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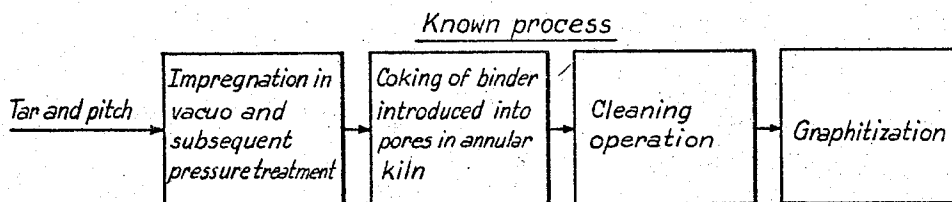
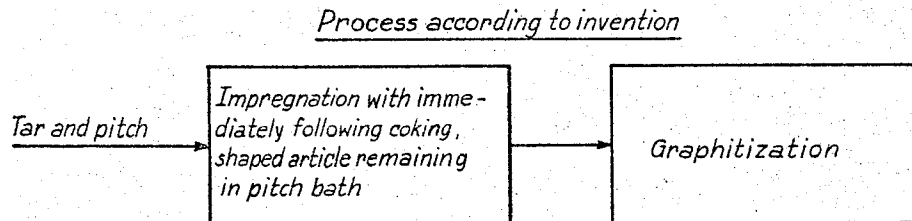
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*I. Compression of shaped carbon articles by impregnation with pitch and subsequent coking**II. Compression of shaped carbon articles by impregnation in pitch bath and immediately following coking in one operation*INVENTOR:  
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1

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## SHAPED BODIES OF CARBON AND PROCESS FOR PREPARING SAME

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The present invention relates to shaped bodies and a process for preparing same. It is known to compress prebaked carbon or graphitized shaped bodies which due to their special way of being prepared are always porous, by impregnating them with tar, pitch or resins and by coking the infiltrated impregnating agent in a subsequent heat treatment. Prebaked shaped bodies of carbon are such bodies as have slowly been heated to a temperature of at least 750° C. The upper heating limit may be at about 1300° C. It largely depends upon the material of the receptacle in which the bodies are heated. In addition to a considerable reduction of the pore volume and the reduced permeability for gases and liquids connected therewith, the impregnation with subsequent coking helps to increase considerably the tensile strength. The reduction of the pore volume is accompanied by an improved electrical conductivity and a raised resistance to oxidation.

In order to reach this effect the following procedure was applied hitherto:

In the first phase of the process liquid pitch is soaked into the pores of the prebaked impregnation material by applying a vacuum. Generally the pitch is charged onto the evacuated goods to be impregnated under maintenance of the appropriate temperatures, i.e. of about 150° C. to about 200° C., and the penetration of the liquid impregnating agent is accelerated by working under pressure, of, for instance, about 6-8 atmospheres. When the impregnation is well performed the open pores of the shaped body are filled to 96%-98% with the impregnating agent. Then the impregnation material is introduced into an electrode baking furnace, in order to coke the pitch penetrated into the pores. The coke formed in this baking process under reducing conditions supports the structure of the shaped body and effects an improvement of the values of the tensile strength of about 25-40% compared with non-impregnated material. The impregnation and the following coking may be repeated whereby the obtained compression is reduced with each treatment.

The impregnation of graphitized shaped bodies is realized in the same manner. According to the intended use the pitch present in the pores is only coked in the baking furnace or it is, in addition, subsequently graphitized. Coking and graphitizing of the impregnating agent can also be effected in one operating phase in the graphitizing furnace.

When the known coking processes are applied, the material in the baking furnace is embedded in a layer of coke powder and subjected to a baking process of several weeks. The expected quantity of coke depositing in the pores can be ascertained by the degree of impregnation and the coking value of the used impregnating agent. It has been found out that the actual values are always less the calculated values, i.e. that a large part of the pitch laboriously pressed into the pores is lost when the usual manner of coking is applied. This

2

lost portion is considerable and generally amounts to about 25-30%, in the most unfavorable case even to about 50% of the pitch quantity soaked in. These losses are nearly exclusively due to the fact that during the heating in the annular furnace the volume of the pitch is increased with the progressively higher temperatures and flows out of the pores. At temperatures of more than 150° C. the pitch used for the impregnation is so highly fluid that, at the margins, it flows out of the larger pores without any expansion pressure being effective, and is soaked into the heaped up coke powder. This powder impregnated with pitch, when being coked, bakes to a compact mass which can be removed from the shaped bodies of coal only with difficulties.

