

# COLLOIDAL GRAPHITE. ITS PREPARATION, PROPERTIES, and DIVERSIFIED USES *in* INDUSTRY

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*A comprehensive survey of colloidal graphite as known to modern industry, in which its development is traced from its earliest conception by E. G. Acheson. How the Biblical story of the use of straw in brick making bears directly on the birth of this unique material is explained. A brief description of the nature of colloids and the laws which they obey, precedes a detailed discussion of the modern industrial uses of colloidal graphite. X-ray and electron diffraction procedures are also discussed. How these new tools of science explain some hitherto little-understood phases of graphite lubrication is revealed. The article is concluded with a survey of the uses of colloidal graphite in applied electronics and experimental biology.*



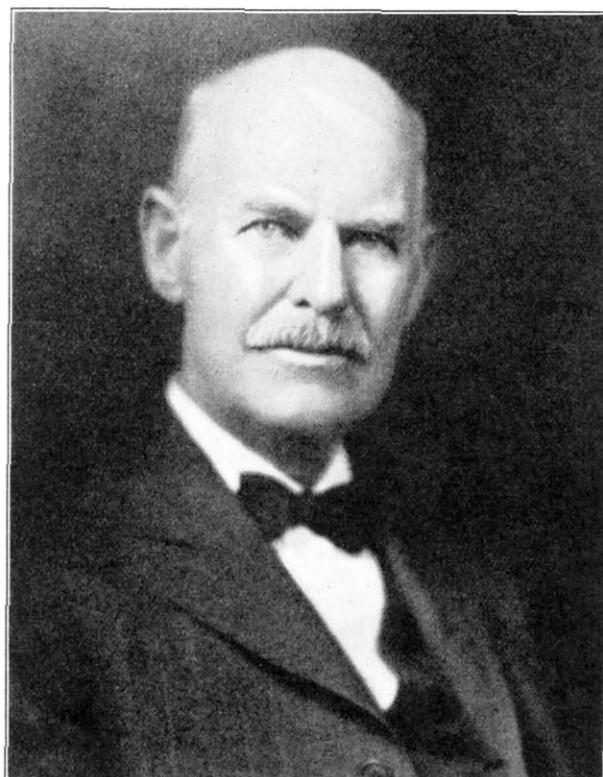
## HISTORICAL

AS AN outgrowth of his work on silicon carbide ("Carborundum"), Edward Goodrich Acheson, in 1896, invented the first successful process for the commercial manufacture of artificial<sup>1</sup> graphite. He discovered that any form of amorphous carbon, when placed in an electric furnace and subjected to a temperature of approximately 3000°C., was converted into the graphite allotrope. Graphite, so produced, could, dependent upon the raw material employed, be obtained in a state of almost perfect purity.

Although most of his early production was in the form of rods and plates for electrode use, Acheson was of the firm belief that his graphite, because of its high degree of purity, could, despite its somewhat higher cost, compete with the natural varieties being mined extensively in Ceylon, Madagascar, Mexico, and domestically in the State of New York.

The greatest outlet for mined graphite, during that period, was the crucible trade. The manufacture of steel had already become a flourishing industry and the demand which it created for crucibles of sturdy construction had reached considerable proportions. Acheson, fully aware of the requirements for an article of

this type, directed his attention to a search for a suitable bonding material for his graphite. After conducting a series of unsuccessful tests with American clays, he learned that those engaged in crucible manufacture were employing, as binders, clays imported



*Underwood and Underwood*  
EDWARD GOODRICH ACHESON (1856-1931)

Discoverer of "Carborundum"; the first to produce synthetic graphite commercially and the originator of colloidal graphite.

from Germany. These, because of their high degree of plasticity and greater tensile strength, were far superior to domestic earths.

This difference in performance aroused Acheson's curiosity, and created within him a desire to learn

<sup>1</sup> Artificial in the same sense that manufactured ice is artificial.

why two clays of similar chemical composition should vary so widely in physical properties. In the course of his study, he found that the German clays were, for the most part, of sedimentary origin, while the domestic varieties with which he had worked were residual. He concluded that whatever change the more plastic sedimentary clays underwent probably occurred while they were being carried from their original beds to the point where they were ultimately deposited. Working on the theory that the vegetable matter contained in the water effecting the transfer might be responsible, Acheson proceeded to carry the problem to his laboratory. Here he started a new line of research which embodied the treatment of kaolin with aqueous solutions of numerous organic compounds, trying in the course of his work such materials as phenol, creosote, gallo-tannic acid, catechu, and extracts of straw. While the majority of his tests yielded negative results. Acheson was encouraged by the trials made with gallo-tannic acid, catechu, and straw. He found, for example, that clay, when pugged with tannin-like bodies, produced a plastic mass which could be molded with a minimum amount of water to produce a dried clod that possessed greater hardness and a higher tensile strength than it was hitherto possible to obtain with the American earths that had been brought to his attention.

The effect of vegetable matter on clay was truly astonishing and led Acheson to make an extensive search of the literature to determine whether any investigators had reported a similar observation. It should be remembered that Acheson was a stranger to the art of clay working, which fact proved valuable in that he was not influenced by the efforts of others. After a lengthy study of the literature on ceramics failed to yield the information he sought, Acheson recalled the Biblical story dealing with the brick-making exploits of the Egyptians as set forth in the fifth chapter of Exodus. Acheson's thoughts in this connection follow.

