A UNIQUE GEOPHYSICAL PHENOMENON, TRINIDAD ASPHALT, INTERESTING FROM THE POINT OF VIEW OF DISPERSOID CHEMISTRY

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The asphalt, found in a deposit of many millions of tons in the crater of an old mud spring or geyser in the Island of Trinidad, B. W. I., is a unique geophysical phenomenon and one which must be interpreted by the principles of dispersoid or colloidal chemistry. Over an area of more than a hundred acres and to a depth of more than 135 feet the asphalt exists in this crater as an astonishingly uniform material. It is in process of formation at the present time. It consists of a complex system of several phases, gaseous, liquid and solid, organic and inorganic, more or less in equilibrium, displaying colloidal properties of industrial as well as scientific interest. The asphalt owes its origin to certain geological conditions existing side by side in that locality. Oil sands occur at different depths, which contain vast quantities of petroleum as has been demonstrated by the many wells which have been successfully sunk, a petroleum of unique character, differing from any previously known, and of a highly asphaltic nature. Rising toward the surface along some line of least resistance the petroleum meets the paste of fine silica and clay which forms the mud of the spring. With this the oil becomes emulsified, probably by the action of the natural gas which accompanies it at very high pressure. In the lapse of time the entire crater of the spring has been filled with the resulting material and it has overflowed the rim, running down the slopes to the sea. Fresh material is in process of formation today and issues at several points on the surface of the deposit of a consistency so soft that it can be readily moulded into balls with the hands, without adhering to them, owing to the free water with which it is associated. This so-called "soft pitch" is also accompanied with natural gas of unusual com-

position, containing in addition to the hydrocarbons usually found in such gas, carbon dioxide and hydrogen sulphide, in some localities in the neighborhood of the deposit, as much as 33 percent of the former and 3.5 percent of the latter. At the same time the soft pitch itself is evolving gas, either the result of the release of pressure or of a reaction going on between the bitumen and the mineral matter it contains, this gas consisting largely of hydrogen sulphide and carbon dioxide, probably the latter cause, as it continues for years after the material has been exposed to the air, while if the soft asphalt is sealed up in a tin can the latter will explode in the course of time from the gas pressure developed.

The main mass or older form of the asphalt in the crater is sufficiently hard to make it possible to flake it out in large pieces of from 50 to 100 pounds in weight. In this form it resembles an exaggerated Swiss cheese owing to the gas cavities it contains. While brittle enough for this, an excavation of some depth at any point is filled up and obliterated in twenty-four hours by the flow of asphalt from the adjoining material. Large masses of the asphalt taken from the deposit and kept in storage, without lateral support, present all the features of the glacial flow of ice.

The asphalt, therefore, originating in a soft condition, as demonstrated by the fresh material, which is constantly being formed and which emerges near the center of the deposit, becomes hard in the course of a year or two. The cause of this and of the evolution of the gas which is observed may be attributed to the presence of a catalyzer. As will be shown, the asphalt contains clay in a highly dispersed condition, carrying adsorbed ferrous sulphate, which may play such a rôle.

As long ago as 1891 and again in 1895, the writer made a personal inspection of the deposit and collected specimens of the asphalt at various points on the surface and to a depth of 135 feet, the latter with the aid of a wash drill. In connection with this operation it was found that the mass of asphalt was in a constant state of motion owing to the evolution of

gas, as evidence of which the drill was tilted to such an angle that the boring could not be continued beyond the depth reached. The same fact was also demonstrated by driving a line of wooden plugs in the surface of the deposit and noticing their displacement in the course of time.

It was found from an examination of the specimens representing the material as it exists in different parts of the deposits, that it contains everywhere 29 percent of water, which proves to be of thermal origin and of remarkable character, in that there was found to be present in solution, on evaporation of some of it obtained in the early methods of drying and refining the material, about 20 grams of different salts per liter, and that these were of a somewhat surprising character. Although the principal salts are chlorides and sulphates of soda, there is also present ferrous sulphate in sufficient amount to give the water a strong acid reaction, together with sulphate of ammonia and small percentages of iodides and borates. Attempts to separate this water from the crude asphalt, by the use of solvents for the bitumen, were not successful, as it was found to be closely held by the clay and mineral matter of the material. It does not rise to the surface of the solvent. The sample examined was, therefore, obtained from refining stills in which the material was heated and melted and is, in consequence, somewhat altered and concentrated by the conditions to which it has been subjected. It is a notable fact, however, that on pulverizing the crude asphalt and exposing it to the air for some hours, all the water is lost which does not exist as water of hydration of the clay.

