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T. M. BENZIGER
GRAPHITE EXTRUSIONS

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2 Sheets-Sheet 1

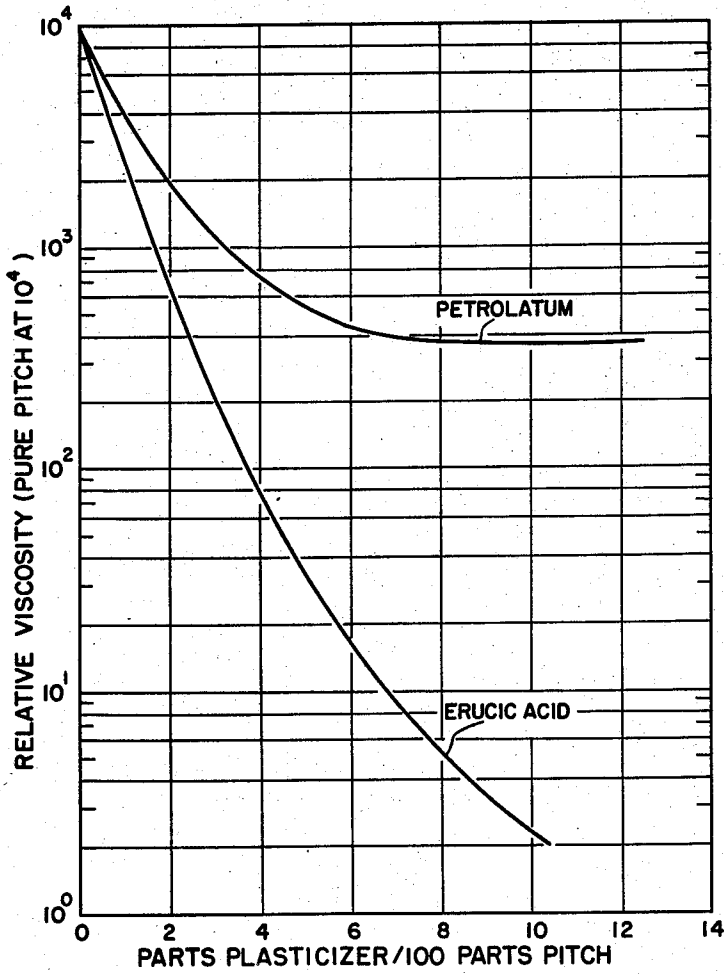


Fig. 1

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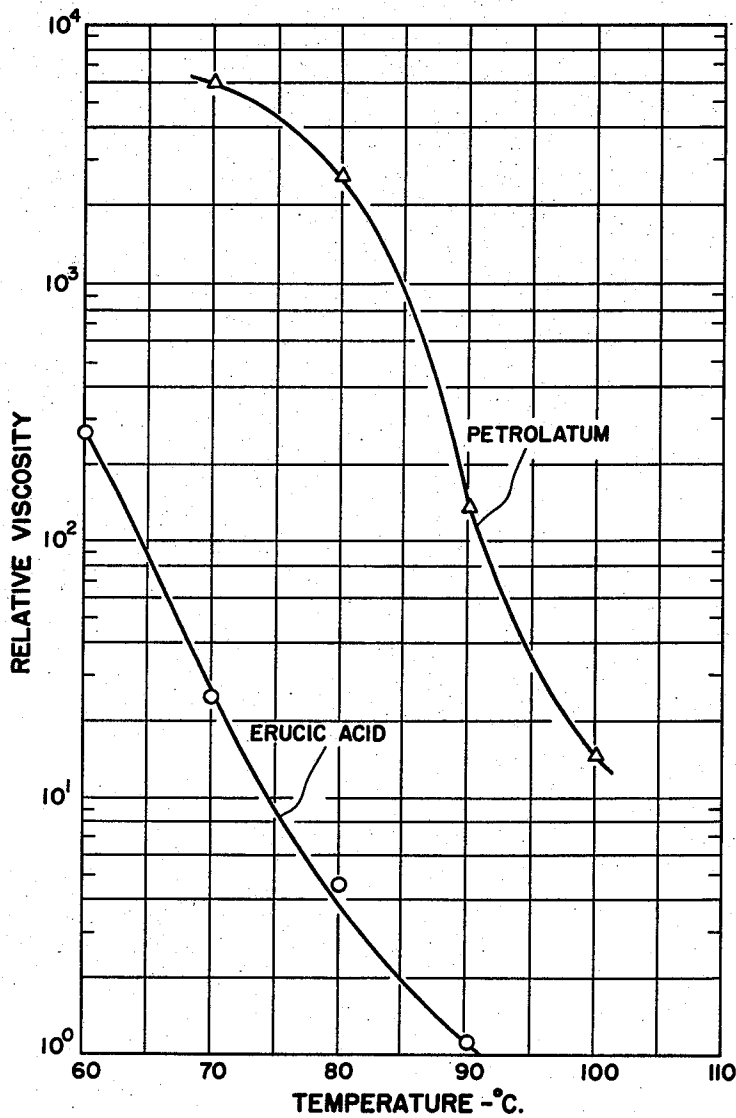


Fig. 2

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GRAPHITE EXTRUSIONS

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1 Claim. (Cl. 106—56)

This invention relates to a method of extruding continuous shapes from carbonaceous mixtures and in particular to a superior material from which endless extrusions of carbonaceous mixtures can be made.

