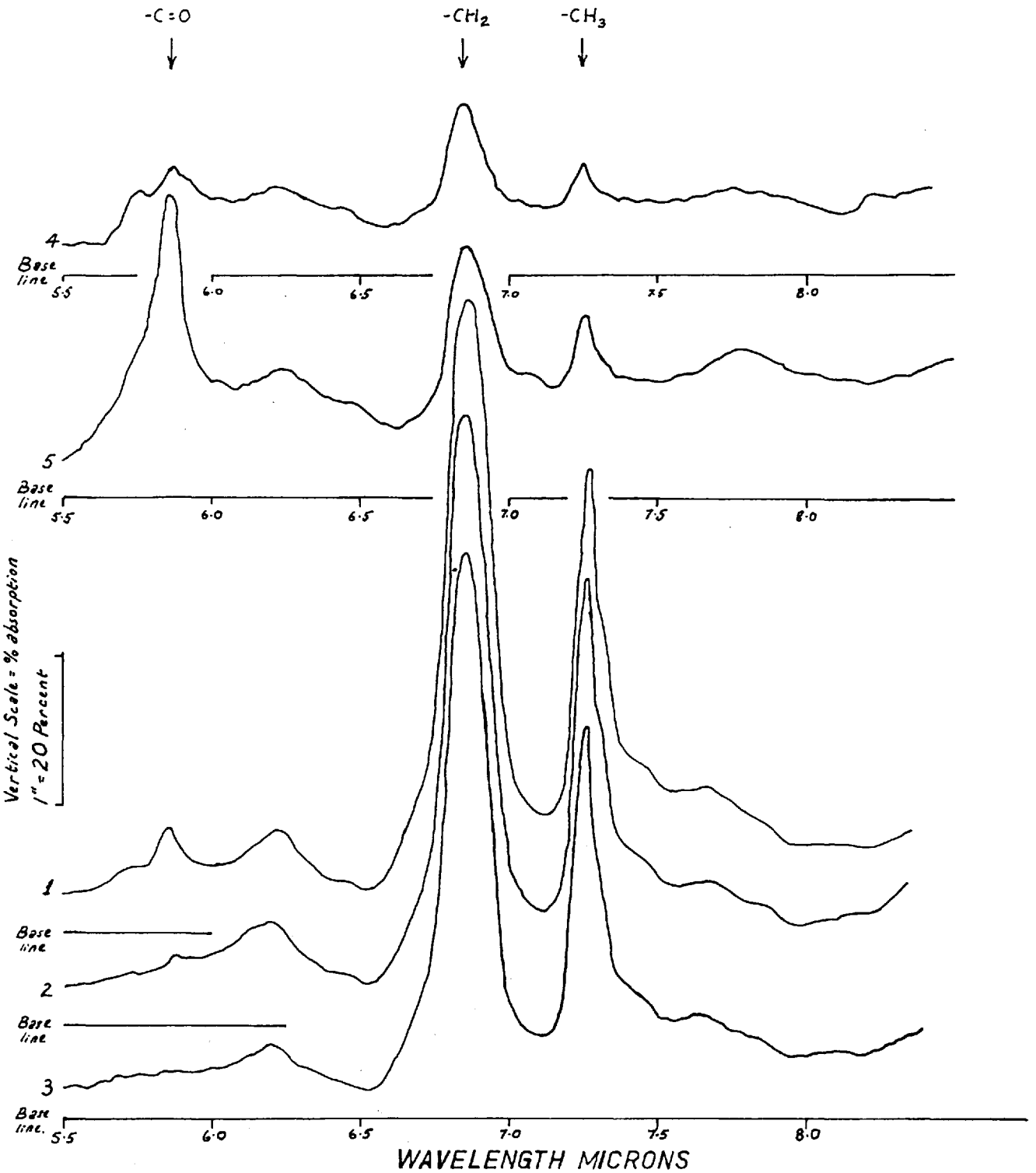
Extraction of the supernatant residual solutions from the damp Gault-adsorption complex samples, followed by evaporation and gravimetric determinations of the residue, showed that the percentage of oil components removed increased from 5 to 10% as the ratio of the weight of damp clay to oil solution increased. In ultra-violet light the fluorescence of the extracted residues of the residual solution showed a gradation from a light grey-green through to a deep royal-blue as the percentage of oil components adsorbed increased. Similar results were obtained with damp Fuller's Earth.

The infra-red spectra of two of the solution residues after contact with damp Fuller's Earth, together with the

FIG. 25

Spectrum number

1 Infra-red spectrum of Socorro oil.
2 Infra-red spectrum of oil remaining in heptane solution after contact with 0·25gm. of damp Fuller's Earth.
3 Infra-red spectrum of oil remaining in heptane solution after contact with 8·0gm. of damp Fuller's Earth.
4 Infra-red spectrum of oil eluted by benzene from composite damp Fuller's Earth samples
5 Infra-red spectrum of oil components eluted by benzene-acetone from composite damp Fuller's Earth samples.



infra-red spectra of the original Socorro oil, are shown in Fig. 25. The only significant change noticeable in a comparison of the three spectra is the reduction and final elimination of the carbonyl group peak at 5.85 microns with the increase in percentage oil adsorption.

After the extraction of the supernatant residual solutions, five of the damp Fuller's Earth samples (approximate equivalent dry weights at 110°C of 4, 2, 1, 0.5, 0.25 gm.) were poured, together with any remaining residual solution, into a 10 cm. by 1 cm. chromatographic column in the order of descending weights, i.e. the heaviest first. The column was allowed to drain down and then washed by an excess of pure n-heptane to remove all traces of the remaining residual solutions, as determined by the absence of light blue fluorescence in the effluent. Following this the column was eluted firstly with benzene, and then a benzene-acetone mixture, 6.3% of the total Socorro oil in the original standard oil solutions being recovered.

After evaporating the eluent the benzene fraction was a dark brown viscous liquid with a bright red fluorescence under ultra-violet light; the benzene-acetone fraction was a very dark brown to black tarry material, giving a dull red fluorescence in ultra-violet light. Strong infra-red absorption bands at 5.85 microns indicated the presence of a carbonyl group in the two eluted fractions, especially

for the benzene-acetone eluate where the peak is higher than the $-CH_2$ and $-CH_3$ absorption bands of the spectrum (Fig. 25, spectrum 5).

The total percentage weight of material recovered (6.3%) is only semi-quantitative, since it is the result of a series of batch adsorption samples which varied in their individual adsorption percentages. It is, however, an approximate average, and agrees with the 5 to 10% of oil components adsorbed by damp clays as calculated from the residual solution extracts.

Since the character of the adsorption phenomena taking place appeared primarily to be related to the presence of a large adsorbed water-oil interface rather than to the specific adsorption properties of the dry adsorbents, it was decided that percolation of the oil through a column of damp adsorbent would result in an improved isolation and a better subsequent recovery of the adsorbed components. Such separations are analogous to partition chromatography where an inert material supports a stationary liquid. The stationary liquid phase causes a differential separation of a mobile phase based on the variation of the partition coefficients of the constituents of the mobile phase with respect to the stationary liquid. It is only an analogy, however, since the separation mechanism is probably controlled more by the adsorption of oil components at the

oil-water interface rather than by differential solution, although the latter phenomenon may also play its part to some extent.

In each experiment a 10 cm. by 1 cm. chromatographic column was filled with damp Fuller's Earth by sedimenting through n-heptane. The columns when full contained approximately 8 gm. of damp clay. A Socorro oil sample in n-heptane was then introduced at the top of the column, and the column washed with excess pure n-heptane, followed in succession by benzene and benzene-acetone as eluents. In a later experiment benzene-methanol was used as the second eluent, in place of benzene-acetone, as a control to prove that the carbonyl groups present in the eluted material was not due to contamination from acetone solvent.

The results of three percolations are shown in Table XXII.

Table XXII

Fuller's Earth Percolated Samples.	A	B	C
Weight of oil (gm.)	0.6500	0.1595	0.1749
Percentage weight eluted by n-heptane	95.06	90.10	90.00
" " " " benzene	1.32	3.51	3.09
" " " " benzene-acetone	2.16	3.51	--
" " " " benzene-methanol	--	--	2.86
" " remaining unrecovered	1.46	2.88	4.05

The infra-red absorption spectra of the three eluted fractions from sample A, and the benzene and benzene-acetone

