

# UNITED STATES PATENT OFFICE

2,645,583

## METHOD OF PREPARING CARBON BASE PASTES

Stefan Stanko, Saint-Jean de Maurienne, France,  
 assignor to Pechiney-Compagnie de Produits  
 Chimiques et Electrometallurgiques

No Drawing. Application July 14, 1949, Serial  
 No. 104,797. In France May 30, 1949

6 Claims. (Cl. 106—56)

1

This invention relates to the preparation of carbon-base pastes, more particularly pastes made of agglomerated carbon particles of the type used in various branches of industry and especially in electro-thermal and electrolytic manufacturing processes, for the manufacture of current-supply electrodes. Also, agglomerated carbon is sometimes used in forming the internal lining of electric furnaces and electrolysis cells.

Such agglomerated carbon compositions are made from pastes, which comprise carbon powder mixed with a binder and then shaped in molds. Some types of agglomerated compositions are fired in special furnaces prior to their use in electrothermal manufacturing operations or in electrolysis cells, the said firing step sometimes even being pursued to the point of graphitizing the agglomerated carbon particles. In other cases, the agglomerated carbon particles are subjected to firing within the electrothermal furnace or the electrolysis cell during actual operation, as in the case for instance of continuous electrodes of the Söderberg type.

However, regardless of the particular use to which they may subsequently be put, the quality of such agglomerated products essentially depends on the quality of the carbon pastes from which they are formed.

It is well known in this connection that, in addition to the choice or control of the granulometric composition of the carbonaceous product and the type of binder used, it is important that the particles of the carbonaceous product in contact with the binder should be effectively wetted by said binder throughout the entire surface of each individual particle, if it is desired that the final electrodes resulting from said paste should possess optimum characteristics. It is only when the particles or grains are thoroughly wetted by the binder that a desirably intimate bond is secured between the paste constituents and that it is possible to eliminate the mechanical losses which occur in service with inadequate bonded pastes. It is further known that in order to obtain as thorough as possible a wetting of the dry carbonaceous material by the binder, said carbonaceous material, which generally comprises a mixture of different sizes of particles, is first bodily introduced into a mixer or the like, then heated to a predetermined temperature, and the binder is thereafter introduced and the mixing operation is continued until a homogeneous mass is obtained.

However the procedure just described, while universally followed, presents a number of shortcomings. The finer particles form a stable

2

suspension with the binder, and said suspension, in which the said fine particles comprise the dispersed phase, follows the laws generally prevailing in nonhomogeneous liquids. As the concentration of fines increases in the suspension, the suspension increases in viscosity so that, for a sufficient concentration of fines in the suspension, the viscosity number of the suspension reaches a value which is a multiple of the viscosity of pitch. In mixing with the binder carbonaceous materials having various particle sizes, the suspension of fines in the binder reaches such a high viscosity value that it becomes unable of wetting the entire surface of the particles and can only partially, if at all, fill the pores thereof. In addition, the pores of the particles are initially filled with finer particles which prevent the penetration of the pitch or of the fines-pitch suspension. This effect by itself may cause formation, within the mass, of totally unwetted agglomerates of particles. Such a paste does not possess a desirably intimate bond between its constituents, and the parts molded therefrom will not possess optimum characteristics after firing. An incomplete wetting of the grain surfaces, and/or the presence of entirely unwetted particles in the mixture results in losses occurring in the utilisation of electrodes made from such compositions, said losses assuming the form of a production of coal-dust.

It is an object of this invention to provide an agglomerated carbon-base composition which is generally free of the above defects. According to my invention, the carbonaceous material, ground to the form of a carbon dust comprising particles of various sizes, is separated into two fractions, a cruder and a finer fraction. The cruder fraction, which may range in weight from 30% to 75% of the total weight of coal dust, is separately mixed with the binder until all of its constituent particles are thoroughly wetted by the binder; the balance of finer carbonaceous material is then added, and mixing is continued until a final mixture of highest possible homogeneity is obtained.

The carbonaceous starting material used may vary to a large extent depending on the characteristics desired in the final paste. When petroleum coke and pitch coke are used, as in the production of high purity electrodes, particles are obtained after the grinding step in which the pores may reach comparatively large sizes, e. g. 0.3 mm. and more. When such coke materials are used to make carbon pastes according to the invention, separation of the dust into two fractions is so effected that the small-

3

est-sized grains of the cruder fraction will be similar in size to the pores of the largest-sized grains therein. On the other hand, if the carbonaceous starting material used is metallurgical coke or anthracite, which once ground provides particles in which the pores are exceedingly small, the separation of the dust batch into two fractions should be so accomplished that the smallest-sized grains of the cruder fraction should have a dimension of about 0.2 mm.; for, should this minimum limit be exceeded, the resulting suspension formed with the particles during the mixing step would be so viscous that it would not insure a complete wetting of the grains. The subsequently added fines act to saturate the binder and form a suspension therewith, and a final paste is thus produced in which the pores of the particles and the gaps between the particles are completely filled and in which the surface of all the grains is completely wetted. A thoroughly bonded paste is thus obtained and one in which the structure is thoroughly uniform, and, after baking, the resulting molded part is found to possess optimum characteristics.