Apart from the loss of precious carbon substance hereby caused reduction of the effect intended by the impregnation of the prebaked shaped body represents a great disadvantage of the known manner of operation. In the case of thin plates and tubes as well as shaped bodies with a system of pores of a larger diameter often one half, only, of the originally soaked-in pitch is coked within the pores themselves.

I have found that shaped and prebaked carbon bodies, which may also be graphitized, can be impregnated and baked until coking of the impregnating agent is effected by keeping the shaped bodies immersed in pitch during the coking procedure according to the invention. It is, therefore suitable to place them into a bath of liquid pitch.

When operating according to the present invention the pitch present in the state of resoftening is hindered from flowing out by the hydrostatic pressure of the ambient liquid pitch. In this manner, especially the compression of the marginal portions is best guaranteed, this being particularly necessary for obtaining a high tensile strength. When removing the coked residues of excess pitch which surround the shaped bodies, it has surprisingly been found that the residues break away easily and the shaped bodies do not need any additional cleaning. The pitch coke resulting therefrom represents an excellent raw material which can directly be used for the production of electrodes.

The significant differences between the process of the invention and the known process will become further apparent by reference to the accompanying drawing.

The following table shows, for comparison, some physical properties of carbon shaped bodies which after impregnation with soft pitch (softening point according to Krämer-Sarnow 55° C.) have been coked in compliance with the normal vacuum pressure process once in the usual manner under coke powder and once, according to the invention, in a pitch bath.

### Example 1

Six baked round carbon bodies each having a diameter of 128 mm. and a length of 300 mm. were subjected to subatmospheric pressure in a vessel and subsequently covered, at 180° C., with soft pitch having a softening point of 55° C. according to Krämer-Sarnow. After breaking the vacuum, the system comprising carbon bodies and pitch was maintained under a gauge pressure of 8 atmospheres for one hour. After being freed from excess pitch and adhering pitch film, the carbon bodies were weighed. Thereupon three of the bodies were subjected to coking in an annular furnace under coke powder in the usual manner (treatment A) and the remaining three were placed into a bath of liquid pitch and coked (treatment B) under otherwise equal conditions. The losses of weight in the baking operation,

the bulk densities and the pore volumes were measured and are tabulated immediately below:

| Treatment | Losses of Weight in Baking, percent | Bulk Density (Weight per unit of vol.), kg./liter | Volume of Pores, percent |
|-----------|-------------------------------------|---------------------------------------------------|--------------------------|
| A-----    | 6.7                                 | 1.70                                              | 14.6                     |
| A-----    | 8.0                                 | 1.69                                              | 14.3                     |
| A-----    | 7.4                                 | 1.70                                              | 14.3                     |
| B-----    | 5.5                                 | 1.75                                              | 11.6                     |
| B-----    | 5.4                                 | 1.76                                              | 11.7                     |
| B-----    | 5.9                                 | 1.75                                              | 11.7                     |

When operating without losses and based on a coking value of 60% for the pitch used, a reduction of the pore volume of 6.5-7% absolute is calculated for a shaped body having an initial volume of the pores of 18-20% and having been completely impregnated. As in the above example the pore volume of the bodies coked under pitch is reduced by 2.7% absolute, the yielded improvement amounts to 40% relatively considered.

The coking procedure according to the invention may, on the one hand, be applied when shaped carbon bodies are concerned which have been impregnated, by a special treatment, in an installation working under a vacuum and pressure. It has the advantage of depositing a greater amount of coke and effecting a corresponding improvement of the quality of the product, as shown in Example 1.

On the other hand, however, it is possible to combine in one process the impregnation and the coking when applying the process according to the invention. This is an especially simple solution from the technical point of view. For this purpose, prebaked shaped bodies which are not yet impregnated are placed into liquid pitch, the quantity of which is so calculated that after complete filling of the pores the impregnated material is still just covered by pitch. As the temperatures in the electrode baking furnaces rise but very slowly, the liquid pitch is given enough time to penetrate into the pores. The special advantage of this variation of the process also resides in the fact that, apart from the iron tanks for the reception of the pitch material to be impregnated there-

port and energy, compared with the working procedure in separate stages.