FIG. 26

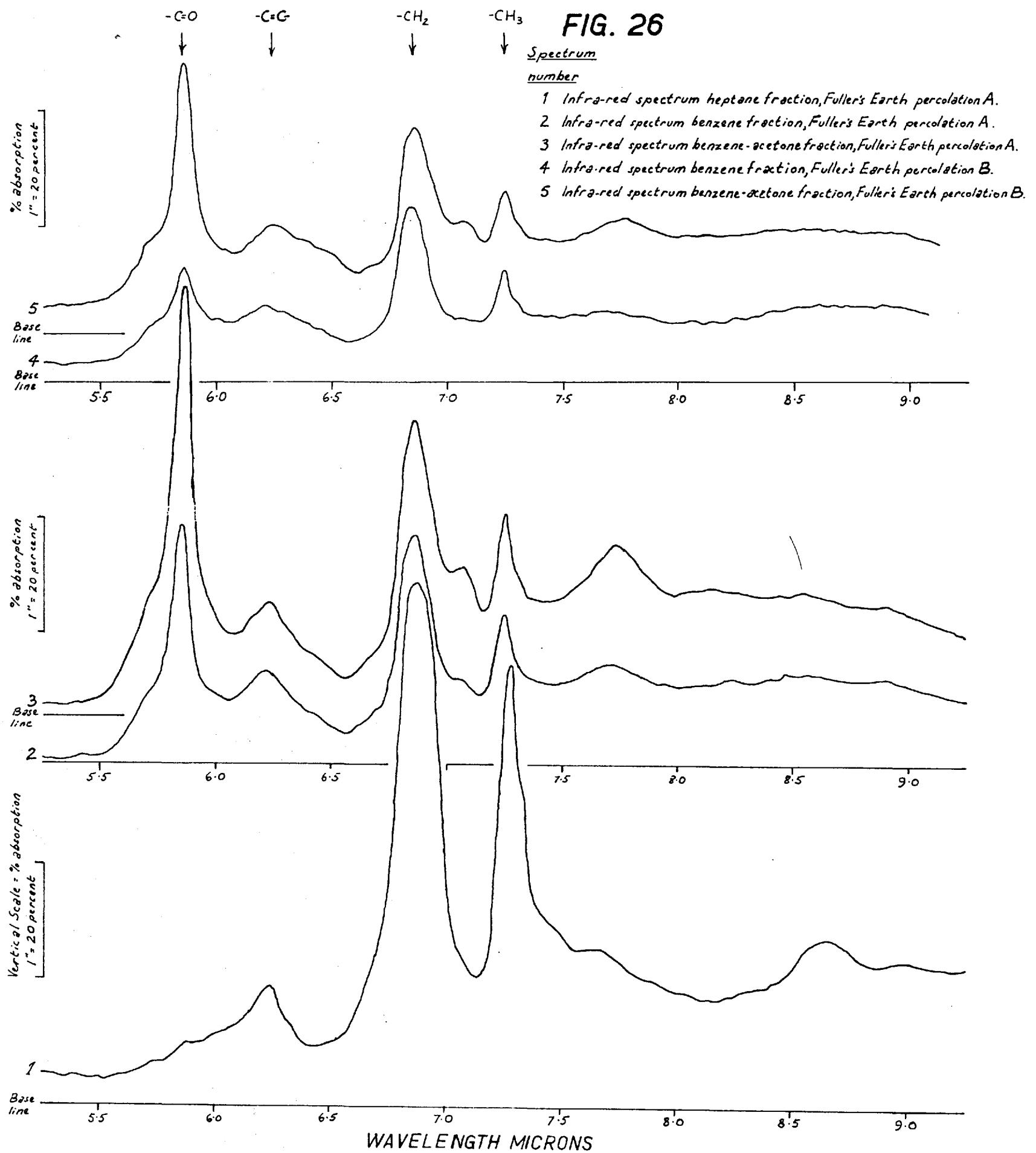
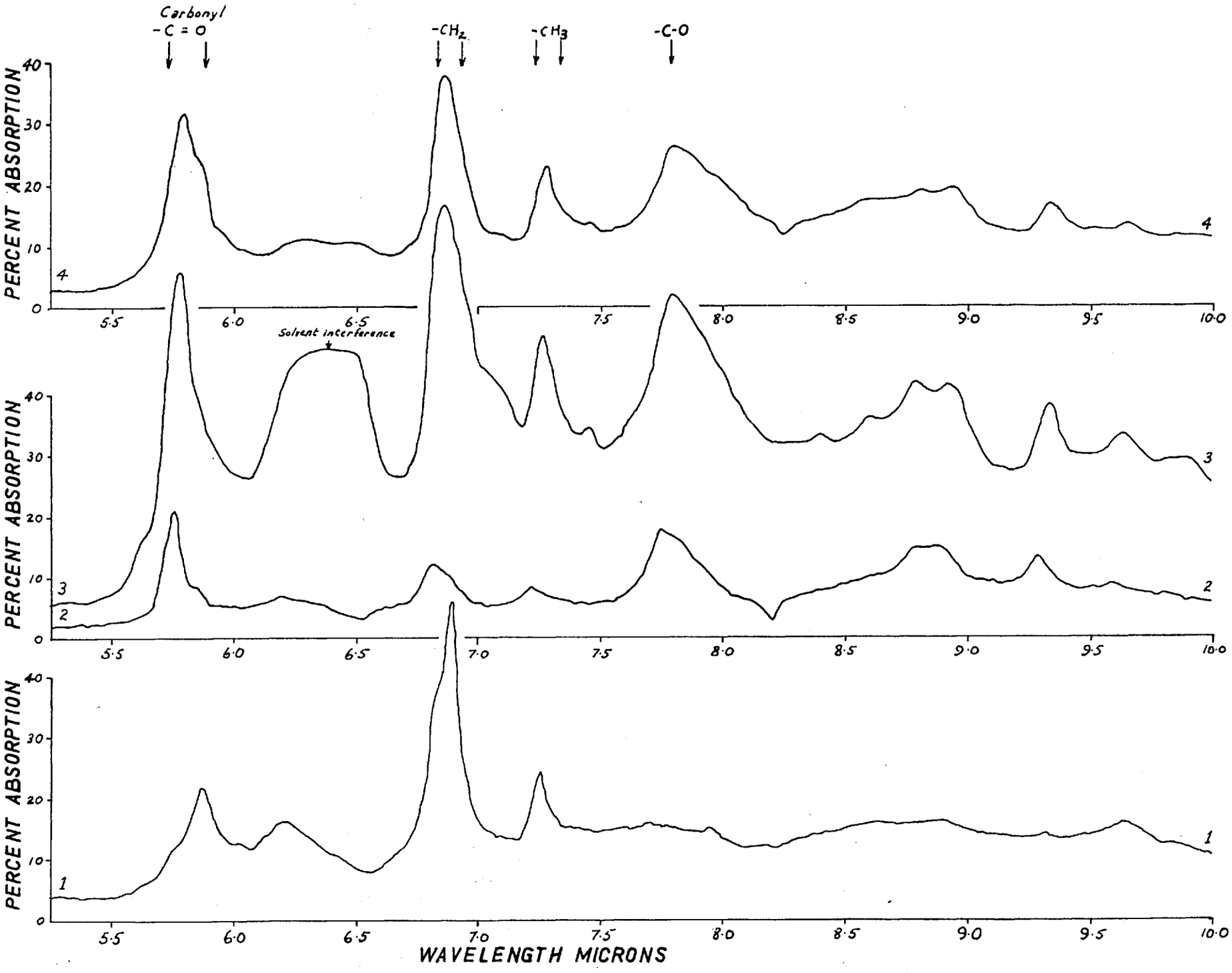

-C=O
-C=C-
-CH2
-CH3
Spectrum number
1 Infra-red spectrum heptane fraction, Fuller's Earth percolation A.
2 Infra-red spectrum benzene fraction, Fuller's Earth percolation A.
3 Infra-red spectrum benzene-acetone fraction, Fuller's Earth percolation A.
4 Infra-red spectrum benzene fraction, Fuller's Earth percolation B.
5 Infra-red spectrum benzene-acetone fraction, Fuller's Earth percolation B.
% absorption 1" = 20 percent
Base line
Vertical Scale = % absorption 1" = 20 percent
5·5
6·0
6·5
7·0
7·5
8·0
8·5
9·0
WAVELENGTH MICRONS

Fig. 27

FIG. 27

Infra-red absorption spectra of fractions eluted from damp Fuller's Earth percolation C.

Spectrum number	
1	Benzene eluted fraction.
2	Benzene - methanol eluted fraction.
3	Pyridine - acetone fraction.
4	Fraction washed from extruded damp clay by acetone - chloroform.



fractions of sample B are shown in Fig. 26. The use of benzene-methanol (4 to 1 by volume) in sample C failed to elute as much adsorbed material as the benzene-acetone used in sample B, and in order to improve the recovery an attempt was made to elute further the unrecovered adsorbed material with a pyridine-acetone mixture. This was only partially successful since fluid flow practically stopped and even a pressure of 20 lb. per sq. in. applied for forty-eight hours gave only an insignificant amount of material. Further extraction was attempted by extruding the column and washing the clay with an acetone-chloroform mixture, and again only a trace of adsorbed material was recovered. The infra-red spectra of all these extracts, however, are shown in Fig. 27. From an examination of these spectra it is seen that, with the exception of the benzene fraction, there is a -CO peak at 7.8 microns in addition to the usual carbonyl peak.

The variation in the percentage weight of the fractions eluted in percolations A and B for different weights of oil on the same weight of adsorbent may be explained as follows:-

Let the total amount of polar material present in an oil which can be removed by adsorption and retained on the adsorbent in the presence of a non-polar solvent, such as n-heptane, be X% of the total original oil. Furthermore, if the maximum capacity of unit weight of the adsorbent used to remove this material is A gm./gm., then N gm. of adsorbent

will be capable of adsorbing NA gm. of the polar material. Thus if a charge of M gm. of oil is percolated through the adsorbent it will contain MX/100 gm. of the polar material, and provided MX/100 is equal to or less than NA then no polar material will be present in the non-polar solvent effluent; i.e. $M/N \leq 100A/X$.

However, when M/N is greater than 100A/X some of the polar material will remain in the non-polar solvent and pass through and out of the column. That retained by the adsorbent will be limited to NA; that removed will be (MX/100 - NA), and the proportion retained will be (NA/M)100 as a percentage of the original charge.

Up to the critical ratio of M/N all the polar material will be retained, giving a constant percentage retention; above this value a diminishing percentage will be retained.

In practice, however, the situation is complicated by the fact that the specific adsorption capacity, A, of the adsorbent is not constant for a given polar material, but varies with the concentration of the material in the percolating solution at any given time during the course of the percolation. This is often expressed by the Freundlich equation $A = kC^{1/n}$, where C is the concentration of the polar material in the solution, and k and n are constants. Furthermore, there are a series of increasingly polar materials present in the oil, each having its own

concentration-adsorption relationship with the adsorbent. As the concentration of the more polar materials in the oil decreases with continued adsorption during percolation, they are gradually superseded down the column by less polar materials of higher concentration until all the available adsorption capacity is exhausted. Thus, equilibrium between the adsorbent and a series of increasingly polar adsorbates in the percolating solution is a function of A x C x P where P is the polarity of a given adsorbate of concentration C in the percolating solution. The use of more polar solvents as eluents, e.g. benzene followed by benzene-acetone, changes this state of equilibrium and the solvents displace the polar material on the adsorbent by being adsorbed themselves and/or the preferential solubility of adsorbed material for these solvents as compared with their solubility in the original non-polar solvent.

In percolation A only 5% of the original charge is not eluted by n-heptane as against 10% in percolation B. In terms of actual weight, however, percolation A has retained twice as much material as percolation B. This means that for a given fraction, the material adsorbed in percolation A is more polar than the material in the equivalent fraction of percolation B.

Verification that the material adsorbed in percolation A was more polar than that in the equivalent fractions of

percolation B, was obtained from their respective infra-red spectra, by comparing the relative carbonyl group content, in effect the polarity, of the various eluted fractions. The proportion of carbonyl group present in one fraction relative to another was found from the ratio of the height of the carbonyl absorption peak at 5.85 microns to an absorption peak which remains approximately constant throughout the spectra of the eluted fractions. The absorption peaks chosen were at 6.2 - 6.25 microns caused by the presence of aromatic conjugated double bonds, and the side chain $-CH_3$ peak at 7.25 microns, the ratio together with their respective fraction are shown in Table XXIII.

Table XXIII

	Percolation A.			Percolation B.		
Fraction	% of original	Absorption Ratio. 5.85μ / 6.25μ	5.85μ / 7.25μ	% of original	Absorption Ratio. 5.85μ / 6.25μ	5.85μ / 7.25μ
Benzene	1.32	2.60	1.60	3.51	1.43	1.0
Benzene-acetone.	2.16	3.75	2.08	3.51	2.58	1.88

For comparative purposes an experiment similar to percolation C was carried out using activated silica gel that had been exposed to an atmosphere of 75% relative humidity controlled in the usual way. A benzene-methanol mixture was again used in place of benzene-acetone to

avoid any doubts as to the origin of any carbonyl groups in the fractions recovered.

The results of this experiment are shown in Table XXIV.

Table XXIV

"Mildly Wetted" Silica Gel Sample.

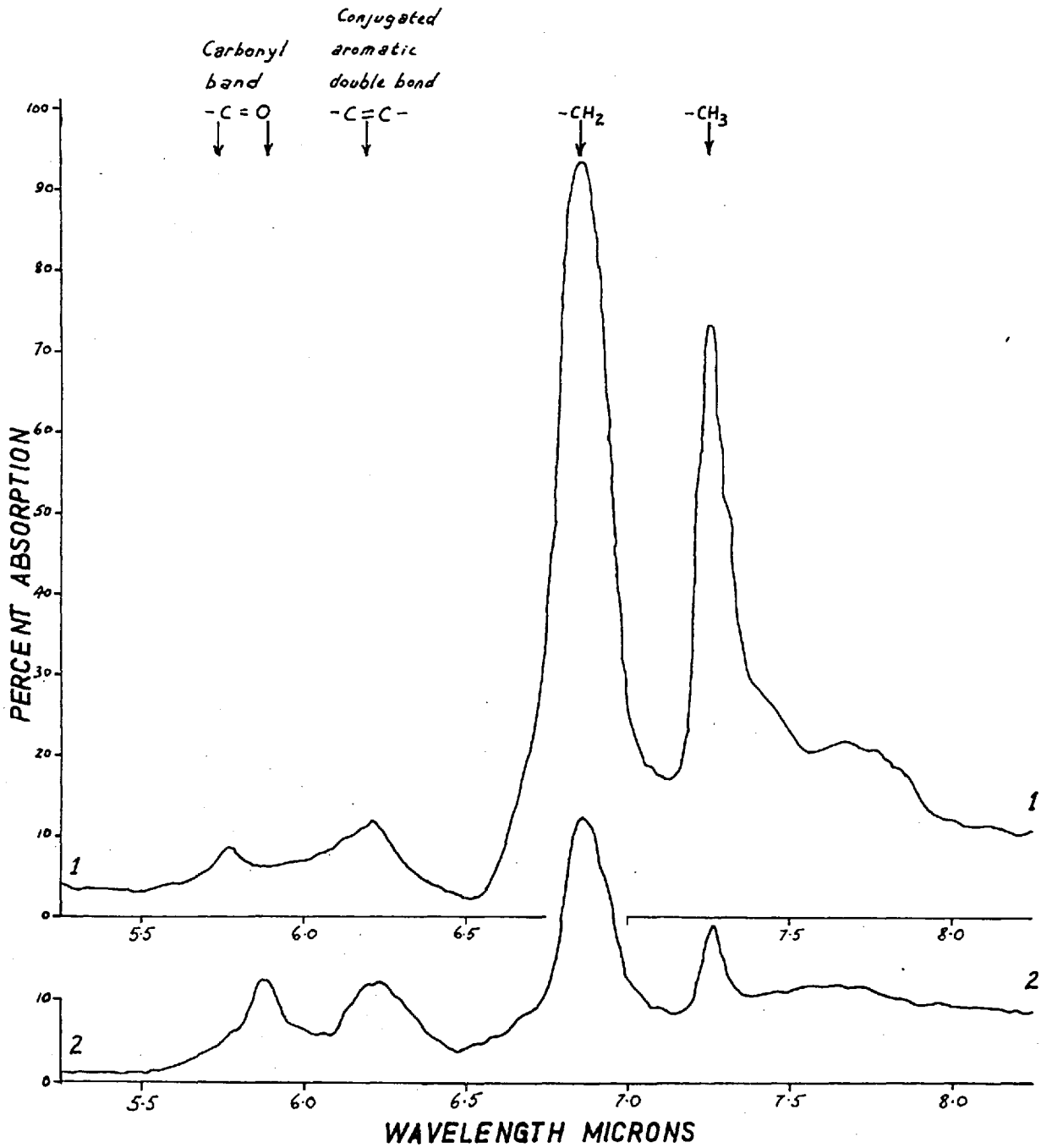
Weight of oil (gm.)	0.1933
Percentage weight eluted by n-heptane	86.7
" " " " benzene	6.31
" " " " benzene-methanol	2.84
" " remaining unrecovered	4.15