The specimens thus dried at their source were examined in the United States, with results, averages of which are given in the accompanying table.

The method of examination consisted in extracting the bitumen with carbon disulphide and ignition of the residue for the determination of mineral matter. By this method of analysis it was found that over 9 percent of material remained undetermined. For some years this was looked upon as being organic matter not soluble in carbon disulphide, but further

AVERAGE COMPOSITION OF TRINIDAD LAKE PITCH IN CIRCLES

	Bitumen by CS ₂ percent	Mineral matter percent	Undeter- mined percent
Circle 2, 200 ft. from center	55.02	35.41	9.57
Circle 4, 400 ft. from center	54.99	35.40	9.61
Circle 6, 600 ft. from center	54.84	35.49	9.67
Circle 8, 800 ft. from center	54.66	35.56	9.78
Circle 10, 1000 ft. from center	54.78	35.44	9.78
Circle 12, 1100 ft. from center	54.62	35.45	9.93
General average	54.92	35.46	9.72
Circle 14, 1400 ft. from center	53.86	36.38	9.76

researches showed that it is, in fact, water of hydration of the clay, a small percentage of bitumen absorbed by the latter and not removed by carbon disulphide, and of volatile salts lost on ignition. This has been discussed in a paper entitled "The Proximate Composition and Physical Structure of Trinidad Asphalt," presented before the American Society for Testing Materials and appearing in the proceedings of the Society, Vol. 6, 509 (1908).

The results of the preceding analyses show plainly the fact that the enormous mass, many millions of tons, of the crude asphalt found in the deposit, is of astonishingly uniform composition, and that the conditions under which it was and is being formed involve a certain equilibrium between the components which the writer will not attempt, as yet, to explain.

The proximate composition of the crude material is as follows:

	Crude Trinidad asphalt
Water and gas	29.0
Bitumen soluble in cold carbon disulphide	39.0
Bitumen adsorbed and retained by the disperse mineral matter	0.3
Mineral matter on ignition with tricalcium phosphate	27.2
Water of hydration of clay	4.2

The character of the gas and the water in the crude asphalt has already been mentioned. The mineral matter obtained on ignition consists of impalpably fine silica, clay, and the residue of the salts contained in the water which are not volatile. The silica exists as sharp transparent flakes having all the appearance, under the microscope, of having existed in solution in water under pressure, on releasing which it has separated in its present form, as suggested by Dr. Carl Barus. The particles of silica are much larger, naturally, than those of the clay, but the largest are no greater than 0.26 mm in diameter. By treatment of the mineral matter obtained on ignition with strong hydrochloric acid, it can be obtained in a perfectly white condition, the iron readily going into solution, probably, being largely derived from the ferrous sulphate existing in the water. The insoluble portion amounts to 85 percent.

In the study of the asphalt efforts were made for many years to prepare from it, by means of solvents, a bitumen free from mineral matter. None of these was successful, a certain amount of it remaining in a solution made with any solvent which completely dissolved the bitumen. At the same time this was not to be detected under the ordinary microscope. An explanation was not discovered until recently, when it was found, on examining a solution of the crude asphalt or of the dried material in pure carbon disulphide, which had been allowed to settle for some weeks or months, and even when it had been centrifuged for some hours, that it contained mineral matter to the extent of 2 percent or more, which, with the aid of the ultra-microscope, was revealed as particles in the high state of motion, characteristic of highly dispersed solids. This accounts for the fact that they could not be removed by ordinary filtration or by centrifugal force, nor could they be entirely removed by passing once through a Chamberland filter. By repeated use of such a filter, the colloidal material becomes agglomerated and clogs the pores to such an extent that it forms an ultra filter and can be collected. It has been found to consist largely of bitumen

adsorbed by clay and other mineral matter existing in the highly dispersed condition in which it occurs. On ignition of this material the residue amounted to 20.5 percent, which, of course, owing to the loss of water of hydration of the clay and the volatile inorganic matter, is much smaller than the actual amount of hydrated mineral matter present. This figure is evidence of the peculiarly high adsorptive power of the disperse solid colloids and, probably, also of a selective adsorption, as will appear later.

If the disperse material immediately after filtration is treated with carbon disulphide it is again dispersed as a sol, which may, therefore, be denominated a bitusol.

If while still adhering to the Chamberland filter it is further washed with disulphide removing some of the bitumen, it no longer becomes a sol on taking up with the disulphide, showing that the bitumen has acted as a protective colloid.