"The accepted theory of using the straw fibre as a binding agent for the clay had never appealed to me, and it now seemed likely that those ancient people were familiar with the effect I had discovered. I procured some oat straw, boiled it in water, decanted the resultant reddish brown liquid, and mixed it with clay. The result was like that produced with gallo-tannic acid, and equal to the best I had obtained. This explained why the straw was used, and why the Children of Israel were successful in substituting stubble for straw, a course that would hardly be possible were the fibre of the straw depended upon as a bond for the clay, but quite feasible where the extract of the plant was used."

In view of this reasoning Acheson concluded that "Egyptianized Clay" would be a fitting name for straw-treated earths.

This new discovery, despite its seeming importance, proved to be of little immediate value. It was found, in the course of subsequent work, that electric furnace graphite was too pure and lacked the physical structure required to render it suitable for crucible fabrication. Furthermore, when Acheson endeavored to utilize the

"Egyptianized" product in the making of ceramic ware, shrinkage of articles produced with it was greater than the industry would tolerate. Also, cracking could not be overcome, with the result that the process failed to gain commercial recognition.

What Acheson had actually accomplished in the treatment of his clay, was to effect a reduction in particle size to a point where much of the material was rendered colloidal. Today it is a well-known fact that a clay with an excessively large amount of fine particles becomes sticky and difficult to work. It is also an accepted fact that fineness or grain is important only to the point where it does not unduly affect other important properties, such as drying conduct, drying shrinkage, warping, tensile or transverse strength, and bonding strength. It is quite possible that Acheson could have overcome the shortcomings of his product had he mixed his clays with coarser material.

The unctuousness of natural graphite had long made it useful as a solid lubricant, either alone or when incorporated with grease. It was especially advantageous for applications where heavy pressures and high temperatures were factors with which one had to contend. Natural graphite, unfortunately, was usually found to be contaminated with abrasive, silicious bodies which made impossible its use in anything but what might be termed coarse mechanisms. Even though refinement methods have steadily improved, it has been practically impossible to produce a final product devoid of objectionable impurities because of the similarity in specific gravity of graphite and the foreign bodies with which it is associated in nature. Acheson's electric-furnace graphite, on the other hand, could be produced, as cited above, in a remarkable state of purity. This advantage, coupled with its unctuousness, made it outstanding for lubrication purposes. Knowing that graphited greases possessed certain advantages over plain greases, he felt a similar beneficial effect would be had in the case of oil lubrication if petroleum bodies could be made to carry graphite in suspension. Powdered graphite, however, whether natural or artificial, with its specific gravity of approximately 2.25 could not, of course, be kept in suspension in mineral oils without constant agitation. It was only when Acheson recalled his early work with clay and its colloidalization—or deflocculation, as he termed it—with vegetable extracts that an achievement of this kind seemed possible.

In 1906 when Acheson duplicated his experiments, using electric-furnace graphite instead of clay, he found that nutgalls, tea leaves, sumac, hemlock bark, oak bark, and similar tannin-rich bodies deflocculated or colloidalized graphite parallel with the manner in which straw extract effected a reduction in the particle size of clay. Although this process yielded stable suspensions of graphite in water (1), Acheson soon learned how to produce equally stable dispersions in mineral oil (2). This work ultimately led to the commercial manufacture of the products marketed under the trademarks "Aquadag" and "Oildag."

## CONCERNING COLLOIDS

The term colloid was originally applied to substances that were jelly-like in form, typified by such things as glue, gelatin, and albumen. This designation, however, was eventually broadened and now includes all matter, regardless of phase, so long as the size of the unit particle is within the arbitrary range of 1-500 millimicrons. The division between the colloidal and non-colloidal realm, however, cannot be clean-cut. Bartell (3) very aptly treats of this point in the introduction of his laboratory manual when he says,

"There does exist a difference of opinion as to the exact limits of magnitude which should be assigned to the individual units, but this difference is not of particular importance, inasmuch as there is no sharp line of demarcation between colloid state and true solution on one hand, nor between colloid state and suspensions on the other. The colloid range which might be assigned to a given material would very probably differ from that which might be assigned to some other type of material of different density or different degree of hydration or with other differences in physical properties."

In the broadest sense one might look upon colloids as "that form of matter which is in the 'twilight zone' between coarse suspensions and substances in true solution."

Colloids are not only characterized by fine particle size but possess other properties peculiar to matter in this state. When a substance is rendered colloidal, the particles acquire an electric charge. Whether this charge is positive or negative<sup>2</sup> depends upon the nature of the material and the relationship of its dielectric constant to that of the medium in which it is dispersed. Probably the outstanding characteristic of a colloidal substance is its ability to remain suspended for indefinite periods, regardless of its density. In liquid systems this apparent disregard of the law of gravity is due to the charge on the particles—since bodies charged alike repel each other—and the fact that the minute masses are constantly being bombarded by molecules of the carrier. This phenomenon, known as Brownian Movement, is visible under the ultramicroscope. When a colloidal solution is contaminated with an electrolyte, the electric charge on the particles is neutralized, resulting in coagulation and ultimate precipitation. Similarly, when a colloid is mixed with a second colloid carrying a charge of opposite sign, co-precipitation takes place.