The most significant points of similarity between this experiment and percolation sample C (Table XXII), are the almost identical values for the benzene-methanol fraction and the unrecovered material. The percentage weight of oil eluted by n-heptane is, however, less than for sample C and the benzene-eluted fraction consequently greater. The explanation of the latter difference, it is felt, lies in the same explanation as the difference in adsorption characteristics of "mildly wetted" Gault clay and "damp" Gault as already described, i.e. the silica gel having first been activated adsorbed a water layer of only molecular dimensions compared with the relatively high water content of the damp Fuller's Earth. Certainly the percentage weight of oil eluted by n-heptane from the mildly wetted silica gel is comparable with that remaining in the

FIG. 28

Infra-red absorption spectra of fractions eluted by heptane, and benzene after percolating Socorro oil through mildly water-wet silica gel.

Spectrum number	
1	Heptane eluted fraction.
2	Benzene eluted fraction.



residual solution after contact with mildly wetted Gault clay prior to water desorption (Fig. 15 spectrum 2). Just as the addition of water to the mildly wetted Gault-oil complex increased the percentage of oil in the residual solution from 83 to 88%, so the higher water content of the damp clay percolation samples allowed a greater percentage of oil to be eluted by n-heptane (90%). Similarly the percentage of oil remaining in the residual solutions after maximum adsorption by the wet and damp clay samples described earlier was of the same order.

With the exception of the side chain $-CH_2$ groups peak at 6.9 microns, the infra-red spectra of the benzene-eluted fractions from percolation C (Fig. 27, spectrum 1) and from the silica gel percolation (Fig. 28, spectrum 2) were very similar. A comparison of the relative polarity of these fractions obtained from absorption peak ratios (Table XXV) indicates, however, that the increase in percentage adsorption on the silica gel sample correlates with a lower polarity of the material retained after heptane elution, i.e. silica gel has a higher adsorption capacity with respect to material in heptane solution than damp Fuller's Earth.

FIG. 29

Infra-red absorption spectra of fractions eluted by heptane, benzene, and benzene-acetone after percolating Socorro oil through activated silica gel.

Spectrum number

1 Heptane eluted fraction.
2 Benzene eluted fraction.
3 Benzene-acetone eluted fraction.

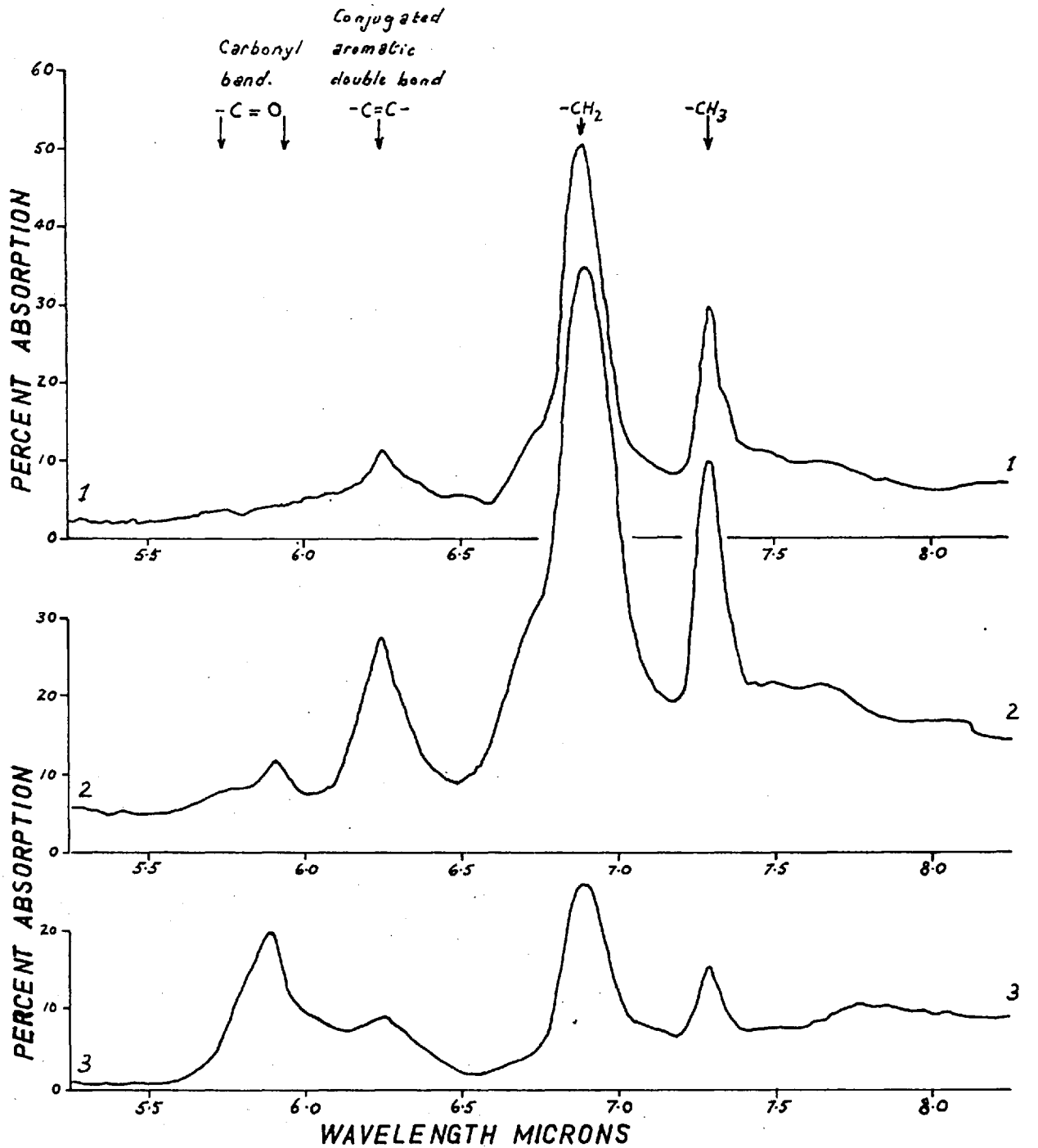


Table XXV

Fraction	Percolation C			Mildly wetted Silica Gel.		
	% of original	Absorption Ratio. 5.85μ / 6.25μ	Absorption Ratio. 5.85μ / 7.25μ	% of original	Absorption Ratio. 5.85μ / 6.25μ	Absorption Ratio. 5.85μ / 7.25μ
Benzene	3.09	1.38	0.92	6.31	1.0	0.63

The similarity of the percentage weight of material in the corresponding benzene-methanol and unrecovered fractions of percolation C and mildly wetted silica gel, on the other hand, suggests that the adsorption capacity of the adsorbents for the components in these fractions, with respect to the eluents used, is greater than the critical charge-adsorbent weight ratio (M/N) referred to above.

The retention on adsorbents containing adsorbed water, of components of a certain structure, i.e. with pronounced carbonyl groupings, is illustrated by the differences in the infra-red spectra of the corresponding fractions eluted from activated silica gel. (Fig. 29). Thus from the respective benzene eluted fractions from mildly wetted silica gel (Fig. 28, spectrum 2) and activated silica gel (Fig 29, spectrum 2) it is seen that the former had much the higher carbonyl absorbtion.

Table XXVI

Percolation through activated Silica Gel.

Weight of oil (gm.)	0.1634
Percentage weight eluted by n-heptane	69.5
" " " " benzene	24.0
" " " " benzene-acetone	4.53
" " remaining unrecovered	1.97

Comparing Table XXVI with the percentage weights of oil recovered from mildly wetted silica gel (Table XXIV) it is further apparent that the activated silica gel can retain a much higher percentage of oil after n-heptane elution, and that the low carbonyl content of the benzene eluted fraction is the result of "dilution" with aromatic hydrocarbons; i.e. the increased adsorption capacity of the activated silica gel results from its higher specific adsorption capacity (A) caused by activation (extreme drying). It is significant that the amount of material retained by the activated silica gel after benzene elution (6.5%) is very similar to that remaining after benzene elution from mildly wetted silica gel (6.91%) and Fuller's Earth sample B and C (6.61% and 6.91%, respectively). This similarity is further confirmed by the form of the infra-red spectrum of part of this retained material (Fig. 29, spectrum 3) which resembles closely the material eluted by polar adsorbents from damp adsorbents.

Comparing the damp Fuller's Earth percolations B and C, (Table XXII) which involved a similar charge-adsorbent weight ratio, it is seen that the benzene-acetone (3 : 1) mixture is a better eluent than benzene-methanol (4 : 1), leaving less unrecovered material on the adsorbent. The preferential desorption by benzene-acetone may be due to the eluent having a functional group (ketonic-carbonyl) similar to that in much of the adsorbed material. Furthermore, from a comparison of the percentage weights of benzene-acetone desorbed material (percolation B), and the unrecovered fraction (percolation C), together with the benzene-methanol desorbed material (percolation C), and the unrecovered fraction (percolation B), it appears that the material eluted by the respective solvent mixture may be of slightly different composition. Support for this hypothesis is provided by the infra-red spectra of the benzene-acetone and benzene-methanol fractions (Fig. 26, spectrum 1, and Fig. 27, spectrum 2) which show several marked differences (Table XXVII).

Table XXVII

Wavelength microns.	5.75	5.85	7.75	8.75 - 8.95
Benzene-acetone Percolation B.	slight shoulder.	very prominent.	weak	absent
Benzene-methanol Percolation C.	very prominent.	slight shoulder.	very prominent.	prominent.

Although the carbonyl grouping is still present in the benzene-methanol fraction, it has shifted its peak from 5.85 to 5.75 microns, indicating a different structural combination, e.g. ester or acid instead of ketone.

Discussion.

From these experiments it may be concluded that the specific adsorption capacity (A) of adsorbents containing adsorbed water is determined by the thickness of the adsorbed water film which surrounds the adsorbent, which in turn limits the ability of the adsorbent to adsorb components below a given polarity. Whether or not such an adsorbent can actually adsorb all the components above this critical polarity depends on the weight of adsorbent and the concentration of the polar material with which it is in contact as explained above, i.e. a "saturation" of the adsorbent is reached after which the remaining adsorbable polar material remains in solution. In other words, in the case of an adsorbent with an adsorbed film of water, the "undersaturation" or "saturation" of the adsorbent with respect to a given concentration of adsorbable polar material, is a function of the available adsorbed water-oil solution interfacial area at which the polar material may be adsorbed.

