428-408. UR 2908 9342 SR

SEARCH ROOM

Patented Aug. 3, 1954

2,685,542

UNITED STATES PATENT OFFICE

2,685,542

REFRACTORY CARBON AND METHOD OF PRODUCING THE SAME

James Woodburn, Jr., Youngstown, and Rawley F. Lynch, Niagara Falls, N. Y., assignors to Great Lakes Carbon Corporation, New York, N. Y., a corporation of Delaware

3406
X2261

No Drawing. Application April 7, 1953, Serial No. 347,387

32 Claims. (Cl. 117—169)

1

This invention relates to methods of producing refractory and oxidation-resistant compositions based upon carbon and graphite. More particularly, this invention relates to methods for preparing carbon and graphitic bodies containing in the pores thereof alkali metal phosphate compositions, the resulting material being resistant to oxidation. The term alkali metal includes the metals sodium, potassium, lithium, rubidium, and cesium. However, for the purpose of this invention, the preferred alkali metal phosphate compounds are those of sodium and potassium.

The use of massive carbon and graphite bodies as refractory material is of long standing in the art, and the application of such material for the construction of furnace and runner linings, mold stock for the pouring or casting of molten metals and other hot molten compositions, is progressively increasing. In many of these applications, a major drawback in the use of carbon and graphite resides in the fact that it is not resistant to oxidation, particularly at temperatures in excess of 500° C. This condition is aggravated in the event that the molten or hot composition itself exerts an oxidizing effect upon the carbon; for example, in the casting of fused alumina. Also, the erosion effect of molten metals upon carbon and graphite is quite pronounced, particularly in an oxidizing atmosphere.

Various attempts have been made to improve the properties of carbon and graphite to render it more resistant to oxidation. For example, it has been the practice to impregnate carbon or graphite with carbonaceous material such as tar or pitch from coal or petroleum sources, or with certain natural or synthetic resinous compositions, followed by carbonizing the impregnant. This procedure increases the apparent density of the base carbon body and reduces its porosity. Such techniques have provided only a partial solution to the problem. In addition, they are quite expensive since the impregnated carbon bodies must be again baked to temperatures in excess of the ultimate service temperature of the carbon stock and for some purposes must be regraphitized to temperatures in excess of 2000° C.

It has also been proposed to impregnate carbon or graphite with phosphoric acid. While this reduces the oxidation of carbon or graphite at low

2

temperatures, we have found that such treatment actually catalyzes oxidation at temperatures in excess of 600° C. Again, others have proposed to incorporate refractory materials; for example, compounds of aluminum, calcium, iron, magnesium, such as the phosphate salts of these metals, directly into the "green" mix prior to formation and baking of the carbon bodies. Such compositions are made up of a small amount of refractory, a small amount of carbonaceous binders such as coal tar or coal tar pitch and a major portion of carbon aggregate. Following an intensive mixing operation in order to evenly distribute the carbonaceous binder, the resulting composition is molded or extruded and baked to temperatures of around 1000° C. Although such compositions have been useful in the manufacture of arc-light carbons; we have found that they do not reduce the tendency toward oxidation, particularly at temperatures in excess of 600° C. Presumably, this is for the reason that the refractory material does not form a continuous phase throughout the baked carbon body, but rather is encased or occluded within a carbon matrix which results from thermal decomposition of the carbonaceous binder.

It is an object of this invention to provide methods for the production of materials of construction based upon carbon and graphite.

It is a further object of the invention to provide methods for the production of massive carbon and graphite bodies or articles having improved resistance to erosion by molten metals and to oxidation by the atmosphere or to hot chemicals which normally oxidize carbon or graphite.

It is a further object of the invention to provide methods for the production of mold-construction material based upon carbon and graphite which has marked resistance to oxidation, particularly up to temperatures of about 800° C.

The above objects as well as others which will become apparent upon understanding of the invention as herein described are achieved by impregnating or depositing in the pores of a previously formed massive carbon or graphite body a composition comprising essentially alkali metal phosphate compound. We have further found that, where M represents one atom of alkali metal, the ratio of M_2O to P_2O_5 in the alkali metal phos-

phate compound impregnant is critical with respect to the ultimate oxidation-resistant properties of the final material. More particularly, we have found that the molar ratio of $M_2O:P_2O_5$ in the alkali metal phosphate compound must be between about 01:1 and about 2.4:1.