Colloids may be divided into two large classes, the lyophilic which evidence great affinity for their carrier, and the lyophobic which are literally carrier-fearing. A lyophilic colloid is said to be reversible, or capable of being resuspended. The lyophobic or irreversible colloids lose their colloidal properties once they have been freed of their carrier. Common lyophilic colloids are gum, glue, gelatin, albumin, agar-agar, and so forth. Lyophobic materials are chiefly inorganic

<sup>2</sup> A charged particle, like an ion, is capable of migrating to an electrode charged oppositely (Electrophoresis). It is thus possible to determine whether the particle charge is positive or negative.

bodies, such as the elements, and inorganic compounds thereof. Since an irreversible colloid lacks the stability possessed by the reversible variety, it is usually necessary to add a protective agent in the form of a lyophilic body. The adsorption of the lyophilic material by the lyophobic alters the surface properties of the latter and exerts other influences which make for greater resistance to the forces responsible for coagulation.

Because of the minuteness of particles composing colloidal materials, they have a large surface area for their mass, causing them to exhibit marked surface energy. It is this property which explains the readiness with which most colloidal materials are adsorbed.

## PREPARATION OF COLLOIDAL GRAPHITE

Colloids of the lyophobic type may be prepared by chemical, mechanical, electrical, or electrochemical means. The method to be chosen depends upon the material to be processed. In the case of simple inorganic compounds, one can resort to oxidation, reduction, hydrolysis, and even simple metathetical reactions. In some instances it may be advantageous to effect diffusion by electrochemical procedures. Where substances do not react readily, or otherwise do not lend themselves to oxidation or reduction, it may be necessary to employ electrical disintegration methods through the agency of a direct current arc. In such cases, where the physical structure of a solid permits, colloidalization may be brought about by mechanical disintegration.

Graphite, being a lamellar material and at the same time quite inert chemically, is usually rendered colloidal by mechanical subdivision. The process of Acheson, already described, is a mechanical one. Plauson (4) resorts to a "colloid" mill or high-speed mechanical disintegrator, using as protectors such compounds as fatty acids, esters, ethers, or ketones of high molecular weight. It is claimed that good suspensions are obtained with this device. If the graphite is subjected to a very prolonged treatment, a colloid is alleged to result.

Ducas (5) forms dispersions of graphite in oil by crushing the latter in the presence of what he terms "natural colloids," particularly petroleum bodies rich in tar. To stabilize aqueous suspensions he uses certain gums and tannates.

Pigache (6) claims to achieve a satisfactory result by subjecting graphite to attrition in the presence of gelatine.

All of these processes are basically not unlike Acheson's original method, the novelty appearing to lie in the technic followed and the lyophilic protective bodies chosen.

Karplus (7) has devised a chemical method of colloidalizing graphite which is based upon Brodie's (8) process of converting graphite into graphitic acid. When graphite is acted upon by strong oxidizing agents, such as a mixture of potassium chlorate and concen-

trated nitric acid at a temperature of 60°C. for several days, there is formed a yellow crystalline solid, referred to as graphitic acid.

When this is subjected to gentle heat, it decomposes with almost explosive violence to what has been termed pyrographitic oxide—a black amorphous residue which bears strong physical resemblance to graphite. The exact composition of this material has been disputed, but Spence (9) considers it to be pure graphite ("Brodie's Graphite"). Karplus claims that by altering both the oxidizing agents and the temperatures at which the reaction is carried on, he is able to bring about physical disruption of graphite crystals without the attendant formation of graphitic acid. This investigator, who employs natural graphite in his process, may be obtaining an effect with his oxidizing mixture

Although graphite is carbon chemically, its properties differ widely from those of amorphous carbon and the diamond. It is an unusually soft material, having a hardness on Moh's scale of between 0.5 and 1.0. The specific gravity of graphite varies somewhat with its source, falling between 2.1 and 2.4. In addition to being highly unctuous, it has a low coefficient of expansion; is a good conductor of heat and electricity; is radio-inactive and highly resistant to electron bombardment.

Chemically, graphite is quite inert, being incombustible at temperatures below 660°C. It is unaffected by the free halogens and shows no tendency to dissolve in acids and alkalies, regardless of concentration.<sup>4</sup> All of these properties, of course, are retained when the material is colloidalized.

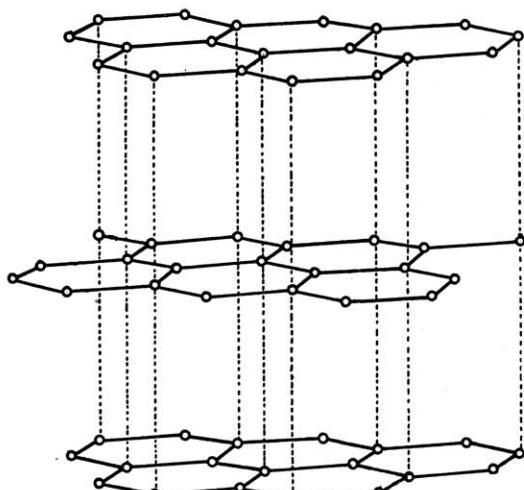


FIGURE 1.—THE ARRANGEMENT OF CARBON ATOMS IN GRAPHITE CRYSTALS AS DEDUCED FROM X-RAY DIFFRACTION EXPERIMENTS

somewhat like that noticed when certain varieties of graphite are moistened with fuming nitric acid. A swelling of the crystals results, forming so-called "graphite worms."<sup>3</sup> It is believed that the capillary structure of natural graphite permits the absorption of the acid. When heated the gases which result from the decomposition of the acid break down the lamellar structure of the graphite to form extremely fine dust (10). Karplus' process, of course, like most that deal with the preparation of colloids, is a wet one throughout.