The crude coal dust fraction may also be first wetted with only part of the total requisite amount of binder, the balance of binder material being added subsequently at the same time as the finer dust fraction is added. The binder may be added in liquid condition, and the mixing operation is then more rapidly completed; however the binder may also be added in solid condition as for instance when the binder used is dry pitch; in such a case, the wetting of the particles can only be accomplished upon liquefying the pitch by application of heat.

In the production of a paste for electrodes, when the method of the invention is used, it is found that in order to obtain an adequately fluid paste, it is necessary to add from 1% to 3% more binder (e. g. pitch) if the particle fraction without fines is first mixed with the binder, and the fines are only added upon completion of the mixing step, than when following the conventional procedure involving simultaneous mixing of the entire batch of particles with the binder. This fact can only be explained in one way, i. e. that when the entire batch is treated with the binder (such as pitch) according to conventional procedure, the entire surface area of the particles is not wetted by the binder, whereas it is wetted to a much greater extent when the procedure of the invention is used.

#### Example I

A batch of carbonaceous material used in the manufacture of Söderberg paste, had the following granulometrical composition:

3-5 mm.	2-3 mm.	1-2 mm.	0.2-1 mm.	0.075-0.2 mm.	0-0.075 mm.
1.7%	1.8%	8.2%	31.2%	10.8%	46.6%

A Söderberg paste, when produced from a pulverized material of the above granulometry by the conventional methods of mixing, should have a pitch content of 28% in order to possess satisfactory fluidity. The above mixture of particles was treated according to the present invention with the binder, which in the case in hand was hard pitch, that is a pitch having a Krämer-Sarnow softening point not less than 70° C. The operating procedure was as follows: the particle frac-

4

tion in the range of from 0.2 to 5 mm. was first mixed with the hard pitch until the pores of the particles were filled and the surface of all the particles entirely wetted. Then the particle fraction of a size less than 0.2 mm. was added, and the mixing was continued until a homogeneous mass was obtained. The resulting Söderberg paste, in order to have satisfying fluidity, should contain 29.5% pitch, i. e. 1.5% more than when the conventional mixing procedure is used.

A Söderberg electrode paste was thus obtained which, after shaping and baking, showed the following characteristics as compared with those of a paste produced according to the conventional mixing practice:

	Electrode obtained by conventional mixing method	Electrode according to the invention
Apparent sp. gravity.....	1.42	1.36
Porosity, Percent.....	25.3	28.4
Resistivity, ohms, mm. sq./mm.....	84	59
Crushing strength, kg./cm. sq.....	268	290

Instead of adding the binder (e. g. pitch) in liquid condition to the divided carbonaceous material, the binder may be added in the solid state. In such case, the grain fraction in the 0.2 to 5 mm. range is first mixed with the solid binder. During this mixing step, heat is applied until the binder is completely liquefied, and only after the cruder particles are completely wetted by the liquefied binder, the particles in the range of sizes finer than 0.2 mm. are added, and mixing of the whole batch is continued until the mixture has attained its highest possible homogeneity.

#### Example II

Baked electrodes used in the electrolytic production of aluminium were manufactured from a petroleum-coke base carbonaceous paste, in which the average size of the pores was of the order of 0.3 mm., the granulometric composition of the coke-dust being as follows:

	Percent
3.33-2.76 mm.....	7
2.76-1.77 mm.....	9
1.77-0.76 mm.....	16
0.76-0.29 mm.....	15
0.29-0.16 mm.....	13
0.16-0.075 mm.....	17
0.075-0 mm.....	23

According to the invention, the particle fraction of from 3.33 to 0.29 mm. was first wetted with the binder, specifically hard pitch as in the foregoing example, then the remaining carbon dust (particles from 0 to 0.29 mm. in size) were added. The batch was thoroughly mixed and the resulting mass was molded under pressure. After firing, an electrode was obtained which has the following characteristics, against the corresponding characteristics of another electrode produced using the conventional mixing procedure:

	Conventional electrode	Improved electrode
Resistivity, ohms, mm. sq./m.....	73	54
Crushing strength, kg./cm. sq.....	245	315

#### Example III

A paste, intended for use as a coating for the internal lining of a furnace, was constituted by a