It should be understood at the outset that our invention contemplates a treatment by various techniques of previously formed, massive, amorphous (or "gas-baked") carbon and/or graphite with solutions which will deposit alkali metal phosphate compound within the internal and surface pores of the base material as distinguished from adding a phosphate compound to a "green" carbon mix followed by baking, the latter having been previously taught in the art.

In a broad embodiment of the invention an amorphous carbon or graphite body is treated with a solution of alkali metal phosphate compound wherein the molar ratio of $M_2O:P_2O_5$ is between about 0.1:1 and about 2.4:1. This solution may contain various compounds which will deposit the required alkali metal phosphate compound upon drying and heating of the resulting treated material; for example, at temperatures from 150° to 500° C. The resulting treated carbon base material is then dried for several hours at about 100° C. followed by a baking operation at temperatures up to 500° C. in order to insure that all of the solvent from the impregnating solution is removed and to decompose hydrated alkali metal phosphate compounds.

The treatment of carbon or graphite with alkali metal phosphate compound may be accomplished by various techniques according to our invention. Eminently satisfactory results and prolonged service-life of the final material are achieved by impregnation. This is accomplished by placing the carbon or graphite base material in a container which is subsequently evacuated to about 25–30 inches mercury. After several minutes a solution containing (or capable of forming) alkali metal phosphate compound is admitted after which the vessel is pressurized to effect partial or total impregnation of the available voids. Ordinarily, a period of 45–120 minutes will be sufficient for this operation. Alternatively, and where complete penetration or impregnation are not essential or necessary, the base carbon or graphite can be coated (as by brushing or spraying) or soaked with solutions which will deposit alkali metal phosphate compound in the surface and/or sub-surface pores of the carbon or graphite. Alternatively, a combination of the foregoing methods can be employed.

The base carbon (or graphite) materials which are impregnated according to our novel process are adequately described, as to their methods of manufacture and properties, in Mantell, Industrial Carbon, second edition, 1946, particularly in chapters XIII and XVI. The methods of manufacturing the base carbon and graphite materials form no part of this invention. Ordinarily, the amorphous or "gas-baked" carbon which may be treated according to our novel process will have an apparent density (grams/cm.^{3}) of 1.4 to 1.6; the graphitic base material will have an apparent density in excess of 1.4 and preferably 1.6 to 1.8. The higher densities of the graphitic material are achieved by employing pitch impregnated gas-baked carbon which is subsequently graphitized.

In a specific embodiment of the invention, an aqueous solution of sodium phosphate compound wherein the molar ratio of $Na_2O:P_2O_5$ is between about 0.1:1 and about 2.4:1, and preferably between about 0.3:1 to 0.6:1, is admitted to a previously evacuated vessel containing pieces of massive graphite having an apparent density of about 1.7. The system is then pressurized at about 100 lbs. per square inch for 45–120 minutes after which the resulting graphitic pieces are dried at 100° C. for 15 to 20 hours. The dried material is then heated at a temperature of 250° C. for 4 hours to insure that the specimen is completely dry. The resulting composition forms an excellent mold or casting stock in the pouring of fused alumina, glass, pig iron and other molten metals. The active or useful life of such a mold is at least two to three times that of regular graphite.

In preparing the solutions of sodium phosphate compound used in the above embodiment of the invention, the following formulations have been found to be particularly useful:

A. Tribasic sodium phosphate (Na_3PO_4) plus sufficient oxy acid of phosphorus (preferably o-phosphoric acid) or ammonium salt of a phosphoric acid to insure that the molar ratio of $Na_2O:P_2O_5$ is between about 0.1 to about 2.4.

B. Monobasic sodium phosphate—NaH_2PO_4—dissolved in aqueous hydrochloric acid.

C. Dibasic sodium phosphate — Na_2HPO_4 — dissolved in aqueous hydrochloric acid.

D. Sodium pyrophosphate—$Na_4P_2O_7$—dissolved in aqueous hydrochloric acid.

E. Pyrodisodium phosphate — $Na_2H_2P_2O_7$ — dissolved in aqueous hydrochloric acid.

F. Sodium metaphosphate—$NaPO_3$—dissolved in aqueous hydrochloric acid.

In addition to the above formulations, the present invention contemplates employing a solution containing sodium hydroxide, carbonate, or sulfide, along with at least one agent of the group consisting of the oxy acids of phosphorus, their anhydrides, ammonium salts and mixtures of such phosphatic materials, providing that the molar ratio of $Na_2O:P_2O_5$ in the solution is between about 0.1:1 and about 2.4:1. The term "acids of phosphorus" include ortho-, meta-, and pyrophosphoric acid; hypophosphoric acid; ortho-, pyro- and hypo-phosphorus acids and the anhydrides of such acids, for example P_2O_3, P_2O_4, P_2O_5 and mixtures thereof. Alternatively, the mono- and dibasic ammonium salts of the above acids and anhydrides can be employed along with the sodium hydroxide, carbonate, or sulfide.