If light naphtha is used as a solvent all the bitumen of the asphalt is not dissolved, that is to say, this is not a universal solvent for all classes of bitumen. With a naphtha of 88° B. density, only 57 percent of the entire bitumen in the air-dried crude asphalt goes into solution, and the solution differs from one made with carbon disulphide in that it carries no disperse solids, showing that the bitumen soluble in naphtha is not adsorbed by the disperse solids in the same manner as that soluble in carbon disulphide alone.

The crude asphalt appears from the preceding observations to consist of a suspension of relatively large size mineral particles in an extremely viscous medium, together with highly dispersed mineral matter in colloid form, intimately mixed with an emulsion of a thermal water with the bitumen present.

If the dried or refined material is treated with a solvent and attempts made to remove the mineral matter, as in the case of the asphalt from the deposit still containing water, the same results are obtained as far as the presence of disperse solids is concerned, showing that its colloidal character is not essentially changed by the heat treatment.

It is of interest to observe that, as an indication of the

amount of colloidal material present in the asphalt, the mineral matter obtained on ignition of the bitumen present in the carbon disulphide solution amounted in the case of the crude material to 8.02 percent after one week's subsidence. After further sedimentation, probably by agglomeration, it fell to 3.4 percent in three months. This shows that a large amount of disperse colloid material is present in the original undried asphalt. In the refined or dried material the original percentage was 4.5 percent after one month's sedimentation, and the changes which were found to go on in the course of time were as follows:

1 month	4.5 percent
2 months	3.0 "
3 "	2.57 "
4 "	2.67 "
5 "	2.74 "
6 "	2.75 "

It appeared to be of interest to determine whether a system such as that found in nature in the case of Trinidad asphalt, could be prepared synthetically with the purer forms of bitumen. For this purpose a crude Bermudez asphalt, which is practically free from mineral matter, was softened at a temperature below that of boiling water and a paste of colloidal clay and water intimately emulsified with it, something which can be done with great readiness.

When this emulsion was treated with carbon disulphide and allowed to settle, treating it in the same way as the crude Trinidad asphalt, it presented under the ultra-microscope the same appearance, the bitumen carrying disperse solid colloids which it had taken from the water, probably due to the greater capacity of the colloidal clay for adsorption of bitumen than of water. When a similar emulsion was made with a very dense asphaltic oil of 0.994 specific gravity, liquid enough to flow at ordinary temperatures, much less of the colloid matter was taken from the water by the bitumen, showing the selective adsorption exercised by the disperse clay.

When the water was removed from the Bermudez emulsion, which has been described, in the same manner as is practiced in refining the crude Trinidad asphalt, a material was obtained containing clay and corresponding to refined Trinidad asphalt. On dissolving in carbon disulphide and centrifuging for one hour, the presence of disperse solid colloids were evident under the ultra-microscope and, on ignition, a residue of clay, 0.67 percent of the bitumen, was recovered, as compared to 2.08 percent in the case of the refined Trinidad asphalt. The difference may be attributed either to the fact that the clay in use in making the synthetical Bermudez product was not as highly colloidal as that associated with the Trinidad bitumen, or to the fact that the bitumen of the Trinidad asphalt is one which is adsorbed more readily and acts as a better protective colloid than that of the Bermudez material or the oils. With the liquid asphaltic bitumen the amount of colloidal clay which was taken up was only sufficient to give a residue of 0.17 percent on representing the clay present as a bitusol.

In addition to the scientific interest in the presence of solid disperse matter to such an extent in the Trinidad Lake asphalt, it is of great importance from an industrial point of view, since the presence of such a large amount of material in a suspensoid and dispersoid state adds enormously to the surface energy developed by the material, and this has been shown to be of great importance in the construction of asphalt surfaces. At the same time the great powers of adsorption of the disperse solid colloids present contribute an additional feature of value. Such an asphalt presents greater viscosity, smaller ductility and susceptibility to temperature changes than bitumens in which disperse solids are not naturally present, and the lack of which is made up in practice by the addition of an ordinary mineral dust which cannot present the same surface area as that provided by the highly dispersed colloids which are contained in Trinidad asphalt.

From the data presented it appears that in Trinidad asphalt we have a unique geophysical phenomenon and one

which it will be of interest to study further for the purpose of explaining its origin and constitution.

In conclusion the writer desires to thank Dr. Philip Schneeberger, who has aided him efficiently in the more recent laboratory work, which has supplied the data contained in this paper.

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