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## MANUFACTURE OF CARBONACEOUS MOLDING COMPOSITIONS

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This invention relates to improvements in the manufacture of carbonaceous moulding compositions suitable for extrusion.

There is a wide variety of articles which can with advantage be shaped by extrusion; these include rods, bars, tubes or pipes of rectangular, polygonal, circular or elliptical section or of more complex shapes. It is highly desirable to produce as final products moulded carbon articles which have been fired and which are strong, tough, resistant to solvents to acids or to alkalies, which can stand high temperatures and are free from bubbles or from visible porosity. For the manufacture of carbon articles the dry powder-moulding technique, such for example as that described in United States patent application Serial No. 622,934, now Patent No. 2,461,365 has certain advantages. One of these advantages is the ability to fire the moulded shapes at relatively rapid rates of temperature rise without causing intumescence. At the same time the moulding of dry powders imposes limitations on the shapes that can be produced. One object of this invention is to produce from coal a composition which may conveniently be moulded by extrusion. Another object is to produce such a composition which, after moulding, may be heated rapidly without intumescence taking place. A further object is to produce from such a composition strong, tough, moulded carbon articles which are of simple or of complex shape.

According to the present invention, a method of making a carbonaceous moulding composition, especially an extrusible composition, consists in mixing at an elevated temperature subdivided coal and a softening agent as hereinafter defined.

The coals suitable for use in this invention are those having up to 25% volatile matter on the dry ash-free basis, preferably between 6% and 20%. The particle size of the sub-divided coal may be about 80 to 150 mesh British Standard sieve, but gradings of coarser and finer particles may be employed according to the type of moulded product it is desired to make.

A suitable temperature for the mixing operation is from 60–180° C. It is advantageous to digest the mixture for a considerable period, say 4–8 hours.

The expression "softening agent" used herein means a material which exercises a solvent action upon the coal and comprises at least one of the following: Coal tar middle oil, coal tar heavy oil, coal tar anthracene oil, coal tar pitch (including specially treated pitches which are neutral); aromatic compounds which are hydrocarbons or derivatives of benzene, naphthalene, anthracene, phenanthrene or like aromatic hydrocarbons, such derivatives including phthalic acid-esters, aryl esters of phosphoric acid; naphthenic and heterocyclic compounds; petroleum residues, soft bitumen; and chlorinated paraffin waxes.

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The proportion of softening agent may conveniently be from 10% to 30% by weight of the mixture. In order to reduce the consistency of the moulding composition or "dough" there may be added to the mixture after cooling a light oil such, for example, as a solvent naphtha.

The mixing at an elevated temperature of the coal powder and softening agent produces a reaction on the coal which appreciably increases the swelling properties of the mixture above that of the coal used, and in the case of non-agglutinating coals allows a strong, coherent product to be made by subsequent moulding and heating. It is a feature of this invention that such products can be made from non-agglutinating coals of anthracite and semi-anthracite character. However such non-agglutinating coals may be blended with coals of more agglutinating or of strongly agglutinating quality such as a strongly coking coal.

By the addition of the softening agent the volatility and swelling properties of the composition are increased above those of the coal used, when there are used agglutinating coals which can be subdivided, moulded and heated so as to give a strong, coherent product. The result is that in order to avoid intumescence it will be necessary for the heating to be carried out at a slower rate than would have been necessary if the coal had not been submitted to the pretreatment described. We have found, however, that by adding to the mixture an oxidizing or dehydrogenating agent, the rate of heating of the resultant composition after moulding may be substantially equal to the rate at which the coal alone could have been heated without intumescence taking place e. g. 1° C. to 2° C. per minute. The dehydrogenating agent, for example sulphur or selenium or nitrobenzene, must be of such a

character and must be added in such a manner (e. g. after cooling of the mixture) that it does not react with the mixture to a significant extent, and hence does not harden the mixture, until after moulding has been completed.

Accordingly, the invention includes a method of making a carbonaceous moulding composition, especially an extrusible composition, which method consists in mixing at an elevated temperature subdivided coal and a softening agent as hereinbefore defined and adding to the mixture after it has cooled an oxidizing or dehydrogenating agent such as sulphur, or selenium or such as nitrobenzene.

To avoid a reaction which would impair the moulding properties of the composition, the mixture should be cooled to a temperature below that at which as experimentally determined, reaction between the particular agent used and a particular mixture takes place. The addition of the dehydrogenating agent may be made in any suitable mixing machine. Intimate admixture is important.

If desired there may also be added to the mixture a swell inhibitor such for example as finely subdivided natural graphite which contributes to the flow properties of the composition.

In order to manufacture strong, useful moulded products it is necessary to submit the composition to a shaping and to a heating operation. The invention includes, therefore, a method of making a moulded carbon product which method consists in submitting a composition made as above-described to a moulding or shaping operation and heating the shaped article under non-oxidizing conditions to a temperature of at least 550° C., and preferably above 700° C.