#### PROPERTIES OF GRAPHITE

Both the mined and manufactured varieties of graphite possess important properties which make this allotropic form of carbon valuable for many diversified uses in industry.

<sup>3</sup> Electric-furnace graphite, unlike the natural product, does not display intumescence when treated with nitric acid.

#### PRACTICAL APPLICATIONS OF GRAPHITE: LUBRICATION

Because of the greasy feel possessed by graphite, its suitability as a dry lubricant has long been recognized. Being a solid which is highly resistant to oxidation and, at the same time, chemically stable under conditions that are destructive to fluid lubricants, graphite is of considerable value as a friction reducer in many industrial applications. This is especially the case where high temperatures are involved; where fluid lubricants are absorbed, as in the case of wood bearings and shafts; and in looms used for the production of laces and textiles where the fabrics being woven are liable to stain from oils and greases.

Carefully machined parts, even though seemingly smooth, reveal, under the microscope, surfaces made up of a multitude of projections and depressions. It is this roughness of the rubbing surfaces that is mainly responsible for friction and wear. If the depressions are filled in or the projections leveled, the coefficient of friction<sup>5</sup> is reduced.

Dry graphite, in dust form, when injected between bearings and shafts acts to some extent as a smoothing and polishing agent. When abrasion takes place between unpolished surfaces there is a tendency for the projections of one rubbing member to shear off the peaks of the opposing member. However, when abrasion occurs between parts lubricated with graphite, the particles of the latter, which are weak in cohesive properties, suffer rupture rather than the strongly coherent metallic faces.

Adam (12) clearly explains the mechanics of dry graphite lubrication in terms of the structure of the graphite crystal. (See Figure 1.) He says,

<sup>4</sup> Graphite is oxidized to a slight degree to CO, CO<sub>2</sub>, and graphitic acid by KClO<sub>3</sub> plus HNO<sub>3</sub>, CrO<sub>3</sub> plus H<sub>2</sub>SO<sub>4</sub>, and KMnO<sub>4</sub> plus H<sub>2</sub>SO<sub>4</sub>. In each case, however, it is the oxidizing agent rather than the acid that is responsible for the conversion.

<sup>5</sup> Archbutt and Deeley (11) describe the coefficient of friction as "that value which when multiplied by the pressure normal to the surface in contact gives the measure of the maximum frictional resistance to motion." For example, if a slider weighing 2240 lbs. requires a force of 350 lbs. to put it into motion, the coefficient of friction is 0.156, *i.e.*,  $\frac{350}{2240} = 0.156$ .

"Graphite consists of plane sheets of carbon atoms, of indefinite and large extent, exceedingly tightly linked together in the sheets; each sheet is, however, rather loosely attached to the next sheet parallel to it, and sliding or separation can easily take place. It is known, from studies of electron diffraction, that graphite is easily attached to metal surfaces, these sheets being parallel to the surface; the sheets afford protection against seizure between the metals. When real contact occurs, it will be between the outside of the sheets of graphite and not between the metals. When separation occurs, graphite is the weakest link in the bridge, and breakage occurs in the graphite and not in the metal."

The electron diffraction studies to which Adam alludes have been carried on by several investigators, particularly Finch and his co-workers (13).

When a single beam of electrons is made to impinge upon a surface it is deflected into a series of beams, the directions of which are governed by the arrangement of the atoms comprising the surface. This comparatively new technic for examining matter provides not only a means of identifying substances but offers a method for determining the orientation of atoms comprising a surface. Electron diffraction methods differ from X-ray procedures in that electrons are poor in penetrating power and hence are, by necessity, confined to surface explorations.<sup>6</sup> This method has been employed to prove the existence of graphoid surfaces on friction parts which have been consistently lubricated with oil containing colloidal graphite.

The cast iron from which the motor blocks of internal combustion engines are made is reasonably rich in free graphite. The electron diffraction camera shows that when such iron is subjected to a rubbing action the graphite flakes are spread over the surface to provide a film possessing low friction properties. (See Figure 2.) Finch and Zahoorbux (14), in commenting on this point, say,

"The presence of graphite in cast iron accounts for its self-lubricating properties, but in certain cases this graphite supply is inadequate and can only be replenished by the opening of fresh pores as the result of wear, unless an external source of graphite is furnished. Indeed, it has become usual to add small amounts of colloidal graphite to the lubricating oil for graphite-free metals as well as for cast iron. An orientated graphite layer is soon formed on a bearing surface run-in with such a graphitized oil. The authors have found that a bearing, neither of whose elements is cast iron, but which has been lubricated with graphitized oil, can run without damage or seizure in a dry condition for a much longer period than one previously lubricated only with plain ungraphitized oil. Since under normal running conditions the oil film at some point or other continually undergoes momentary rupture, the chief function of the graphite is to prevent 'pick-up' during these brief periods of oil-film breakdown."