Thus the adsorption of the polar components at what is, in effect, a water-oil interface is subject to the same laws and conditions which govern adsorption by liquids (see Chapter I). The adsorbed uni-molecular films which form at the stabilized

water-oil interface consist of molecules which may be either soluble or very sparingly soluble in the bulk phase. Hence the use of a non-polar solvent such as n-heptane tends to promote maximum adsorption of these materials at the interface.

The concentration of material in these films is further dependent on the concentration of the material in the bulk of the solution, and is related to it by the Gibbs equation which for low concentrations of a solute may be written:-

$$\Gamma = \frac{-c}{RT} \frac{d}{dc}$$

where Γ = the surface excess or the concentrations at the interface between two phases of a solute present in one or both of the phases, in excess of that which would be present if the two phases were completely homogeneous up to an interface of zero thickness.

c = the concentration of the solute in the bulk of the solution and γ = the interfacial tension.

With an increase in the concentration of the bulk phase it is seen that an increase in the concentration of material in the adsorbed film also occurs, and since this is of uni-molecular thickness and constant area, a closer packing of the adsorbed molecules takes place in accordance with the film gas law. This is apparently the state of affairs existing in the percolation experiments where an increase in oil concentration

of the solution in Fuller's Earth percolation A, causes a closer packing of the adsorbed material on the available interface, i.e. twice as much material was adsorbed as in percolations B and C. Similarly since the interface available is limited, only the more highly polar of the total adsorbable polar material present in the bulk solution could be adsorbed. With the reduction of the oil concentration in the percolating solutions in B and C, the interfacial area per unit weight of oil in solution is increased approximately four times, but only half as much material is adsorbed (by weight) compared with percolation A. Similarly as there is now plenty of available interface the molecules in the film are not so closely packed and the less polar material, which remained in solution in percolation A, can now be adsorbed.

Summarizing, it therefore appears that the adsorption of water-insoluble organic material present in oils by an adsorbent which has first adsorbed water, is dependent on the following factors:-

1) The concentration and polarity of the various adsorbates present in the oil phase.

2) The thickness of the adsorbed, orientated water layer which surrounds the adsorbent, this being a function of the hydration properties of the adsorbent and the amount of water present in the system.

3) The extent of the surface area (interface) existing between the orientated water and the oil phase, which is a function of the quantity of adsorbent, its specific surface area, and the quantity of oil.

In these experiments the organic material adsorbed from an oil by wet and damp adsorbents was found to contain:-

a) One or more polar carbonyl groups in addition to their normal organic carbon-hydrogen structural groups - shown by infra-red absorption spectra.

b) Porphyrins, indicated by the strong red fluorescence in ultra-violet light of the recovered polar fractions.

It was also observed that up to 10% of an oil could be adsorbed from solution in a non-polar hydrocarbon solvent, by wet and damp clays.

Chapter VI.

DISCUSSION OF RESULTS AND THEIR RELATIONS TO SOME OF THE PROBLEMS OF PETROLEUM GEOLOGY.

At the start of the work, the nature of any relationship between crude oil, water and fine-grained mineral matter was uncertain, although at first sight interaction between non-polar hydrocarbons and the highly hydrated surface of a clay seemed unlikely. It appeared possible that the relationship between oil and water-wet-clay would be similar to that arising on shaking a pure hydrocarbon with distilled water, i.e. there would be temporary dispersion of oil into spherical droplets, followed by gravity separation into two separate continuous phases. The fundamental errors in the above reasoning are firstly, that crude oil is not entirely composed of non-polar hydrocarbons, and secondly, that not all the clays are highly hydrated. Although the preliminary experiments in which dilute crude oil-in-water dispersions were sedimented by clay slurries indicated the probability of an interaction, it was not until the experiments involving two different oils and four different kinds of clay had been carried out that the final proof was obtained. In these experiments, a check was kept on the quantities of the three phases present prior to the addition of excess water. The proportions involved, as a percentage weight of the total, i.e. after the addition of oil, but prior to the addition

of excess water, are shown in Table XXVIII.

Table XXVIII

Oil	Clay	Dry Clay % weight		Distilled Water-Clay % weight			Brine-Clay % weight		
		Dry Clay	Oil	Dry Clay	Water	Oil	Dry Clay	Brine	Oil
Mercedes	Aquagel	48	52	30	57	13	43	42	15
	Fuller's Earth	60	40	34	53	13	34	58	8
	Gault	46	54	43	41	16	44	48	8
	China Clay	40	60	34	48	18	25	56	19
Socorro	Aquagel	46	54	30	54	16	38	39	23
	Fuller's Earth	50	50	35	53	12	30	52	18
	Gault	50	50	40	37	23	37	40	23
	China Clay	39	61	35	49	16	26	56	18

The main point to be noted is that the proportions of clay and oil, and clay, water and oil in the original mixtures are of the same order and, therefore, the differences in behaviour between the various systems must be due principally to the properties of the clays and oils. An outstanding feature was that Aquagel (sodium montmorillonite) was the only clay which allowed oil to escape from both dry and wet clays as approximately spherical globules on the addition of excess water. Even in this case, the escaping globules did not coalesce at the surface of the water, presumably because of the protective

colloid action of small clay particles adhering to their surfaces. The other oil-saturated oven-dried clays did not disperse, nor was the oil flushed out, on the addition of water, although some readjustment of the Socorro oil within the clays did occur. Similarly, in the initially water-wet samples mixed with oil no clay dispersion or oil flushing occurred, the oil being retained as discrete film-like particles intimately mixed with the clays.

The following explanation in terms of interfacial tensions, appears to account for the differences noted in the observations relating to oven-dried and water-wet clays:- If oil spreads over a solid surface by displacing water, then the spreading coefficient S in the equation, $S = \gamma_{WS} - \gamma_{OW} - \gamma_{OS}$, must be positive, where $_{WS}$, $_{OW}$ and $_{OS}$, are the water-solid (clay), oil-water and oil-solid interfacial tensions, respectively. Assuming that the oil-water interfacial tension remains approximately constant, spreading of oil against water in the water-wet samples (or water against oil in the dry-clay samples) will depend on the relative magnitudes of the oil-solid and water-solid interfacial tensions. In the case of Mercedes oil-Fuller's Earth, -Gault, and -China Clay, the adhesion of oil to the dry clays (due to the adsorption of oil components) prevented its displacement by water; there was only readjustment but no clay dispersion when water was added to Socorro oil saturated

complexes. These clays, therefore, have comparatively low oil-solid interfacial tensions. Oven-dried Aquagel saturated with oil, on the other hand, imbibed water quite readily, dispersing the clay and allowing the oil to form quite large spherical globules, some of which were immediately released to the overlying water (many of the others remaining were easily released by very gentle tapping of the tube). Thus Aquagel has a very low water-solid interfacial tension, and water spreads on the clay forcing the oil to contract into globules.

When the clays are initially water- or brine-wet, the situation is reversed and the oil, dispersed into droplets by stirring, spreads as a film when intimately mixed with Fuller's Earth, Gault and China Clay, i.e. the sum of the oil-water and oil-solid interfacial tensions is less than the water-solid interfacial tension. Similarly, the low water-solid interfacial tension of Aquagel ensures that no oil spreading occurs, the oil for the most part remaining as largish spherical globules. As in the case of the oil-saturated dry Aquagel, however, a small amount of fine clay particles does adhere to the relatively large globules, preventing coalescence of the oil. The presence of the particles on the oil globules is probably due to extensive localized adsorption of oil components which is sufficient to overcome the hydrophilic properties of the few fine particles attached.

With regard to the different types of oil, it was noticeable that Mercedes oil adhered much more strongly to dry clays (Fuller's Earth, etc.) than did Socorro oil. This is apparently due to the greater adsorption of oil components from Mercedes oil than from Socorro oil, since the clay-oil ratios were similar for a given clay (Table XXVIII), as were the specific gravities of the oils (Table V). The readjustment and concentration of Socorro oil at the top of the dry clay samples on the addition of water further suggests that increased adsorption had taken place on the clay remaining in contact with the oil so as to prevent any further displacement from the clay, i.e. the clay-oil ratio had in effect been reduced. Furthermore the oil-stained layer directly below the Socorro oil in the dry clay samples, shows that adsorption of oil components by clays can take place without the clay surface becoming sufficiently hydrophobic to prevent partial water imbibition. The adsorbed oil components remaining after the displacement of the oil phase proper were, however, sufficient to prevent the water from dispersing the clay, i.e. Fuller's Earth, Gault and China Clay.

Evidence that wet clays can also adsorb oil components without the clay surface being preferentially oil-wet was provided by the discoloration of water- and brine-wet Aquagel after the addition of excess water had caused the

displacement of oil (discoloration of the oven-dried Aquagel was also observed after the water displacement of oil). Although the adsorption of oil components was obviously not extensive enough to prevent the further hydration and swelling of Aquagel it may, however, have reduced its hydration properties as compared with a straightforward Aquagel-water system, but this was not investigated.

Further proof of adsorption by wet clays was the cracking of the sample tubes on mixing oil with wet clays, which occurred in eleven out of the twelve samples involving three-layer, expanding lattice type clays (internal as well as external surface areas) i.e. Aquagel, Fuller's Earth and Gault. This phenomenon is apparently caused by a heat of wetting effect believed to result from a change in state of the water directly adjacent to the adsorbing surface of the clay, either by displacement of adsorbed water, and/or the orientation of adsorbed oil components on the internal surfaces of the clay (Grim, 1953).

The percentages of adsorbed oil components retained, after the addition of excess water, by dry Fuller's Earth and Gault clay-oil solution complexes and a mildly water-wetted Gault clay-oil solution complex were determined and found to be approximately 15% for initially dry clays and 11% for the mildly wetted sample. It was also found that

FIG. 30

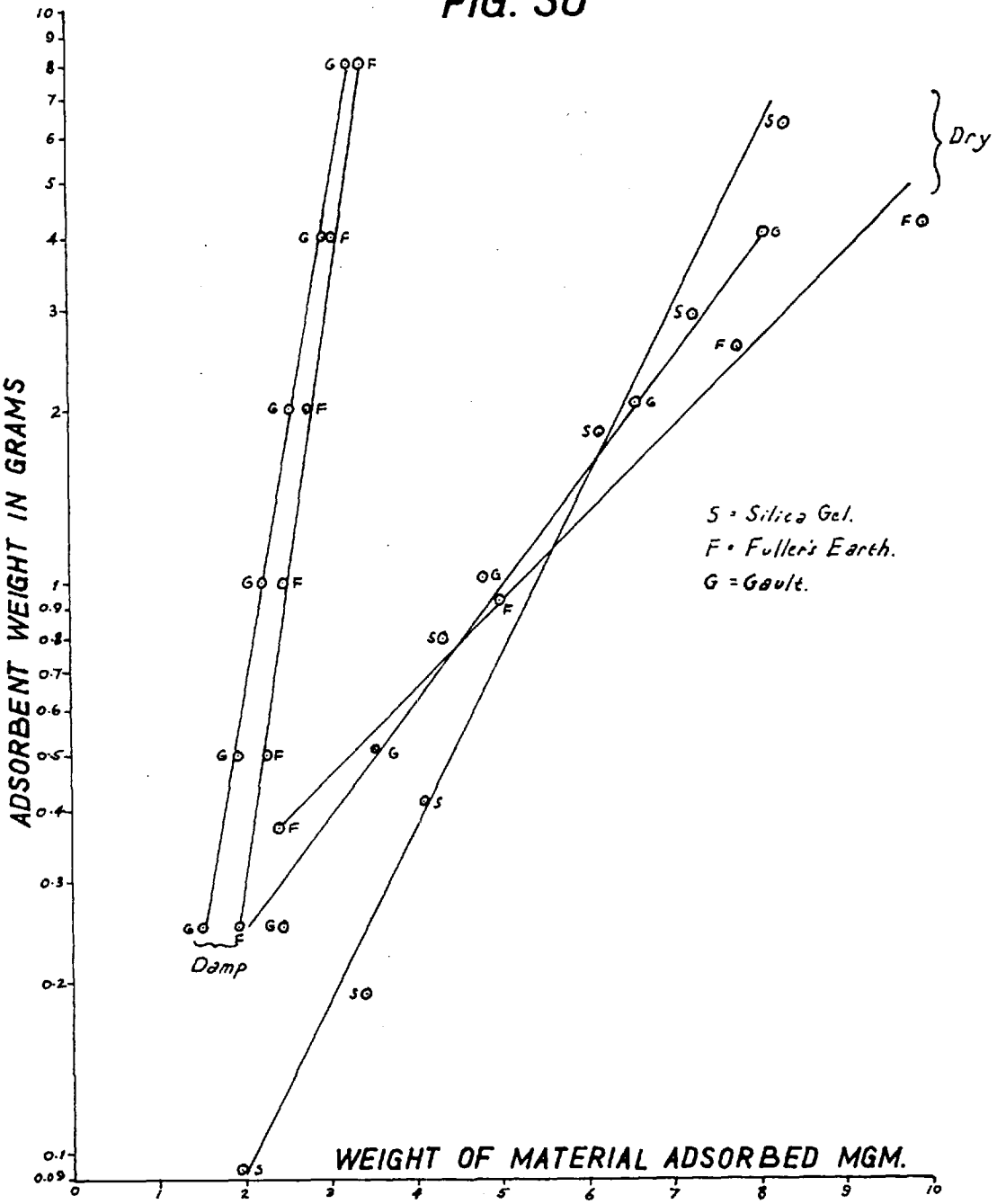


FIG. 30a
(After Ferguson, 1960)