With the advent of the reactor and rocket propulsion arts there has been a demand for intricate extruded graphite shapes which may be made in any desired length. These shapes can be used in the graphite lattice of thermal nuclear reactors or can be used in high temperature applications in the reaction zone of rockets. It can be seen that by using extruded shapes in, for example, heterogeneous reactors, a great deal of machining effort can be saved over the prior art method of making such lattices.

In the prior art, carbonaceous mixtures have been extruded prior to graphitization, but with severe limitations because of the type of lubricants used. The carbonaceous or "green" mixtures have incorporated lubricants which act to reduce the power required in the extrusion process. However, since the type of lubricant used has been of the relatively non-volatile fraction of petroleum stock, the lubricant has had limited miscibility with the binder in the carbonaceous mixture. Thus, the prior art lubricants have acted as gross lubricants only, and do not encourage the formation of intimately bound, coherent extruded shapes. Therefore, the lubricants of the prior art have not been suitable for screw extruders but only for a limited application in ram-extruders which, of course, limits the length of the extruded piece.

Other lubricants of the prior art which have been used in an attempt to improve on petrolatum are colloidal suspensions in graphite. It has been found, for example, that a colloidal suspension of graphite in oil is a fair extrusion lubricant. This can be colloidal graphite suspended in glycerine which is known by the trade name Glydag, or can be colloidal graphite in petroleum oil, known as Oildag, or could be colloidal graphite in castor oil, known as Castordag. However, these lubricants do not yield the results of the present invention.

By this invention a lubricant which is miscible with the binder in the green carbonaceous mixture is disclosed which causes such a vast improvement in the physical properties of these mixtures that it is possible to extrude sound, coherent shapes of intricate cross section with a continuous screw extruder.

Since reactor applications generally require a graphite which has high purity, it is desirable that the lubricant either become graphite in the graphitizing process, or else volatilize without leaving a non-carbon residue. The lubricant of this invention has these desirable properties.

It is therefore an object of this invention to provide a lubricant for carbonaceous mixtures which is miscible with the binder of the mixtures.

It is a further object of this invention to provide a lubricating agent for carbonaceous mixtures which is capable of either being graphitized or volatilized.

It is a further object of this invention to provide a

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lubricating agent for green carbonaceous mixtures which improve the flow properties of said mixtures so remarkably that carbonaceous shapes may be extruded with a continuous screw extruder.

Further objects of this invention will be apparent from the specification, claim and appended drawings hereby made a part of the specification in which:

Figure 1 shows a graph of the relative viscosity between pitch plus a lubricant of the prior art and pitch plus erucic acid, a lubricant of this invention.

Figure 2 shows a graph of the relative viscosities between two carbonaceous mixtures, one using a lubricant of this invention, the other using a lubricant of the prior art.

Graphite is usually made from a "green" mixture of coal-tar pitch, used as a binder, and forms of carbon for filler such as petroleum coke, graphite flour or carbon black. If this mixture is to be extruded before graphitizing, it is necessary to add a lubricant to lower its viscosity. If the lubricant has a low solubility in the binder portion of the above mixture the extruded piece will have poor mechanical strength and coherence, since the immiscible lubricant phase prevents the intimate bonding between filler particles and the binder. If the lubricant has a high solubility in the mixture, the extruded piece is more likely to have good handling properties as well as good extruding properties as the binder particles can wet the filler particles and because the lubricant then allows individual particles of the mixture to flow relative to each other with considerable ease.

By this invention, a lubricant which is vastly superior to any lubricant of the prior art is disclosed.

This lubricant is any one of the family of fatty acids, although of this family, erucic acid has been found to be superior to all. The fatty acids lower the viscosity of the carbonaceous mixtures and being soluble in the binder portion of the mixture, they have a high solubility in the mixture with the result that the extruded piece is remarkably flexible.

Figure 1 shows a graph of the viscosity of a pitch lubricated with erucic acid as compared to petrolatum. As can be seen, the erucic acid lowers the viscosity by as much as a factor of 200.

Figure 2 shows the relative effectiveness of erucic acid compared to petrolatum for a carbonaceous mixture composed of 22 parts by weight coal tar pitch, 49 parts by weight petroleum coke, 27 parts by weight carbon black and 2 parts by weight lubricant. Note that a temperature of 80° C., the viscosity of the carbonaceous mixture with erucic acid is lower by a factor of 700 compared to petrolatum. At 90° C. the fatty acid mixture has a viscosity only 1% that of the petrolatum-based mixture.

With this drastically lowered viscosity it is possible to feed this mixture into a continuous screw extruder and consequently the length of extruded shapes which may be made, are unlimited.