In subsequent work Finch and Whitmore (15) made studies to determine why a surface which had been lubricated with colloidal-graphited oil is able to run without injury for a considerable period of time after the oil supply had been interrupted. They

found that during the formation of the Beilby layer (16) any graphite which may be present in the lubricant is virtually kneaded into the plastic metal, thus becoming entrapped in the amorphous surface layer. Previously, it was difficult to understand why extremely thin layers of adsorbed graphite were able to provide extended lubrication in the absence of fluid

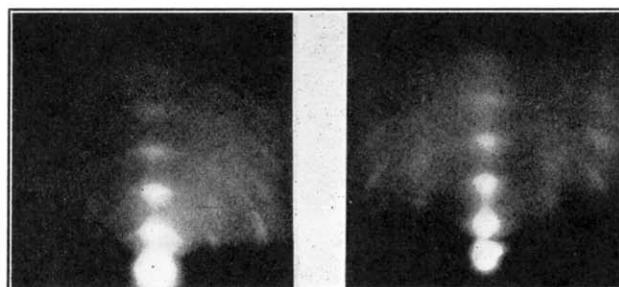


FIGURE 2

*A* represents the type of electron diffraction pattern obtained when cast iron is abraded. *B* is the pattern produced when an electron beam impinges upon a graphoid surface. Note similarity of figures obtained. In *A* the graphite is supplied by the cast iron, while in *B*, colloidal-graphited lubricant is responsible for the characteristic graphite pattern. The series of vertical spots indicates that the graphite particles are oriented, as is always the case when a graphite surface is subjected to a rubbing action.

lubricants. The observations of Finch and Whitmore thus offer a plausible explanation. These investigators, in summarizing their efforts, state,

"These experiments show that graphite is actually absorbed into the amorphous surface layer of the metal formed during running-in with an oil containing colloidal graphite. It remains to explain how this occurs. We know that running-in consists essentially in the formation, by a liquid-like flow of the metallic surface, of an amorphous, *i.e.*, vitreous-like, Beilby layer on the bearing surface. If, as is the case when a graphited lubricant is used, an adherent film of graphite is present on the metal surface when flow is occurring, it is not difficult to see how graphite can become occluded, by 'rolling-in,' as it were, into the flowed layer. This view is supported by the fact that the greatest amount of graphite absorption by the Beilby layer occurs in the metals which flow most easily."

The value of graphite as a solid lubricant is of major importance in connection with devices operating at high temperatures, typical of which are: baking oven chains, kiln cars, glass-making machinery, and so forth (17). For such applications it is customary to use colloidal graphite dispersed in a fairly volatile oil having good penetrating properties. The petroleum carrier serves primarily as a vehicle to convey the graphite to remote parts. When subjected to heat, the oil distils off, leaving the graphite as a residue to function as a dry lubricant.

The presence of a solid lubricant, colloidally suspended in an oil, is of great value where boundary or thin film conditions prevail. New machinery having

<sup>6</sup> For a review of electron diffraction research *cf.* CLARK, G. L., AND E. WOLTHUIS, "A résumé of electron diffraction," *J. Chem. Educ.*, 15, 64-75 (1938).

unusually close-fitting parts, mechanisms operating under severe temperatures and pressures, and devices in general suffering a diminished oil supply, offer typical examples.

When a friction surface is lubricated with colloidal-graphitized oil, adsorption of the graphite takes place through the surface energy of the metal coming into play (18). This graphoid film, in addition to discouraging friction, because of its ability to satisfy surface energy, displays a pronounced affinity for any oil that may be brought in contact therewith. Bachmann and Brieger (19), in the course of their research to determine if there existed a relationship between the lubricating quality of oils and their heats of wetting with metals, found that the forces acting between graphite and oil are more than seven times as great as those existing between copper and oil. Inasmuch as a surface that is more readily wetted is one that is more difficult to wipe clean, it follows that oil films that are spread upon graphoid surfaces are less liable to rupture than those in contact with metallic bodies. The affinity between graphite and oil is a most useful property under severe operating conditions and may explain the ability of graphite to raise the critical temperature<sup>7</sup> of oils as much as fifteen to twenty degrees Centigrade (20).

#### WIRE DRAWING

Colloidal graphite's unusual qualities as a dry lubricant have enabled it to play an important part in the development of tungsten as a filament material for incandescent lamps. After a group of scientists working at the General Electric Company's laboratories at Schenectady, New York, had achieved the seemingly impossible feat of producing ductile tungsten, they were still confronted with difficulties which prevented them from commercializing their discovery. In the working of tungsten, after its reduction in rod form from its oxide in a hydrogen atmosphere, it is swaged repeatedly until its cross-section approaches the diameter of a coarse wire. The metal in this form is then subjected to a number of draws through diamond dies until the wire size is that of the filaments found in present-day lamps. These delicate strands, unfortunately, during the early days of tungsten drawing, broke with frequent regularity in their passage through the carefully drilled diamonds. Furthermore, these costly dies wore excessively, requiring their constant replacement. It was felt that if a satisfactory wire-drawing lubricant could be obtained, both die wear and wire breakage could be minimized.

The manner in which colloidal graphite dispersed in water ultimately solved this problem and made possible the production of tungsten filaments on a huge scale is described by Colin G. Fink (21), one of the chemists at the General Electric Laboratories engaged on this project,

<sup>7</sup> The critical temperature of an oil is that temperature above which it ceases to function as a lubricant.