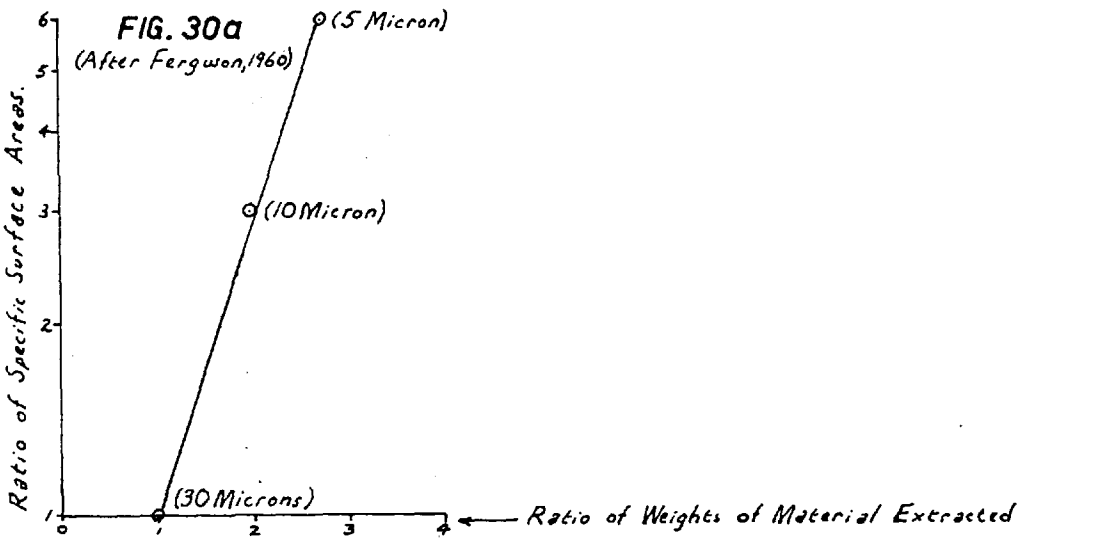
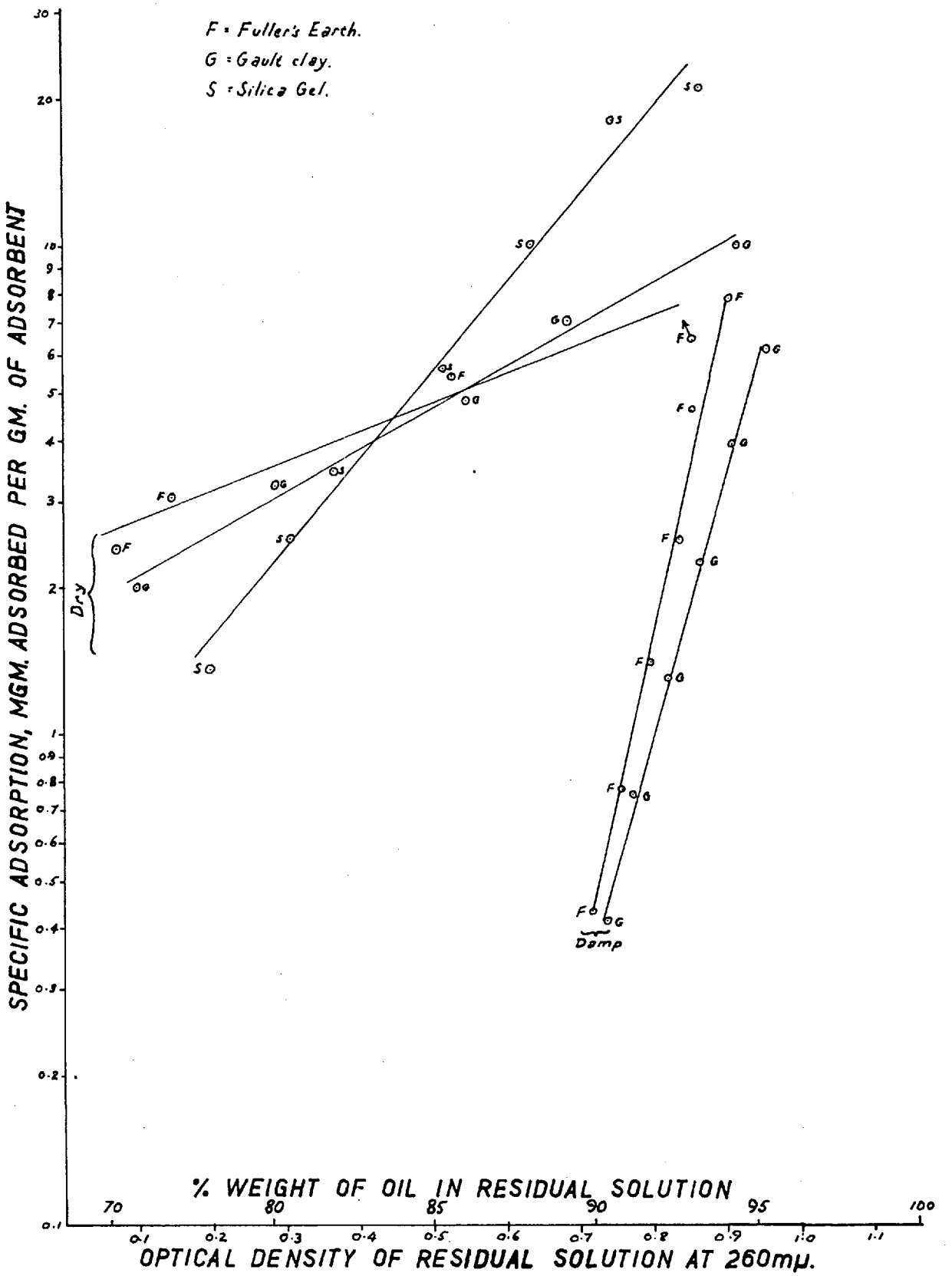


FIG. 31


F = Fuller's Earth.
G = Gault clay.
S = Silica Gel.
SPECIFIC ADSORPTION, MGM. ADSORBED PER GM. OF ADSORBENT
Dry
Damp
% WEIGHT OF OIL IN RESIDUAL SOLUTION
OPTICAL DENSITY OF RESIDUAL SOLUTION AT 260mμ.

water-saturated Fuller's Earth samples were capable of adsorbing up to 10% of the oil originally present in a non-polar solvent when the wet clay and oil solution were thoroughly shaken together. These percentages represent an approach to the maximum possible adsorption of oil components for clays initially associated with different amounts of water, i.e. initially dry, mildly wet and water saturated clays, and indicate that the percentage of oil components able to remain adsorbed in the presence of excess water decreases as the initial water content of the clay increases.

Regardless of the influence of water content on the adsorption capacity of clays for oil components, the extent of adsorption in any given system will depend on the relative concentrations of oil and clay present. Fig. 30 shows the relationship which exists between adsorbent weight and material adsorbed for three dry adsorbent-standard oil solution, and two damp adsorbent-standard oil solution systems. Thus, although the amount of material adsorbed from a fixed volume of a standard solution increases with increase in adsorbent weight, the specific adsorption (mgm./gm. of adsorbent) decreases. A consequence of this relationship is shown in Fig. 31, where specific adsorption is seen to increase logarithmically as the percentage of oil removed by adsorption from a standard solution decreases linearly.

For a given oil concentration, therefore, the greatest percentage adsorption of oil will occur when the solution is in contact with a large amount of a given adsorbent, i.e. low oil-adsorbent weight ratio However, since the specific adsorption is low in such a situation the material adsorbed will have comparatively little influence on the wetting properties of the adsorbent. If, on the other hand, the oil-adsorbent weight ratio is high, then the percentage of adsorption of oil will be low, but the specific adsorption will be much greater than for the previous low oil-adsorbent ratio, and it is therefore much more likely that the wetting properties of the adsorbent surface will be altered in favour of the oil.

Briefly the following inter-related factors control the extent of adsorption and the wetting phenomena in the crude oil-water-fine-grained mineral matter systems investigated:

a) The type of mineral matter.

b) The type of crude oil.

c) The clay-oil weight ratio.

The effects of changes in the properties of the aqueous phase were not investigated beyond using an electrolyte solution in some of the qualitative experiments. This appeared to behave in the same manner as water alone.

There is little doubt, however, that variations in the physico-chemical properties of the aqueous phase would be an additional factor to those already listed, e.g. ph changes would certainly affect both clay and oil, and hence their interaction.

The changes in the ultra-violet absorption spectra of residual oil solutions after adsorption of material by damp and saturated clays indicated that the adsorption was of a selective nature. This was confirmed when the material recovered by organic solvents from damp clays was found to contain polar carbonyl groups and porphyrins, its general appearance and properties suggesting that it was associated with the asphaltic and resinous compounds present in crude oils. Some of the material (approximately 2% of the oil) could not be recovered by the eluting solvents used and appears to be very tenaciously held by the damp clay complexes. This is in keeping with the ability of the hydrophilic Aquagel to adsorb certain oil components without becoming sufficiently hydrophobic to be oil-wet, the material remaining adsorbed even after the displacement by water of the bulk of the oil phase during clay hydration.

From the results obtained it appears that a combination of adsorption processes exists, one process being the complete or partial displacement (reduction in thickness) of the adsorbed water layer by the highly adsorbed oil

components (chemisorption, perhaps), the second process, probably a consequence of the reduction in thickness of the adsorbed water layer, being the formation of complex adsorbed films at the oil-solid (clay) or oil-adsorbed water layer (reduced) interface by the less polar material. Thus the adsorption of oil components by Aquagel did not reduce the thickness of the adsorbed water layer sufficiently to allow complex adsorbed films to form at the oil-adsorbed water layer interface.

The Origin and Accumulation of Petroleum.

The formation of an accumulation of crude oil has, in recent years, been suggested to be the result of selective extraction of hydrocarbons and certain non-hydrocarbons dispersed within fine-grained sediments, followed by the concentration of the extracts within the reservoir rock. Whether the dispersed hydrocarbons are present in the sediments at the time of deposition, or are formed from the non-hydrocarbon organic matter in the sediments during burial and compaction, or, what appears more likely, arise in both these ways, is not at present certain. It seems beyond doubt that the mechanism of selective extraction involves the intrastratal flow of water concomitant with burial and compaction of the sediments. The idea of the association of flowing water with the formation of an oil accumulation is not new, but recent investigations into the composition

and distribution of sedimentary organic matter soluble in organic solvents, together with advances in knowledge of the composition of crude oils, have led to a better understanding of the nature of the association.