The details of this manner of operating are described in the following example:

#### Example 2

100 kgs. of prebaked shaped carbon bodies of different form are evacuated in an iron vessel placed in a chamber under vacuum and covered by 60.0 kgs. of liquid soft pitch of 135° C. The filling height of the pitch is so calculated that the pitch surface exceeds the filling level of the coal bodies by 50 mm.

The filled vessel is introduced into an annular furnace and coked within 22 days in the normal baking cycle.

As the coking soft pitch results in a coke cake showing numerous fissures, it is possible to loosen the impregnated shaped bodies without difficulty from the coke when the process is finished. After this treatment the shaped bodies had a weight of 106.4 kgs., which is equal to an increase of weight of 6.4% referred to the starting weight. The yield of pitch coke amounts to 31.0 kgs. corresponding to 51.7% of utilizable coke, referred to the pitch introduced.

The following example refers to shaped carbon bodies having one small dimension, for instance thin-walled tubes, rings, thin plates or rods of small diameter. In this case the known processes proved to be insufficient. According to the new process, however, impregnation and the coking, free of losses, is possible without any difficulties, as can be seen from data in the table of Example 3.

#### Example 3

Two prebaked carbon tubes having an external diameter of 40 mm., a wall thickness of 8 mm. and a length of 139 and 141 mm. respectively were used. As described in the foregoing example, the first sample was impregnated in the pitch bath and coked in one phase. The second sample was impregnated according to the method described in Example 1 and then coked under coke powder. The greater efficiency of the process according to the invention is to be seen in the following table giving the technological data.

| Kind of process                                                                           | test material                                                       | before the treatment |                        |                 | after the treatment |                 |         |                        |                 |
|-------------------------------------------------------------------------------------------|---------------------------------------------------------------------|----------------------|------------------------|-----------------|---------------------|-----------------|---------|------------------------|-----------------|
|                                                                                           |                                                                     | weight, grams        | weight per unit volume | volume of pores | weight, gr.         | weight increase |         | weight per unit volume | volume of pores |
|                                                                                           |                                                                     |                      |                        |                 |                     | gr.             | percent |                        |                 |
| according to invent. impregnated in 1 phase, coked under pitch without applying a vacuum. | tube of 40 mm. ext. $\phi$ , 24 mm. int. $\phi$ baked 139 mm. long. | 164.9                | 1.51                   | 22.5            | 184.5               | 19.6            | 11.9    | 1.72                   | 13.5            |
| Impregnated in an apparatus under vacuum and pressure coked under a packing mass.         | tube of 40 mm. ext. $\phi$ , 24 mm. int. $\phi$ baked 141 mm. long. | 165.4                | 1.49                   | 23.0            | 180.8               | 15.4            | 9.4     | 1.67                   | 17.1            |

with, no complicated pressure or vacuum installations are necessary. The fact that the preheating period in the annular furnace extends over a long period—about four days with raising of the temperature from about 100° C.

The following Example 4 shows the application of the invention in the case of using a graphitized coal tube and clearly demonstrates the high efficiency of the process when applied for graphitized bodies:

#### Example 4

| Process                                                                                | test material                                                                | before the treatment |                        |                 | after the treatment |                 |         |                      |                 |
|----------------------------------------------------------------------------------------|------------------------------------------------------------------------------|----------------------|------------------------|-----------------|---------------------|-----------------|---------|----------------------|-----------------|
|                                                                                        |                                                                              | weight, grams        | weight per unit volume | volume of pores | weight, grams       | weight increase |         | weight per unit vol. | volume of pores |
|                                                                                        |                                                                              |                      |                        |                 |                     | gr.             | percent |                      |                 |
| according to the invention impregnated and coked in 1 phase without applying a vacuum. | graphitized tube 48.6 mm. ext. $\phi$ , 33.4 mm. int. $\phi$ , 248 mm. long. | 366                  | 1.51                   | 24.3            | 413.6               | 47.6            | 13.0    | 1.70                 | 14.0            |

to about 500° C.—renders a good impregnation possible and, furthermore, helps to save expenses for labor, trans-

According to the invention it is especially easy to densify carbon and graphite crucibles, the prebaked cru-

cibles being filled with liquid or also with cool pitch and placed into the baking furnace. As the crucibles themselves serve as receptacles, special vessels are not necessary. The advantages of the process according to the invention are not restricted to its application when thin plates or thin-walled tubes are concerned; bodies of good properties are also obtained when the process is applied to larger dimensioned bodies, as shown by the Example 5.