"Hot drawing of metals through diamond dies was not an art that had been practiced or developed at that time and while in the midst of this search for a suitable lubricant I happened to come to New York over the week-end to visit my father. While in New York I attended a lecture given by Dr. Acheson at the old Chemists' Club rooms. Dr. Acheson at this lecture described his discovery of 'Aquadag.' I remember distinctly how he referred to the Egyptians using straw in making brick and suggested that it was the tannic acid in the straw that had such a marked effect on the properties of the clay they employed. In like manner this principle was applied to 'Aquadag.' Dr. Acheson demonstrated before us some of the remarkable properties of 'Aquadag' and at the completion of the lecture I went up to him and got the small can of 'Aquadag' from which he had taken samples for demonstration. Returning to Schenectady the following Monday morning, I immediately tried out this 'Aquadag' on the tungsten wire drawing and, to my great pleasure and satisfaction, the lubricant problem was solved. The 'Aquadag' formed a very close, adherent film on the rod and wire, very much resembling polished ebony as the wire came out of the die. From that day on till the present, 'Aquadag' has been used for this purpose by tungsten wire producers all over the world."

#### INSULATORS

Another novel use for films formed with aqueous dispersions of colloidal graphite is embodied in the manufacture of Pyrex suspension-type insulators (22). It was discovered that the metallic parts in contact with the glass had to be lubricated to discourage seizure between these dissimilar materials. After the assembly of an insulator a slight but definite movement takes place between the glass and metal portions because of differences in their expansion. Mechanical movements are also set up due to the strain to which the insulator is subjected in use.

Oil was first used to reduce the friction set up, but proved unsatisfactory as it had a tendency to volatilize and gas under the heat generated when the insulator was assembled with molten alloy. Furthermore, the rupture of the oil film under high-tension currents promoted electrical failures. When a film of graphite was substituted for oil, a conducting, dry lubricant was provided which eliminated both mechanical and electrical difficulties.

#### COPPER OXIDE RECTIFIERS

Manufacturers of copper oxide rectifiers employ colloidal graphite to improve contact between the discs and plates comprising these devices. The rather rough crystalline cuprous oxide surface upon which the rectification of alternating current depends, must make close permanent contact with adjacent discs, or plates (23). Originally, an attempt to accomplish this was made by inserting soft metal washers between the discs which, in the small types of rectifiers, are assembled on a rod carrying a nut to permit the application of pressure. The flow of soft alloy under the conditions was imperceptible, however, resulting in the adoption of colloidal graphite as a filler for the cavities between the crystals. The spraying of the cuprous oxide surface with colloidal-graphited water produced a leveling action, which gave the desired results.

The plates used in the large rectifying units (see Figure 3) are first treated with graphite and subsequently sprayed with molten metal.

#### RESISTANCES

The conductivity of a graphite coating or layer varies with its density and with the proximity of the particles of which it is composed. A thin film, for example, is quite resistant to the passage of an electric current. If such a film is gently buffed, thus orienting the individual particles, or if it is subjected to pressure, its conductivity is improved. This fact is utilized by the radio industry (24-30) in the production of both variable and fixed resistors of the type represented by tone controls, volume controls, and grid leaks.

#### ELECTRON EMISSION

Being a conductor of electricity, graphite finds many uses in the electrical industry, particularly in the field of applied electronics. These uses are extended when the graphite is in the colloidal form.

Colloidal-graphited water applied to solids by dipping, brushing, or spraying forms tenaciously affixed graphite films which, in addition to being conductive, are homogeneous, opaque, have a high black body factor, are resistant to electrical bombardment, are not radioactive, possess a low coefficient of expansion and, under certain conditions, are capable of absorbing gases. Those familiar with the vacuum tube industry appreciate the importance of such coatings in the manufacture of electric discharge devices.

It is common practice, in the making of radio tubes, to spray the grids of certain classes of tubes with colloidal graphite in water for the purpose of discouraging the emission of secondary or undesired primary electrons.<sup>8</sup> If the grid is negatively charged so that it cannot receive electrons from the filament directly, it can emit electrons by thermionic emission, which depends upon its being heated to a high temperature, or photoelectrically, due to the light from the filament, or upon X-rays produced in the tube resulting from the impact of electrons at the anode. If, in power tubes, the grid is used at positive potential with respect to the cathode, trouble may arise from secondary emission, *i. e.*, electrons emitted as a result of electron impact of the grid.

Graphite is useful in tending to retard these undesirable forms of emission. In the case of primary emission, its dark color is effective. A black body radiates heat more readily than a polished metal surface. Hence, a grid that has been sprayed with graphite remains cool and thus shows less tendency to emit electrons thermionically.

In the case of secondary emission, carbon in its several forms is markedly resistant to bombardment so that when a grid carries a graphite coating, the metal

<sup>8</sup> For a discussion of the emission of electricity from solids see HOAG, J. B., "Electron physics," D. Van Nostrand Co., Inc., New York City, 1929, p. 24.

constituting the same is sheathed from the onslaught of electrons.