In a further embodiment of the invention an amorphous carbon or graphite body may be impregnated according to the method mentioned above by employing a "double-impregnation" technique. This involves alternately impregnating the base material with a solution of at least one agent of the group consisting of the oxy acids of phosphorus, their anhydrides, ammonium salts and mixtures of such phosphatic materials, and another solution containing a sodium phosphate such as Na_3PO_4 dissolved in hydrochloric acid, or alternatively a solution containing sodium hydroxide, carbonate, or sulfide, which is reactive with the phosphatic agent to form sodium phosphate compound. The relative amounts of impregnating solutions admitted into the pores of the carbon base body are controlled so that the molar ratio of $Na_2O:P_2O_5$ of the final sodium phosphate compound which is formed therein by interaction between the solutes is between about 0.1:1 and about 2.4:1 and preferably between 0.3:1 and 0.6:1. The various acids of phosphorus, phosphorus anhydrides and ammonium

salts of such compositions as hereinbefore set forth are also applicable to this embodiment of the invention. We have found that a solution containing essentially ortho-phosphoric acid and another solution containing sodium phosphate dissolved in hydrochloric acid are particularly effective in practicing this embodiment of the invention.

In practicing the invention in accordance with the "double-impregnation" technique, it is our practice to dry the carbon base material after each impregnation, usually at 100° C. but often at 250° C. prior to conducting the second impregnation which causes deposition of sodium phosphate compound in the pores of the previously impregnated carbon body. The technique of impregnation involving evacuation and pressurizing of the container is substantially as set forth hereinabove.

In a further embodiment of the invention massive carbon and/or graphite pieces are treated with solutions which will contain (or which will deposit in the pores of the base material under heat treatment) sodium phosphate compound by employing sub-surface treatment techniques. These may involve applying the solutions to the base material by immersion and soaking; by brushing; or by spraying. These treatments will be of sufficient duration, and the solutions in sufficient quantity to apply the solution to the surface or sub-surface portions of the base material in order to deposit therein a desired amount of sodium phosphate compound. The "double-impregnation" technique can also be employed in connection with these procedures, and the carbon base material is usually dried at 100° C., and often at 250° C., between treatment with the individual solutions. While such techniques have been found to be useful for some applications, it will be obvious that the resulting compositions will be effective only as long as the surface or sub-surface remain substantially intact and unexposed to the action of oxidizing agents. For best results and optimum service life, we prefer to employ the previously described impregnation techniques.

In manufacturing the compositions described herein in accordance with our novel process, we contemplate employing one or a plurality of treatments, either with the "single" or "double" impregnation techniques or by spraying or soaking. For example, a solution of sodium phosphate (Na_3PO_4) dissolved in phosphoric acid to give a molar ratio of $Na_2O:P_2O_5$ of between 0.1:1 and 2.4:1 can be used as the impregnating solution in several treatments of the carbon base material. We have found that two or three impregnations with solutions of sodium phosphate compound result in a refractory carbon-base material which is particularly resistant to prolonged exposure (i. e. over two hours) to an oxidizing atmosphere at temperatures in excess of 700° C. Alternatively, when employing the "double" impregnation technique, a series of alternate impregnations can be conducted using any of the aforementioned phosphatic solutions and sodium hydroxide, carbonate, or sulfide solutions reactive therewith to deposit sodium phosphate compound in the pores of the carbon body. We have found that it is possible to effect four to five of such "double" impregnations with attendant significant increase in weight of the final, dried composition. Impregnations in excess of this number result in only minute increases in weight and are usually not justified from an economical standpoint.

The amount of sodium phosphate compound (dry basis after heating to 250° C.) deposited in the base material will depend upon the ultimate use of the refractory product. Generally, from one to ten per cent by weight of the compound, based upon the carbon, will suffice.