#### Example 5

| Process                                                                    | test material                             | before the treatment |                        |                 | after the treatment |                 |         |                      |
|----------------------------------------------------------------------------|-------------------------------------------|----------------------|------------------------|-----------------|---------------------|-----------------|---------|----------------------|
|                                                                            |                                           | weight, kg.          | weight per unit volume | volume of pores | weight, kgs.        | weight increase |         | weight per unit vol. |
|                                                                            |                                           |                      |                        |                 |                     | kgs.            | percent |                      |
| according to the invention impregnated in one phase and coked under pitch. | round body 195 mm. $\phi$ , 245 mm. long. | 12.02                | 1.64                   | 18.0            | 12.75               | 0.73            | 6.1     | 1.75                 |
|                                                                            |                                           |                      |                        |                 |                     |                 |         | 12.4                 |

The comparative values tabulated in the following Example 6 show the superiority of the process according to the invention also as regards the values of tensile strength.

#### Example 6

| Kind of test material                     | bending strength, kg/cm. <sup>2</sup> |                                                                                |                                                                                  |
|-------------------------------------------|---------------------------------------|--------------------------------------------------------------------------------|----------------------------------------------------------------------------------|
|                                           | non-treated sample                    | impregnated in the apparatus under vacuum and pressure coked under coke powder | according to the invention impregnated under liquid pitch and coked in one phase |
| rods of 40 x 40 mm., 120 mm., long baked: |                                       |                                                                                |                                                                                  |
| sample I.....                             | 193                                   | 246                                                                            | 263                                                                              |
| sample II.....                            | 198                                   | 251                                                                            | 277                                                                              |

In certain cases the filling under vacuum of the vessels charged with impregnated material may be of advantage. In order to facilitate penetration of the impregnating agent it is suitable, in the case of cylindrical bodies, to remove, in a thin layer, the skin which is formed during the baking procedure, or, when prismatic shaped bodies are concerned, to scratch the skin at spaced intervals in order to make it more permeable to the pitch. Example 7 illustrates the better effect to be obtained by abrading the baking skin.

#### Example 7

| Process                                                                    | test material                                   |              | increase in weight percent | weight per unit volume | volume of pores |
|----------------------------------------------------------------------------|-------------------------------------------------|--------------|----------------------------|------------------------|-----------------|
| According to the invention in one phase impregnated and coked under pitch. | rods of 50 x 50 mm. baked with baking skin.     | 1st test.... | 6.4                        | 1.67                   | 16.2            |
|                                                                            |                                                 | 2nd test.... | 6.3                        | -----                  | -----           |
|                                                                            |                                                 | 3rd test.... | 5.9                        | -----                  | -----           |
|                                                                            | rods of 50 x 50 mm. baked, baking skin abraded. | 1st test.... | 8.2                        | 1.69                   | 14.9            |
|                                                                            |                                                 | 2nd test.... | 7.8                        | -----                  | -----           |
|                                                                            |                                                 | 3rd test.... | 7.9                        | -----                  | -----           |

#### I claim:

1. A process for treating a prebaked and shaped carbon body which comprises impregnating and immersing a prebaked shaped carbon body with and in a bath of liquid pitch, baking the impregnated and still immersed body until coking of the impregnated pitch is effected, and thereafter separating the baked body from the carbonaceous matter formed from the bath of liquid pitch during the baking step.

2. A process as defined in claim 1 wherein the impregnation is effected by subjecting the carbon body to re-

duced pressure and then immersing it in a bath of liquid pitch.

3. The process defined in claim 1, wherein the impregnation and the coking are effected by immersion of the prebaked shaped body in a vessel containing pitch and placing the vessel in a baking furnace.

4. The process defined in claim 3, including the subsequent step of graphitizing the body.

5. The process defined in claim 4, wherein the impregnation is effected by charging liquid pitch under vacuum into the vessel containing the preshaped coal body.

6. A process for treating a prebaked and shaped carbon body which comprises removing a portion of the skin formed on said body in the prebaking operation, impregnating and immersing said prebaked shaped carbon body with and in a bath of liquid pitch, baking the impregnated and still immersed body until coking of the impregnated pitch is effected, and thereafter separating the baked body from the carbonaceous matter formed from the bath of liquid pitch during the baking step.

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