In view of the low concentration of hydrocarbons in source sediments (1 part per 1,000 or less), it appears unlikely that the volume changes (5 to 1 or less), and differential pressure gradients that occur during compaction could alone force out physically adsorbed or even free hydrocarbons against the interfacial forces which tend to cause their retention in the sediments, i.e. by large amounts of inorganic particles having large surface areas.

According to current ideas the hydrocarbons are transported in solution from the source rock by the water squeezed out during compaction, the hydrocarbons being dissolved in water as a result of solubilization by colloidal electrolytes, co-solvency, and hydrotropy the last arising from the presence, in solution, of the more water-soluble organic non-hydrocarbons (Baker, 1959, 1960a; Meinschein, 1959). It has been suggested that after release from solution, in porous, permeable reservoir-type sediments, by a mechanism yet to be determined with certainty, the dispersed or emulsified hydrocarbon and non-hydrocarbon droplets are leached by water because of different rates of motion of the oil droplets and water. This inter-change

of organic material with leaching water results in concentration of the organic-soluble hydrocarbons in the oil phase and transfer of the more water soluble non-hydrocarbons to the water phase (emulsion chromatography), the efficiency of the inter-change being enhanced by the large surface to volume ratio of the "emulsion" droplets. Differences in the rate of movement of the oil droplets and water due to viscosity and surface forces, allow this exchange to continue until the droplet finally reaches a location where it is in hydrodynamic equilibrium with the water phase. A certain minimum pore size is presumably required for the movement of oil droplets or emulsions through an aquifer. In fine-grained sediments such as shales the movement of a dispersed oil phase, if it exists as such, would be negligible or extremely slow. This criterion, therefore, restricts the location of major crude oil deposits to coarse-grained permeable sediments, which is undoubtedly the case (Meinschein, 1959).

Baker (1959) has further observed for hydrocarbons being solubilized by colloidal electrolytes that in highly saline waters the solubility of paraffin hydrocarbons is markedly increased, but that the solubility of aromatic hydrocarbons is decreased as compared with less saline waters. Baker, therefore, suggests that crude oils initially collecting from saline waters will be relatively

more paraffinic than oils collecting from fresh water. As a rule the older and/or deeper, more paraffinic, oils are associated with more saline formation waters, whereas the younger and/or shallower, more cyclic, oils are associated with less saline waters, the words old and young applying only to the age of the reservoir rock in which the oil is now found.

Thus it is seen that the solution and flow of the dispersed fluid hydrocarbons and non-hydrocarbon organic matter are subject to several types of distribution phenomena between the liquid and solid phases present. This is particularly true of the fine-grained sediments where the large surface areas have a very considerable influence on the interfacial relationships existing between the phases. Hence adsorption, partition, ion exchange, foam and emulsion chromatography are all likely to play a part in determining the final distribution of oil components in crude oils, in addition to the solubility relationships of the water and organic material (Nagy, 1960).

A theory such as Baker's, which postulates the formation of a crude oil accumulation as selective concentration of hydrocarbons within the reservoir rock, is supported by the interaction of crude oil and water-wet fine-grained sediments when the two are mixed together in water.

If crude oils existed as such in the fine-grained sediments prior to their primary migration it is very difficult to see how they could have migrated without some mechanism, e.g. solubilization, which could change the interfacial relationship sufficiently to allow the crude oil to move through the water-wet sediments. The work of Reisberg and Doscher (1957) already referred to, suggests ways in which the interfacial relationships may be changed, but these also involve the solubilization of part of the surface active components responsible for the retention of crude oil on water-wet solids.

The hydrocarbons and non-hydrocarbons recovered by solvent extraction from fine-grained sediments in close proximity to reservoirs, i.e. source rocks, might be considered as the material "deposited" or retained under the conditions prevailing in the sediment system over the period of time that oil was accumulating in the reservoir. If, as seems likely, this is the case, then a distributional difference in the components of crude oils and the organic materials in sediments is to be expected. It would appear, therefore, that the solvent action of the water passing through the sediments, particularly if it contains colloidal electrolytes, will be analogous to the flow of an oil solution through a column of damp adsorbent, since the

solution of organic matter in the micelles of colloidal electrolytes is analogous to differential solubility between immiscible hydrocarbon solvents and water, i.e. there is a partition effect. Furthermore, if the adsorbent is such that it has a similar surface, i.e. water-wet, to that of the sediments, then the material retained or adsorbed from the oil solution should have certain characteristics in common with the material retained by fine-grained sediments. This has in fact been found to be the case for the oil solutions used in the experimental work already described.

The infra-red spectra of the chromatographic fractions of both organic extracts from sediments and crude oils have often been compared in the literature with a view to detecting any significant differences between the equivalent fractions eluted. Of particular interest are the comparisons of the aromatic fractions normally obtained by eluting an activated adsorbent column with benzene. Theoretically only pure aromatic hydrocarbons should be present in this fraction, any non-hydrocarbons being retained on the adsorbent. Although, in general, this is true for the benzene-eluted fractions of crude oil chromatographic separations, it is not strictly true for the equivalent benzene-eluted fraction from sediment extract separations. Stevens et al. (1956), Orr and Emery (1956) and Bonnett (1958)

all report significant carbonyl group absorption bands (5.75 to 5.85 microns) in the infra-red spectra of the benzene fractions of organic extracts from sediments.

A comparison of the benzene-eluted fractions of crude oils and their presumed source rock sediment extracts by means of their respective infra-red spectra was made by Bonnett (1958), and generally speaking there was good agreement for oils and sediment extracts from Kuwait and from Ecuador. The principal difference between the spectra of the oils and the extracts, however, lay in the much stronger carbonyl group absorption bands of the sediment extract fractions. Of particular interest with respect to the results obtained in the percolation experiments already described, was the choice of the Ecuador samples, the oil being the Socorro oil used in the percolation experiments and an extract from the Socorro shale which surrounds the Socorro oil reservoir.

Since the elution by benzene of the organic extract from sediments removes components containing carbonyl groups from activated adsorbents, the adsorbents must have weak powers for retaining these components. On the other hand, the same type of component was poorly represented in the equivalent fraction obtained from similar separations of crude oils, i.e. it was not present in the oils to so great an extent. If this applies to all crudes the low content

of compounds with carbonyl groups cannot be attributed solely to the relative polarity demonstrated in the presence of highly active, i.e. dry, adsorbents. In the light of the results of the percolation experiments, namely the association of carbonyl groups with water-wetted surfaces, it seems that there is selective removal of the carbonyl-containing components by an organic phase--aqueous phase interface. The presence of these components in fractions of the organic extracts from sediments, therefore, suggests that the conditions necessary for retention are provided by interfaces in the initially water-wetted sediment which is analogous to the damp clay in the percolation experiments.

According to McBain and Hutchinson (1955) the mechanism of hydrocarbon solubilization by colloidal electrolyte solution is analogous to the differential solubility of a component between two immiscible liquids, the micelles of the colloidal electrolyte behaving as an immiscible phase with respect to the surrounding "pure" water. Thus the quantity of material solubilized in the interior of the micelles depends upon the solubility properties of hydrocarbons with respect to the micelles alone (organic phase) and to pure water (surrounding aqueous phase), in addition to the quantity and type of micelles available. The solubility properties of hydrocarbons in micelles are,

furthermore, analogous to the solubility of hydrocarbons in hydrocarbon solvents, e.g. oils in heptane or benzene. This phenomenon is apparently due to the association, in the interior of the micelles, of the hydrocarbon groups which form part of the colloidal electrolyte molecules. Thus in a continuous dynamic system similar to that found in the flow of compaction water containing colloidal electrolytes, the efficiency of extraction of hydrocarbons dispersed in the fine-grained sediments is governed by the quantity of hydrocarbons initially present, i.e. concentration, and two interdependent partition effects:

1) The relative solubility of the hydrocarbons in "pure" water, i.e. aqueous phase.
2) The relative solubility of the hydrocarbons in the colloidal micelles, i.e. the water-immiscible organic phase.

Whilst solubilization causes a selective extraction of hydrocarbons from sedimentary organic matter in general, there is also, to some extent, a selective extraction of individual hydrocarbons or groups of hydrocarbons with respect to their relative solubility properties and concentrations.

Thus if a hydrocarbon is of low molecular weight, i.e. reasonably soluble in water and highly soluble in the micelles, and of initially low concentration in the sediment

relative to the total hydrocarbons present, then the efficiency of extraction from the sediment will be high as a result of its comparative ease of solution in water. The solution of low molecular weight hydrocarbons in water will, in turn, be promoted by their removal from the water by the partition effect with the micelles. On the other hand, for a hydrocarbon of relatively high initial concentration and high molecular weight, i.e. very poor water solubility, and only reasonably soluble in the micelles, the efficiency of extraction will be low, since in addition to its poor water solubility characteristics, its solubility in the micelles is low compared with low molecular weight hydrocarbons, i.e. the further solution of the hydrocarbon in water is not so readily promoted by removal of the hydrocarbon from water by the micelles. Furthermore, in the case of certain high molecular weight hydrocarbons this situation may be further complicated by the antagonistic action of insoluble amphipathic, i.e. non-hydrocarbon, surface active material, whose hydrophobic structure is similar to that of the high molecular weight hydrocarbons in question. Hence, such water soluble characteristics as the hydrocarbons might normally possess are opposed by a tendency for the hydrocarbons to be adsorbed on amphipathic material, i.e. a further distribution (partition) effect is added to the system.

The above reasoning may explain the failure of Brenneman and Smith (1958) to find low molecular weight organic material, (i.e. boiling below 200°C) in source rock sediment extracts, and also the good agreement found between the structural-type distribution of the higher boiling point aromatics (above 200°C) in source rock extracts and crude oils. In the first instance highly efficient extraction of the available low molecular weight hydrocarbons may have taken place, whilst the extraction of high molecular weight aromatics was controlled by some distribution effect which applied equally to the sediments and the micelles. It appears that such an effect might be caused by amphipathic material whose hydrocarbon structure was similar to the structure of the aromatic hydrocarbons and also to the hydrocarbon structure of the amphipathic material forming the colloidal micelles. The amphipathic material could, in fact, be similar to the carbonyl-containing components associated with the benzene-eluted (aromatic) fraction of sediment organic extracts, and the carbonyl-containing material retained from crude oil by damp adsorbents. Further work on this point is necessary, however, before such a conjecture can be substantiated.

The principal difference between crude oil fractions boiling above 200°C and the organic extracts of their presumed source rocks concerns their respective non-hydrocarbon,

oxygen, nitrogen and sulphur organic components. For an equivalent molecular-weight range they occur in considerably greater amounts in the organic extracts. The oxygen content for the extracts varies from 1.8 to 7.7%, compared to less than 1% for most oils. The functional groups of the oxygenated compounds from the extracts show that two-thirds to three-quarters are represented by esters, whereas for oils only one-twentieth to one-eighth is so represented. The remaining groups in the oxygenated portion of the extracts are mainly carbonyl and alcohol groupings with minor acidic groups. The oxygen in petroleums is apparently combined in other ways, however, since only a quarter to a half of it is accounted for by these functional groups (Brenneman and Smith, 1958).

The Recovery of Representative Organic Extracts from Sediments.

It seems likely that the reason why extracts of the organic matter in sediments have a larger non-hydrocarbon content than crude oil is in part, at least, a consequence of the use of polar solvents (acetone and methanol) in addition to a hydrocarbon solvent (benzene). It would be interesting to compare the distribution of hydrocarbons and non-hydrocarbons in crude oils and in organic extracts from sediments when hydrocarbon solvents alone were used for extraction of the sediment, since after the percolation of topped crude oil through damp clays the more polar oxygenated

components are retained on the clays even after washing with pure hydrocarbon solvents (n-heptane, and benzene). In addition the percolation of both oils and extracts through damp clay prior to a comparison of their hydrocarbon distributions might throw some light on the nature of the association of hydrocarbon and non-hydrocarbon components of the oils and extracts. A further useful comparison would probably be obtained if, after the normal extraction procedure using polar solvents, the extract obtained was similarly percolated through damp clay.