5

mixture of 25% anthracite and 75% metallurgical coke, of the following granulometrical composition:

	Percent
5.54-2.67 mm.....	3
2.67-1.77 mm.....	6
1.77-0.99 mm.....	5
0.99-0.45 mm.....	21
0.45-0.19 mm.....	21
0.19-0.075 mm.....	23
0.075-0 mm.....	21

The anthracite used was not porous and the pores of the metallurgical coke were less than 0.2 mm. in size. According to the invention, the particle fraction of from 5.54 to 0.19 mm. was first wetted with the binder. The binder used in this example specifically comprised soft pitch, i. e. pitch having a Krämer-Sarnow softening point in the range of from 40° C. to 50° C. Then the particle fraction including the sizes from 0 to 0.19 mm. was added and the whole batch was intimately mixed.

Example IV

Electrode pastes intended for use in electrothermal production processes comprised a mixture of 70% anthracite and 30% metallurgical coke, having the following granulometric composition:

	Percent
25.4-11.9 mm.....	6
11.9-5.54 mm.....	7
5.54-2.67 mm.....	17
2.67-1.77 mm.....	5
1.77-0.99 mm.....	4
0.99-0.45 mm.....	4
0.45-0.19 mm.....	8
0.19-0.09 mm.....	22
0.09-0 mm.....	27

The anthracite used was not porous, and the metallurgical coke constituent provided the finer grains, less than 0.16 mm. in size. Thus the carbon particles were practically free of pores. According to the invention, the particle fraction of from 25.4 to 0.19 mm. was first wetted with the binder. The binder composition used by way of example in this operation comprised a mixture of hard pitch and coal-tar. Then the grain fractions in the range of sizes from 0 to 0.19 mm. were added and the whole batch intimately mixed. An electrode paste was thus obtained which, after molding and firing, gave the following comparative test results:

	Conventional electrode	Improved electrode
Resistivity, ohms, mm. sq./m.....	61	51
Crushing strength, kg./cm. sq.....	295	375

Example V

A carbon paste for graphitized electrodes comprised, by way of example, petrol coke of the following granulometric composition:

	Percent
1.30-0.62 mm.....	22
0.62-0.29 mm.....	21
0.29-0.16 mm.....	7
0.16-0.10 mm.....	18
0.10-0.075 mm.....	4
0.075-0.058 mm.....	4
0.058-0.050 mm.....	4
0.050-0 mm.....	20

6

The average dimension of the pores was about 0.3 mm. According to the invention, the particles in the range of sizes of from 1.3 to 0.29 mm. were first wetted with the binder, which in this instance was hard pitch. Then the particle fractions in the range of from 0 to 0.29 mm. were added and the whole batch intimately mixed together. An electrode paste was obtained giving the following comparative test results:

	Conventional electrode paste	Improved electrode paste
Apparent specific gravity.....	1.675	1.718

It will of course be understood that the invention is in no way limited to the details of procedure and compositions specifically mentioned in the above examples, and that the scope of the invention is to be construed as defined exclusively by the ensuing claims.

What I claim is:

1. Method of producing a carbon paste from a batch of finely divided solid carbonaceous material and a binder for said carbonaceous material wherein the carbonaceous material consists of particles of various sizes, which comprises the steps of separating the batch of carbonaceous material into two fractions constituted respectively of relatively coarse particles and fines whereby the smallest-sized particles in said fraction of relatively coarse particles are substantially similar in size to that of the pores of the largest-sized particles therein, mixing said binder with the fraction of coarse particles until substantially all of said coarse particles are wetted by said binder, adding the fines to the wetted coarse particles and continuing the mixing operation until no further noticeable increase in the homogeneity of the resultant mixture is observed.
2. A method according to claim 1, characterized in that the separated fraction of relatively coarse particles represents about 30 to 75% by weight of the total amount of the batch of finely divided carbonaceous material.
3. A method according to claim 1, wherein the smallest-sized particles of said fraction of relatively coarse particles have a dimension substantially equal to 0.2 mm.
4. A method according to claim 1, wherein said fraction of relatively coarse particles is wetted with only a portion of the total amount of binder used in the preparation of the paste, and the balance of said binder is added together with said fines.
5. A method according to claim 1, wherein said binder is added in liquid condition.
6. A method according to claim 1, wherein the fraction of relatively coarse particles is mixed with a binder in solid condition, heat is applied to fluidify said binder during mixing to thoroughly wet said coarser particles, the fines are added, and the mixing of the entire batch is continued until no further noticeable increase in the homogeneity of the resulting mixture is observed.

STEFAN STANKO.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,317,497	Hinckley	Sept. 30, 1919
2,563,285	Shea et al.	Aug. 7, 1951