#### CATHODE-RAY TUBES

A growing use for aqueous dispersions of colloidal graphite is embodied in the manufacture of the cathode

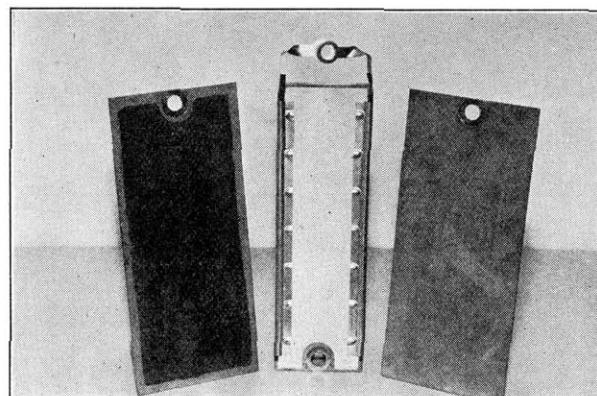


FIGURE 3.—PLATES USED IN COPPER OXIDE RECTIFIER MANUFACTURE

ray tubes employed in oscilloscopes and television receivers. When this type of tube was first introduced, it carried on its walls a ray-focusing anode of silver obtained through the decomposition of a silver salt such as the tartrate. Metallic coatings of this kind, however, were not entirely satisfactory, being expensive, highly reflective and difficult to apply to certain types of glass. Upon replacing such films with graphite (31-32), adequate conductivity was obtained, light reflection was minimized, and higher vacuums achieved as a result of the "getter"<sup>9</sup> properties of carbon. (See Figure 4.)

#### LIGHT SENSITIVE CELLS

The chemical inertness of graphite together with its property of conducting electricity have made it useful as an electrode material in selenium cells. When this latter element is applied to metallic bodies, there is a tendency to form selenides which increase the internal resistance of the cell. Graphite eliminates this difficulty. It is stated (33) that graphite is particularly adaptable to the preparation of cells sensitive to infrared light in which selenium is used with admixtures of heavy metals such as tellurium.

Colloidal graphite is likewise useful in photo-electric cells employing the alkaline metals. In tubes of this kind use is made of its unique property of absorbing cesium and similar alkali metals (34).

#### ELECTROSTATIC SHIELDS

In cases where it is desirable to form electro-static

<sup>9</sup> A "getter" may be defined as any substance which, through chemical or physical processes, removes residual gases from evacuated objects or systems.

shields, colloidal graphite enjoys utility in a wide variety of electrical apparatus, ranging from vacuum tubes to electric pianos.

Porter (35) has compiled with considerable thoroughness the laboratory applications for colloidal graphite, describing in detail how this product is employed to form shields, guard rings, contacts, special electrodes, and so forth.

#### MISCELLANEOUS ELECTRICAL APPLICATIONS

Among the miscellaneous applications for colloidal graphite may be mentioned its utility as a cement for

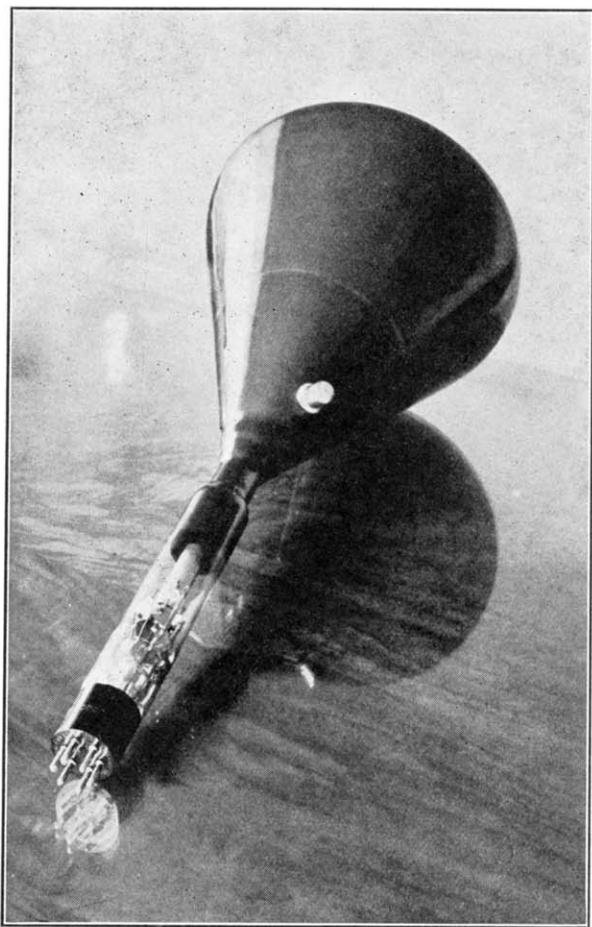


FIGURE 4.—A CATHODE-RAY TUBE OF THE KIND USED IN TELEVISION RECEIVERS. THE DARK LINING ON THE TUBE WALLS COMPRIMES THE RAY-FOCUSING ANODE

connecting the carbon filaments to the lead in wires of therapeutical lamps, as a preventive of corona in the manufacture of alternators (36), as an absorbent of radiation in the building of thermopiles (37), and for rendering non-conductors conductive preparatory to electroplating. It is interesting to note, in this latter connection, that particles of colloidal graphite, like the ions of an electrolyte, may be made to migrate to a pole of opposite charge when subjected to electrolysis.

Fink and Prince (38) have successfully co-deposited copper and graphite to produce low friction metals having a graphite content as high as forty per cent.

#### PARTING COMPOUNDS

The physical structure of graphite responsible for its unctuousness makes it applicable as a parting compound. Accordingly, graphite very effectively prevents the sticking of a variety of objects to the molds in which they are cast or otherwise formed. This applies to glass bottles, rubber tires, die castings, and so forth. In the glass industry it is also used as a parting compound on forming tools and is gradually displacing the beeswax and tallow usually used in this class of work. Graphite, being stable chemically, does not decompose and thus discolor the object being formed, nor does it give rise under heat to acrid fumes so common with animal products.