This retention of the polar material by the sediments after extraction by hydrocarbon solvents alone might well alter extensively the relative distribution of hydrocarbons in the extract as compared with that obtained by the methods used to date. The retained polar components are probably highly surface-active and so will prevent the release of hydrocarbons with which they are closely associated, i.e. indigenous hydrocarbons which have always been intimately mixed with the organic matter and are therefore not likely to have migrated since their formation or deposition, thus allowing a more valid comparison of the sediment and crude oil hydrocarbons.

The extraction of hydrocarbons from ancient sediments by benzene rather than by mixed solvents has recently been advocated by Ferguson (1960). He also found that the amount

of extractable hydrocarbons from a given weight of sediment was dependent on the particle size to which the sediment was pulverized prior to extraction. Thus a sample of 10-micron median size gave up twice as much extractable hydrocarbons as a sample of 30-micron median size, and 5-micron samples gave up a 2.75 times greater extract than 30-micron samples, showing the intimate relationship of the sediment hydrocarbons with the mineral surfaces, probably as a result of a close association with adsorbed non-hydrocarbon components. It would be interesting to know what differences, if any, existed in the distribution of hydrocarbons recovered from these samples of different particle size.

The increase in hydrocarbon recovery with decreasing particle size of the sediment being extracted, shows a close relation with the previous remarks regarding adsorption and clay-oil ratio. Just as the weight of material adsorbed from a solution of fixed concentration increases linearly as the adsorbent weight increases logarithmically (Fig. 30), i.e. the specific adsorption decreases with increasing adsorption, so in the case of extraction (desorption) the weight of material extracted, for a given volume of extracting solvent, will increase as the adsorbent weight increases, but the weight of material extracted per gram of adsorbent will decrease. Increasing the weight of an

adsorbent of fixed specific surface area is to all intents and purposes, the same as keeping the weight of adsorbent fixed and increasing its specific surface area, i.e. in both cases there is an increase in total surface area per gram of solution. Assuming that particles of different size have the same shape, similar reasoning may be applied to the extraction of sediment of different particle size; thus although the ratios of the specific surface areas of the 30, 10 and 5 micron fractions are 1 : 3 : 6, the ratios of the material extracted are only 1: 2 : 2.75, i.e. there is a decrease in specific desorption with increase in total desorption. Although only three points are available, the relationship between specific surface area and weight of material extracted is exactly the same as for adsorption, i.e. semilogarithmic. (Fig. 31a).

Apart from the bearing of sediment particle size in the optimum recovery of organic extracts from a given weight of sediment, there is the additional factor of the adsorbed water content of the sediment which must be taken into account if truly representative extracts are to be obtained. The usual procedure adopted in solvent extraction of fine-grained sediments involves the oven drying of the samples prior to solvent extraction. Such a course of action will remove the adsorbed water and for low volatility organic compounds allow organic-clay complexes to form from

material that was only weakly adsorbed prior to the drying operation; alternatively, volatile material adsorbed prior to drying may be lost by evaporation (Hoffman and Brindley, 1960). Similarly, it is apparent from the ultra-violet spectra of standard oil solutions in contact with a given weight of dry, mildly wetted, and damp Gault clay (Fig. 14, spectra 4 and 6, Fig. 15, spectrum 3, and Fig. 22, spectrum 7, respectively) that the adsorption of both hydrocarbons and non-hydrocarbons increases as the adsorbed water content decreases. Furthermore, the addition of excess water to the dry sample did not displace nearly as much material as was present in the original solution or in the residual solution after contact with damp clay, i.e. some material was irreversibly adsorbed with respect to water.

It might be argued that only the efficiency of non-hydrocarbon recovery would be affected by the removal of adsorbed water, but as already stated the intimate association of non-hydrocarbons with certain hydrocarbon types could also affect the recovery efficiency of the latter. From the above remarks it would appear that the most efficient method of obtaining representative organic extracts from fine-grained samples should take note of the following points:-

1) The storing of samples in an atmosphere of high relative humidity at all times, e.g. over saturated potassium

sulphate solution (relative humidity 97%).

2) The sediments should be powdered as finely as possible in benzene using a ball mill with glass balls as described by Meinschein and Kenny (1957).

3) Solvent extraction should first be carried out with benzene alone, preferably using a counter-current method such as a Soxhlet extractor with a chromatographic column filled with powdered sediment (sedimented into the column in benzene) in place of the usual paper thimble. For better recovery a heating coil around the chromatographic column would be an advantage (temperature not greater than 60°C).

4) After maximum extraction with benzene the extracting solvent in the reservoir could be changed to a suitable constant boiling benzene-methylethyl ketone (62 : 38 weight %) or chloroform-acetone (80 : 20 weight %) mixture without removing the column, and the extraction continued to completion (without the use of the heating coil).

5) After extraction of the damp samples, the sediment could be oven-dried and then extracted again in the usual way, or by refluxing, with the mixed solvents.

In this way comparisons could be made between the hydrocarbons available for possible migration, i.e. those extracted from damp sediments by benzene alone and hydrocarbons

and non-hydrocarbons intimately retained by the sediments and therefore not likely to migrate. The use of a hydrocarbon solvent alone for the extraction of damp sediments is in some ways comparable to the colloidal electrolytes ("immiscible solvents") which have been suggested to be responsible for hydrocarbon migration.

Comparisons of hydrocarbons and non-hydrocarbons extracted from damp sediments by hydrocarbon solvents could be made with equivalent boiling point (molecular weight) fractions of neighbouring crude oils in order to investigate distributional differences. Furthermore, comparisons of the hydrocarbons and non-hydrocarbons extracted from damp sediments by hydrocarbon solvents and similar materials recovered by polar solvents from damp and dry sediments, respectively, together with other investigations of the sediment itself, e.g. surface area, hydration properties and general adsorption characteristics, might be very valuable in source rock evaluation, particularly if carried out on a regional basis.

Variation of Oil Properties and Reservoir Rock Wettability.

The reasons given for differences in oil gravity in oil accumulations in different parts of a depositional basin are controversial, and may only be truly elucidated when more knowledge of the complex geochemistry of organic matter in the sedimentary environment has been gained.

Weeks (1959) has summarized the alternative explanations, which might account for such differences, and it appears that for different geological environments and geographical locations one or other of these explanations may give the dominant factor. Weeks goes on to state that one of the cuases of variation may be due to chromatographic changes taking place during migration. Similarly, Smith et al. (1959), have suggested upward chromatography as an explanation of the systematic variations of sulphur content and correlation index in the Big Spring field, Texas, where oil is produced from Permian sands ranging in depth from 1,300 to 3,000 ft. In this example sulphur content and atomaticity increase with depth, which is the opposite of the usual idea of the deeper oils being more paraffinic. Alternatively, different source material might also account for the systematic variations observed, particularly if there is a progressive change in the sedimentary environment of the source rocks, e.g. slow transgression or regression during the period of sedimentation. An explanation suggested by the same authors for the decreasing sulphur content and correlation index with increasing depth in many of the Gulf Coast and Californian fields is that of upward thermal diffusion of the cyclic hydrocarbons and sulphur compounds, aided, in certain instances, by the presence of surface-active porphyrins which could migrate upwards by

capillarity. Whilst not being in a position to criticise these ideas, it does show that there are chemical and physical processes which can be adduced to explain practically any trends observed.

Perhpas better evidence of oil gravity changes resulting from the selective removal of oil components, i.e. natural chromatography, is provided by the lateral variation of oil properties within one continuous extensive reservoir. This appears to have been demonstrated by Hodgson and Baker (1959) for the selective removal of asphaltic material during the accumulation of oil in a number of Canadian reservoirs. These workers correlated asphaltene, resin, sulphur and metal content in oil produced from different wells, and obtained a distribution which indicated their selective removal in certain directions, from which the direction of oil migration into the reservoirs was postulated. In one of the fields investigated, the Cardium sand (Cretaceous) of the Pembina field, a ten-fold variation of the measured properties was found in transversing the reservoir. It is perhaps significant that this field, which is a stratigraphic trap resulting from the up-dip "shale out" of the Cardium sand, has an argillaceous-sand as its reservoir rock, with the porosity of the sand in a given well controlled by the quantity of argillaceous material present, an empirical correlation between gamma radiation and core analysis porosity

having been established in order to asses porosity from the logs (Justin, 1957). Furthermore, the interstitial water saturation is of the order of only 10% throughout the field, which has led to the suggestion that the sand is oil wet, the interstitial water saturation, however, increases in the usual way with decreasing porosity (increasing shaliness). Taken together it appears that the possible oil-wetting occurs in the areas of highest porosity and permeability, which in turn are the least argillaceous. The presence of asphaltic and resinous material in the oils also bears some relation with the areas of greatest porosity (pay), although insufficient evidence is available to substantiate this fully.

It appears, therefore, that argillaceous material in a reservoir will denude an oil of its polar material without the clay or sand becoming preferentially oil wet, i.e. low specific adsorption, whilst the "cleaner" more porous sands will tend to become preferentially oil-wet due to the high specific adsorption of wetting components. An alternative way of viewing this problem is that clean sands will basically have a lower irreducible water saturation than "dirty" sands, and hence the concentration aspect of oil per unit surface area of reservoir rock is greater for clean sands.

An investigation of clay content and capillary behaviour of Wyoming reservoir sands by Baptist and White (1957), showed that the capillary behaviour of reservoir sands is related to the types and amounts of interstitial clay minerals. Sands containing bentonitic clays had unusually high irreducible water saturations, and water could be imbibed to high percentage pore volume saturations. Sands containing relatively large amounts of kaolinite and illite exhibited these characteristics to a lesser degree than bentonitic sands, but to a greater degree than clay-free sands. This difference is compatible with the results of the present experiments. They also found that irreducible water saturations were not affected by the salinity of the water, suggesting that most residual water is adsorbed on the solid surfaces and held in fine capilliaries, and that only a minor amount is retained as interlayer water within the clay mineral particles. Two of the sands containing small amounts of kaolinite and illite, compared with larger amounts for the other sands tested, but with no montmorillonite, were found to be preferentially oil-wet, which caused the authors to state "it is impossible with present knowledge to separate the behaviour effects due to surface wettability from those due to clay minerals." It would seem, therefore, that in the preferentially oil-wet samples, the small amounts of preferentially water-wet clay that may be present are

insufficient to offset the preferentially oil-wet characteristics of the sand grains themselves. The observation regarding salinity also suggests that adsorption of oil components in the interlayer regions of clay minerals may have prevented swelling.

The protection of clays by the adsorption of oil components has been suggested by Grim (1947) and more recently by Smoot (1959), who, in certain instances, was unable to remove the organic coatings from clays associated with oil-producing formations, even after extended periods of washing in petroleum ether. The adsorbed organic coatings which exist on the surfaces of reservoir rocks, so that the rock surfaces can no longer be contacted by injected water, are the basis of a method for defining and measuring the "relative water wettability" of reservoir rocks (Holbrook and Bernard, 1958). By measuring the quantity of methylene blue dye adsorbed by "fresh" unextracted core, and a similar core after extraction with a 3 to 1 by volume chloroform-methanol solvent mixture (the extracted core being taken as 100% water-wet) the relative water wettability, in terms of percentage surface area of the fresh core that can be contacted by water, was determined. Since the clays constitute the major part of the surface area of a typical core, most dye adsorption takes place on the clay surface so that such tests actually

show the fraction of the clay surface that is wet by water. Provided the tests are made on fresh cores containing their natural residual oil saturations it was shown that the relative percentage surface area of fresh oilfield cores that could not be contacted with water varied from 0% (100% water wet) to 94%, with an average of about 20%, i.e. preferentially water wet. This finding is in agreement with the statement that clays are capable of adsorbing oil components without, for the most part, becoming preferentially oil-wet in the process.

The part played by the oil in the adsorption and preferential oil-wetting of fine-grained (argillaceous) material was referred to when summarizing the practical results. Johansen and Dunning (1959) demonstrated that the displacement energy of water by crude oil in a glass or quartz capillary can be approximately correlated with the presence of asphaltenes in the oils tested, i.e. the precipitation of asphaltenes from a crude oil changed its properties from water displacing to that of being displaced by water. The ability of crude oil to reduce the preferential wettability of an initially highly water-wet core saturated with brine and then flushed with crude oil has been demonstrated by Amott (1959), further indicating the importance of the oil phase in wettability studies.