A preferred technique is to cool the digested mixture, to form a solid billet under mechanical pressure whilst simultaneously extracting air from the cylinder or container within which the billet is formed so that the billet contains no bubbles, then to put the billet into the extrusion press. If an added agent such as sulphur is present extrusion is best effected at room temperature, but with other agents (and even with sulphur) extrusion can be effected in the warm.

*Example I*

300 gm. of a S. Wales semi-anthracite coal (2.3% ash and 7.8% volatile matter on the dry ash-free basis) which had been ground to pass 95% through a 200 mesh B. S. sieve were mixed with 100 gm. of No. 2 anthracene oil in a dough mixer (Z-blade mixer) at a temperature of 160° C.–180° C. After 4 hours' digestion had elapsed the mixture was allowed to cool to below 100° C. whereupon 45 ml. of solvent naphtha were added and mixing continued for a further ½ hour. The composition was then removed from the mixing machine, placed inside the cylinder of an extrusion press and extruded through a ½'' diameter round nozzle into rods 10'' long under a force between 8,000 lb. and 12,000 lb.

The rods were placed inside the muffle of an electrical furnace and were heated in a nitrogen atmosphere at a rate of 2° C. per minute temperature rise to 800° C., this latter temperature being maintained for ½ hour. The rods were removed from the furnace after cooling to about 200° C. under non-oxidizing conditions.

*Example II*

300 gm. of a S. Wales carbonaceous coal (3.1% ash and 17.1% volatile matter on the dry ash-free basis) which had been ground to pass 95% through a 200 mesh B. S. sieve were mixed with 50 gm. of No. 2 anthracene oil and 50 gm. solvent naphtha in a Z-blade mixer at a temperature of 100–110° C. After 2½ hours' digestion had elapsed the mixture was allowed to cool to about 30° C. and a mixture consisting of 50 gm., of finely divided natural graphite, 12 gm. of sulphur (dehydrogenating agent) and 25 gm. of solvent naphtha was added and mixing was continued for a further 1 hour. The composition was removed from the mixing machine and was extruded and heated in the manner described in Example I except that the rate of temperature rise in the heating operation was 1° C. per minute.

It will be understood that if it be desired to produce products of very low porosity, the heating of the extruded shapes may be carried out in a non-oxidizing atmosphere which contains a substantial proportion of a readily-decomposable hydrocarbon gas such as ethylene.

All the swelling number determinations referred to herein are by the method described in British Standard 1016.

We claim:

1. A process for the manufacture of a dough-like extrusible composition consisting mainly of coal from non-bituminous, non-agglutinating coal, which process comprises mixing the coal, 95% of which passes a 200 mesh sieve, with a relatively high boiling softening agent in the amount of 10% to 30% by weight of the mixture, heating the mixture to a temperature between 60° C. and 180° C., digesting the mixture with continued mixing for between 2 and 8 hours, allowing the mixture to cool and thereafter adding and mixing a solvent having a lower boiling point than said softening agent to reduce the consistency of said mixture, which solvent is non-reactive with the aforesaid mixture and is present in a weight less than that of the softening agent.

2. A process for the manufacture of a dough-like extrusible composition consisting mainly of coal from non-bituminous, non-agglutinating coal, which process comprises mixing the coal, 95% of which passes a 200 mesh sieve, with a relatively high boiling softening agent in the amount of 10% to 30% by weight of the mixture and a solvent having a lower boiling point than said softening agent for the softening agent, which solvent is non-reactive with the mixture and is added in a proportion by weight of the coal substantially the same as the proportion of softening agent, heating the mixture to a temperature of 60° C. to 180° C., and continuing mixing the heated mixture for between 2 and 8 hours.

3. A process for the manufacture of a dough-like extrusible composition consisting mainly of coal from non-bituminous, non-agglutinating coal having about 8% volatile matter on a dry ash-free basis, which process comprises mixing the coal, 95% of which passes through a 200 mesh sieve, with anthracene oil in an amount about 25% by weight of the mixture, said mixing being carried out at a temperature of 160° C. to 180° C. for a period of about 4 hours, and thereafter allowing the mixture to cool to below 100° C. and then adding and mixing for about ½ hour solvent naphtha in an amount by weight about half that of the anthracene oil.

4. A process for the manufacture of a dough-like extrusible composition consisting mainly of coal from non-bituminous, non-agglutinating coal having about 17% volatile matter on a dry ash-free basis, which process comprises mixing

the coal, 95% of which passes through a 200 mesh sieve, with anthracene oil and solvent naphtha each in an amount of about 12.5% by weight of the mixture, continuing mixing for about 2½ hours at a temperature of 100° C. to 110° C., thereafter allowing the mixture to cool to about 30° C., adding thereto a mixture consisting of finely-divided natural graphite, sulphur and solvent naphtha in amounts about 12.5%, 3% and 6.25% respectively by weight of the said first mixture, and continuing mixing for about one hour.

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