To prepare a typical carbonaceous mixture of this invention, the following constituents are selected and weighed:

	Grams
Coal tar pitch (No. 30 medium hard).....	450
Petroleum coke (95% minus 200 mesh).....	1000
Carbon Black (Thermax).....	550
Erucic acid.....	41
Benzene.....	600

A mixer of sufficient capacity, preferably a double blade, kneading-type equipped for vacuum and controlled temperature of the range 25° C. to 125° C. is used. With the mixer heating jacket at 70° C., the pitch (in the

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ground state) carbon black, erucic acid and benzene are added and mixed until all of the pitch granules are broken up and smooth. A thin paste is the result. The petroleum coke flour is added and mixing is continued until the batch returns to a dispersed "wet" state. At this point, a vacuum is applied intermittently to remove the benzene. With the benzene removed, the batch becomes quite stiff. Mixing continues in this state for about ½ hour. A vacuum is again applied and in about 15 minutes, the mixture will harden so that it parts cleanly from the mixing blade and breaks up into particles from ¼" to 1" diameter.

Following the mixing, the material is mixed with crushed Dry Ice and allowed to chill to a hard brittle state. It is then crushed to ⅜" maximum particle size and then warmed to room temperature.

These pieces or particles are now put in the hopper of an extruder, either of ram or screw type. The mixture is then extruded as ⅛" diameter rod and chopped to pellets ⅝" long. For this operation, the hopper is evacuated to about 3 mm. Hg and the extrusion die is kept at 300-325° F.

The formed pellets are now ready for final extrusion to the desired shape. They are placed in a hopper of a ram or screw extruder. The hopper is evacuated again and the temperatures in the extruder are as follows:

Temperatures:

Hopper zone.....	180° F.
Screw zone.....	275° F.
Adapter flange.....	250° F.
Die	190° F.

The extrusion rate is about 3 cu. in./min. for a 1½" size extruder.

The extruded piece is then baked and subsequently graphitized.

The foregoing method is typical of the preferred embodiment, though not limiting as a method, as other methods known by those skilled in the art can be applied. For example, it is not at all necessary that benzene be added in the mixing stage, though it does make the mixing easier. The crushing operation can be eliminated if a ram extruder is used for pelletizing, however, for a screw extruder the carbonaceous mixture must be of small enough particles to be "caught" by the screw of the extruder. Again, the pelletizing operation can be eliminated, however, pelletizing has the advantage of helping rid the mixture of low temperature volatiles and aiding uniform extrusion of the final piece when the final extrusion is "fed" from pellets.

Therefore, the use of fatty acids by this invention shows the following advantages:

(1) For comparable extrusion rates appreciably less power is required than for mixtures of the prior art.

(2) Continuous screw extruders may be used. This was heretofore not possible.

(3) The extruded shapes are coherent and strong, allowing easy handling in contrast to weak, brittle shapes obtained with petrolatum-based lubricants.

(4) Mixtures lubricated with fatty acids have superior flow properties as indicated by high extrusion rates and

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physically sound extruded pieces whereas the petroleum lubricated mixtures under comparable conditions have low extrusion rates.

(5) The improved flow properties using fatty acids make it possible to use simplified extrusion dies, as the dies can be of simple contour without intricate approach sections.

Another advantage in using fatty acids as a lubricant is that the density of pieces made by the methods of this invention when graphitized is as high as 1.88 which is considerably higher than the density of graphite extruded by methods of the prior art. High density is of value when extruded shapes are to be used in nuclear reactors as a higher density results in a more compact reactor.

Although the percentage of fatty acid which may be added to a carbonaceous mixture can vary over the useful range of 4 to 10 parts/100 parts pitch as seen by Figure 1, the preferred embodiment has been found to be 7 parts fatty acid to 100 parts pitch. Though, as previously stated, erucic acid is preferred, oleic and stearic are also very suitable, these three representing the preferred acids from the family. Since the extruded piece must have enough mechanical strength to be readily handled, it has not been feasible to add more than about 10 parts fatty acid to 100 parts pitch as the extruded shape tends to become mechanically weak.

Therefore, it is recognized that other carbonaceous mixtures may be used and still be within the teaching of this invention when fatty acids are used in the mixture. Thus, the invention is not limited by the foregoing disclosure, but only by the appended claim.

What is claimed is:

A method for making a carbonaceous mixture readily extrudable, comprising mixing 130 parts by weight of coal-tar pitch, petroleum coke, carbon black, benzene, and a fatty acid in which the coal-tar pitch is present in at least 22 parts, the benzene is present in approximately 30 parts, and the fatty acid is present in at least about 2 parts, stirring a mixture of said carbon black, fatty acid and benzene at a temperature of 70° C. until the mixture is smooth, adding said petroleum coke and continuing the mixing until the batch returns to a dispersed "wet" state, applying a vacuum to said mixture to remove the benzene, mixing the remainder of the batch for about one-half hour, again applying a vacuum and continuing the mixing for about 15 minutes, chilling the mixture by mixing-in crushed Dry Ice, and allowing said mixture to chill to a hard, brittle state, and crushing said hard mixture to ⅜ in. maximum particle size.

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