Thus it would appear that a reservoir with a low specific surface area, i.e. pore surface area per unit volume of pore space, containing an asphaltic oil would tend to be preferentially oil wet, and hence to have a low irreducible water saturation, whilst a reservoir rock with a high specific surface area, e.g. a "dirty" sand containing a light paraffinic base oil would tend to show high preferentially water-wet characteristics.

From the point of view of migration, therefore, a reservoir containing highly asphaltic oil would appear to suggest limited migration from its source rock, i.e. comparatively little migration through fine-grained sediments, with the wetting properties of oil tending to oppose further lateral migration. This does not imply that all crude oils from a localized source are asphaltic since the organic material from which oils are derived will also influence the composition of an oil. Another factor which may influence the composition of a crude oil is secondary enrichment of an oil accumulation with gaseous or low molecular weight liquid hydrocarbons, which would bring about natural precipitation of asphaltenes and so alter the equilibrium of the crude oil-interstitial water-reservoir rock system. The somewhat complementary phenomena of asphalt precipitation and the adsorption of resinous and asphaltic material (Greenlee, 1960) may account for the tar

zones at oil-water contacts, e.g. Burgan Field, Kuwait, and for the tar belts often found in petroliferous basins, e.g. Eastern Venezuela.

Some light paraffinic oils, on the other hand, may reflect a fairly extensive migration history through fine-grained sediments prior to entering the reservoir, and/or through carrier beds, both types of beds being able to deplete them of their non-hydrocarbon content. A low irreducible water saturation in association with an asphaltic oil could be due either to flushing out the water originally in the reservoir at the time of migration or possibly incorporating it in the oil as a very fine water-in-oil emulsion. The latter action may account for some of the very fine, stabilized water-in-oil emulsions encountered during the production of some asphaltic crude oils.

If very fine emulsions are present in some reservoirs, their presence may have been overlooked, since during the determination of interstitial water saturation by distillation, the emulsified water would be reported as connate water. This could be important since rocks with low connate water saturation (as opposed to emulsified water) may be preferentially oil-wet, whereas the distillation results might suggest, by their erroneously high values, that the rock was preferentially water-wet. Whilst the value of interstitial water determined by distillation

would not affect reserve estimates of oil in place, since these are purely volumetric, the interpretation of a comparatively high value as implying water-wet rock could seriously affect views on the recovery factor to be used for obtaining recoverable reserves, particularly if secondary recovery by water-flooding was anticipated. The solution of this problem may be found by comparing interstitial water saturation values determined by distillation and electrical resistivity methods for rocks and prepared samples containing the usual configuration of interstitial water and similar rocks containing very fine water-in-oil emulsions, i.e. the distillation method would give volumetric water content, whilst the resistivity method would provide true connate water (contiguous saturation).

Finally it must be noted that the wetting behaviour of core samples under laboratory conditions may be somewhat different from those under reservoir conditions. Kyte et al. (1961) have observed that some reservoir core samples of intermediate wettability under surface conditions, i.e. they imbibed water only slightly, were found under reservoir conditions (both temperature and pressure) to be strongly water-wet, whilst another sample remained unaffected by the changed conditions. The reduced wetting characteristics of an oil with increasing temperature and pressure, may account in part for the decrease in specific

gravity of oils with increasing depth in some regions, since "young", shallow, asphaltic oils initially retained by their preferential oil-wetting properties, might be more easily displaced with the changed conditions, and possibly lose part of their non-hydrocarbon content during the lateral migration or readjustment which would now be more likely to occur.

Relationship of Crude Oil, Water and Fine-grained Mineral Matter in Fluid Systems.

Fluid systems, used in this context, imply that either water or oil is the continuous phase, the other two being in the dispersed state. Such systems may be roughly divided into the following groups:

Table XXIX

Continuous Phase	Disperse Phase		
	Major	Minor	Examples
Water	Oil	Clay	Oil-in-water emulsion drilling muds.
Water	Clay	Oil	Oil seeping into mud laden waters. Oil entrained in water-base muds during the drilling of oil zones.
Oil	Water	Clay	Water-in-oil emulsion drilling muds. Produced water-in-oil emulsions.
Oil	Clay	Water	Certain oil seeps and Pitch deposits.

There are no fixed boundaries with regard to the major and minor disperse phases, the relative proportions of all three phases being controlled by their physical and chemical properties and the physical or mechanical forces applied to the system as a whole. Some of the examples mentioned have

their properties controlled by additives (e.g. emulsifying agents) which change the relationship of the three phases from that which would exist if the additive were not present, e.g. oil-in-water and water-in-oil drilling muds. In order not to complicate matters further, such controlled systems will be excluded from the discussion, which will be confined to naturally-occurring systems only.

The maximum amount of crude oil that can be complexed with a wet clay in water will depend on the type of oil, the properties of the clay, the degree of dispersion of the oil and clay in water, and the oil-clay ratio. Thus Poirier and Thiel (1941) showed that for a given crude oil, china clay is twice as effective as montmorillonite in causing oil settling; and, furthermore, that for a given clay and oil, the greater the degree of dispersion of clay and oil, the greater the weight of oil that can be sedimented. Basically the quantities involved in this type of relationship, whether the oil is sedimented by clay or the clay floated by the oil, will depend entirely upon the relative concentrations of the clay and oil phases and their respective interfacial properties.

Thus in the case of oil seeping into flowing water with fine-grained mineral matter in dispersion, the oil will gradually become finely dispersed by mechanical forces and adsorbed on the surfaces of the wet clay. If the action

of the stream ceases shortly after contact with the oil, i.e. if it flows into a large body of still fresh water such as a lake, then a part of the clay-oil-water complex will float to the surface, whilst the bulk will be sedimented. On the other hand, if the stream continues its course for a reasonable distance after contact with the oil seep, then the oil will be highly dispersed and sedimented even if flow subsequently ceases, assuming, of course that there is enough suspended sediment in the stream in the first place. Similarly if the stream becomes intermixed with brackish or salt water, the caly-oil complexes will flocculate and sediment. A small amount of oil entering a stream will quickly be dispersed and sedimented, whilst a larger volume will travel a greater distance before final removal of the oil takes place. The distance required for dispersion and sedimentation will vary for the oil-type and the principal clay mineral present in the mineral matter carried along by the stream. Thus an asphaltic oil will quickly be dispersed and sedimented by a stream carrying principally kaolinite, whilst a paraffinic oil in bentonitic argillaceous material will require a longer period. Because of its greater density the sedimentation of asphaltic oil may be easier than for paraffinic oil. Poirier and Thiel found that up to 2.5 cc. per gram of an oil could be sedimented by china clay, 1.35 cc. per gram by bentonite

and 1.12 cc. per gram by calcareous silt. Thus in some cases, hydrocarbons extracted from recent and ancient fine-grained sediments adjacent to petroliferous areas may result from sedimentation of oil from seepages rather than be derived from degraded organic matter present in the sediment.

The entrapment in water-base drilling muds of crude oil released during the drilling of oil zones is analogous to the sedimentation of oil by streams. The oil released will be quickly dispersed due to the turbulence associated with the flow of drilling mud around the bit, and unless it is flowing into the hole at a considerable rate it will quickly be emulsified in the drilling mud. Gas in solution in the oil tends to oppose emulsification, allowing an oil "slick" to form when the mud reaches the surface and is allowed to stand.

Any oil extracted from sediment-laden streams, or from drilling muds, will have slightly different properties from that entering the system due to the selective adsorption of some of its heavier hydrocarbon and non-hydrocarbon components by the wet clays. The extraction of oil by hydrocarbon solvents, e.g. benzene, after emulsification in water-base muds also fails to release all the components present in the oil prior to emulsification, i.e. selective adsorption takes place, as was demonstrated by Zierfuss and Coumou (1956). These workers found that the greater the

amount of oil dispersed in a mud, the greater was the amount that could be extracted as a percentage of the original quantity added, but, as noted before for adsorption and desorption, the amount remaining dispersed (adsorbed) in the mud, in terms of actual weight, increased. They also found that the heavier oil components were the most highly adsorbed, which is in agreement with the present results.

Zierfuss and Coumou also noted that carboxymethylcellulose (CMC), a typical mud additive, reduced the selective adsorption of the oil components by drilling mud clays (bentonites), apparently because it was more strongly adsorbed the the oil components. From the work of Reisberg and Doscher (1957) it would also appear that a reduction of oil adsorption would occur in highly alkaline muds as compared with neutral or slightly alkaline varieties. It is interesting to note in this context that Bobek et al. (1958), investigating the influence of drilling mud filtrates on rock wettability, found that separate solutions containing CMC, lime, and bentonite, flushed through a sandstone core, could change its wettability from preferentially oil-wet to preferentially water-wet.

Small amounts of fine-grained argillaceous material have been observed in crude oils (Witherspoon, 1958), and these will undoubtedly aid the stabilization of water-in-oil emulsions, since in spite of their intimate contact with

oil, it is doubtful if their contact angle with water is zero. It would appear that kaolinite and illite would be the best clay minerals for stabilizing water-in-oil emulsions, because they become preferentially oil-wet more readily than montmorillonite, particularly if the latter has sodium as its exchangeable cation.

Conclusions.

This study had definitely established that there are interactions between crude oil, water, and fine-grained mineral matter. The extent of the interaction between the three phases has been shown to be dependent on the properties of the fine-grained mineral matter and the crude oil in neutral aqueous systems. It has also been shown that an adsorption process is the dominant feature in the interaction between the three phases. The oil components adsorbed by water-wet clays consist principally of porphyrins, and non-hydrocarbons containing carbonyl functional groups. Furthermore, the degree of adsorption of these components and their ability to change the interfacial forces of a given system were found to be dependent on the natural hydration properties of the fine-grained mineral matter, the polar non-hydrocarbon content of the crude oil, and the relative quantities of these two phases at the time of mixing. Similarly the initial liquid contacting dry fine-grained materials, i.e. oil or water, has a significant

effect on subsequent interactions in the system. For a given weight of clay (dry weight) the quantity of oil components adsorbed, i.e. the specific adsorption capacity, was found to increase as the initial adsorbed water content decreased, analogous to clays with different natural hydration properties. Using a topped paraffinic oil from Ecuador, it was found that up to 10% by weight of the oil components present in an oil could be selectively adsorbed if contacted with sufficient damp or wet fine-grained mineral matter. Two distinct adsorption processes appear to account for this phenomenon:

1) The very strong adsorption by the wet mineral matter, probably chemisorption, of approximately 2% of the components of the oil tested, which apparently causes the displacement of adsorbed water from the surface of the fine-grained mineral matter.

2) The physical adsorption and film formation of up to 8% of the oil components at the oil-adsorbed water interface which is probably promoted or enhanced by the reduction of adsorbed water achieved by the initial "chemisorption" process.

The weight of oil components adsorbed from standard oil-in-heptane solutions by damp Fuller's Earth and Gault clay varied from 8 mgm. per gram of clay for a clay-oil

ratio of 7.35 to 0.4 mgm. per gram for a clay-oil ratio of 235. For two water-saturated Fuller's Earth samples, the weight of oil components adsorbed was 0.26 mgm. per gram and 0.19 mgm. per gram for clay-oil ratios of 235 and 470, respectively.

Finally, it is apparent that simple capillary forces are not the only reason for crude oil retention by water-wetted fine-grained mineral matter, since crude oil itself is capable of altering the interfacial forces in an initially water-wet system by the selective adsorption of oil components. The consequence of this adsorption process is that the movement of crude oils through fine-grained mineral matter will, in many instances, appreciably alter the composition of the oil without necessarily affecting the surface properties of the solid matter very drastically. It also appears that the complexes formed by the interaction of dispersed crude oil with fine-grained mineral matter in neutral aqueous systems will cease to exist only if changes in the interfacial forces are brought about via changes in the physico-chemical properties of the aqueous phase, and/or via the introduction of other components into the system.

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