In the making of stereotypes used in the printing field, it is customary to employ as a mold a paper flong, known in the trade as a "dry mat." When these matrices are coated with graphite, it is possible to readily free the stereotype casting without damage to the flong and obtain, at the same time, somewhat better definition than is possible with untreated mats (39-41).

Where there is a tendency for incandescent lamps to stick in their sockets as is frequently experienced with electric signs, on shipboard and in damp or corrosive atmospheres, colloidal graphite applied to the lamp bases forms a protective, lubricating coating which discourages corrosion and makes for their easy removal.

The screw threads of bolts and nuts subjected to high temperatures often give rise to considerable difficulty when an attempt is made to remove them. If these parts carry a coating of graphite, they are not only withdrawn more readily but can, during assembly, be drawn up tighter by virtue of the lubricating properties of the graphite film coming into play. Coatings of this character are used for parting purposes on flanges, gaskets, battery terminals, spark plugs, and so forth.

Colloidal graphite dispersed in light oil or kerosene is beneficial in removing studs from turbine cylinder joints (42) and similar threaded parts.

Many of the so-called penetrating oils used to facilitate the separation of corroded parts, depend upon colloidal graphite for their lubricating qualities (43-44). A penetrant must, of necessity, be of a low viscosity. Often this viscosity is insufficient to withstand the loads and pressures created during disassembly. In preparations such as this the penetrant is used merely as a vehicle for the graphite. Being colloidal the latter is able to enter the porous masses and capillaries of corrosion products without being filtered from its carrier. It is at the seat of corrosion that the graphite can be of greatest benefit in effecting separation.

#### IMPREGNATION AND INCORPORATION

Colloidal graphite, because of the minute size of its

particles, is finding utilization in numerous industries as an impregnating medium.

Grinding wheels (45) have been treated with graphite to give them conductivity, thus making them a part of an electrical circuit controlling grinding operations.

Brake linings (46), clutch facings, and similar friction elements are fields for colloidal graphite. Although the prime purpose of such devices is to create friction, the presence of a small amount of lubricant is important as a preventative of momentary seizing or "chattering."

Packing materials are often impregnated with colloidal graphite to impart lubricity.

Porous bearing materials (47) saturated with lubricating oil are steadily gaining wider adoption in the automotive and mechanical home appliance fields. When such bearing materials are treated with colloidal-graphited oil their efficiency is further increased.

In some instances it is desirable to take advantage of the pigmental value of graphite. It has been so employed for special finishes on a variety of objects.

An English manufacturer of Bible paper adds a small quantity of colloidal graphite to the pulp, while in the beaters, to give increased opacity to his product. It is said that the desired result is achieved without imparting any noticeable tint to the finished stock.

Fabrics are often impregnated with colloidal graphite. One example involves the manufacture of belt stock. A graphite-treated belt on washing machines, refrigerators, and similar equipment, is sufficiently conductive to ground any static charges that may be generated during the operation of the drive.

Because of the difficulty of removal of colloidal graphite absorbed by fabrics, it has become standard practice to use this material, dispersed in both oil and water (48), for the preparation of soiling standards to study the detergent value of soaps and allied laundering preparations.

The fabric used to reinforce laminated resin bearings is sometimes graphite-impregnated to yield a material having a lower coefficient of friction than non-graphited phenol formaldehyde resin.

Colloidal graphite may, of course, be incorporated with other colloids, such as rubber latex. If these two materials are treated jointly with an electrolyte, coprecipitation occurs, resulting in a product which is an intimate mixture of rubber and graphite. Homogene-

ous combinations of other materials can be effected by this scheme (49).

#### BIOLOGICAL APPLICATIONS

Workers in the field of experimental biology find aqueous suspensions of colloidal graphite a useful tool in their research.

Field and Drinker (50), in studying the passage of particulate matter from the blood circulation to the lymphatics, prefer graphite to India ink because of the slowness of graphite agglutination in the blood and the lack of affinity exhibited by it for the vessel walls.

Wangensteen and Cooke (51) conducted work wherein the reticulo-endothelial system of the rabbit was partially blocked in its phagocytic activity by daily intravenous injections of colloidal graphite.

Drinker and Churchill (52) made an extensive study of colloidal graphite as an injection fluid and concluded that such a preparation "possesses qualities essential for physiological injections if employed in perfusion experiments."

Other investigators (53-54) have carried on similar work using graphite as a foreign body in the blood stream.

A most unusual use for oil dispersion of colloidal graphite is brought out in the studies of Hacker (55), who used such a preparation in determining the extent to which oil penetrates the breathing tubes of mosquito larvae. In this work suspensions of lampblack and of carmine in kerosene failed, because the suspended particles were filtered out at the spiracle, or tube entry, permitting the passage of the oil alone. With colloidal-graphited oil, however, the opaque suspensoid was not separated, thus making visible the distribution of the oil within the tubes.

#### CONCLUSION

From the foregoing it is evident that colloidal graphite is a unique material, playing an important rôle in many unrelated lines of endeavor. A material that extends its utility from researches involving the wind-pipe of larvae, through the realm of electronics, to the reduction of friction in huge machines, can well be called unique.

Just as the list of applications for this material, originally designed as a lubricant, has grown extensively in the past decade, so is it expected to lengthen as new fields are uncovered.

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