Comparable results may be obtained by substituting any other alkali metal for sodium in the specific embodiments recited above. However, a preferable substitute would be potassium.

In order to further illustrate the compositions and techniques which constitute the present invention, the following examples will be recited.

A series of solutions with various molar ratios of $Na_2O:P_2O_5$ of from 0 to 3.0 were prepared using 85% phosphoric acid (H_3PO_4) and/or tribasic sodium phosphate crystals ($Na_3PO_4 \cdot 12H_2O$) and mixtures of these materials. All solutions were prepared to provide a solute concentration of 25% by weight; in some cases it was necessary to increase the acidity of the impregnant to effect solution of sodium phosphate compound by means of hydrochloric acid. Sections of graphite (1.7 apparent density) were placed in a container which was evacuated to 29 inches mercury, this condition being maintained for about 45 minutes. The impregnating solution was then admitted to the container in amounts sufficient to cover the graphite, and the system was returned to atmospheric pressure for 45 minutes in the case of a single impregnation and for 120 minutes in the case of two or three impregnations. The resulting impregnated graphite sections were dried at 105° C. for 16 hours and then heated at 250° C. for about 4 hours. We have found it to be essential that the drying operation be conducted rather carefully in order to avoid "sweating" of the graphite sections which results in exudation of the impregnant.

The heated pieces were quartered by machining and subjected to an oxidation test conducted as follows:

The treated graphite along with untreated material is placed in a laboratory muffle furnace on fire clay supports, the furnace having previously been brought up to test temperature. Air is admitted into the furnace at a rate of 2 liters per minute per sample, and the test is conducted for a certain prescribed length of time.

The results of oxidation tests at 750° C. are set forth in Table I for graphite sections impregnated once with a solution containing sodium phosphate and phosphoric acid (and hydrochloric acid where needed to effect solution) in the indicated ratios of $Na_2O:P_2O_5$.

TABLE I

One impregnation

Example No.	Molar Ratio $Na_2O:P_2O_5$	Percent Oxidation (by weight) at 750° C.	
		1 hr.	2 hrs.
1	0.0	23	37
2	0.3	3	7
3	0.6	4	9
4	0.9	10	20
5	1.2	13	25
6	1.8	12	25
7	2.4	14	31
8	3.0	26	47
Blank (untreated)		22	35

The results of oxidation tests for graphite sections impregnated twice are set forth in Table II.

TABLE II

Two impregnations

Example No.	Molar Radio $Na_2O:P_2O_5$	Percent Oxidation (by weight) at 750° C.			
		1 hr.	2 hrs.	3 hrs.	4 hrs.
9	0.0	23	37	53	63
10	0.3	2	4	8	15
11	0.6	3	5	8	15
12	0.9	8	16	25	34
13	1.2	11	19	31	38
14	1.8	17	30	44	57
15	2.4	18	33	49	63
16	3.0	20	47	68	81
Blank (untreated)		22	36	53	66

Similarly, the results of oxidation tests for graphite sections impregnated three times are set forth in Table III.

TABLE III

Three impregnations

Example No.	Molar Ratio $Na_2O:P_2O_5$	Percent Oxidation (by weight) at 750° C.			
		1 hr.	2 hrs.	3 hrs.	4 hrs.
17	0.0	25	37	54	67
18	0.3	3	6	11	19
19	0.6	3	6	12	20
20	0.9	9	21	31	40
21	1.2	13	25	36	44
22	1.8	14	28	45	56
23	2.4	16	33	56	72
24	3.0	28	48	69	87
Blank (untreated)		23	36	55	69

Table IV summarizes the amount of solid impregnant (sodium phosphate compound or phosphoric acid) which was retained in the pores of the graphite after treatment and baking at 250° C.

TABLE IV

Example No.	No. of Impregnations	Percent Increase in Wt. (Av.)
1	1	1
9	2	3
17	3	6
2-8	1	2
10-16	2	3
18-24	3	4

It will be seen from the above data that the amount of oxidation of the treated graphite, particularly where the molar ratio of $Na_2O:P_2O_5$ is between 0.3:1 and 0.6:1, has been reduced about one-fourth to one-tenth that of the untreated material. There is little difference in the oxidation resistance of samples impregnated twice and those impregnated three times. There is, however, a decided improvement in the samples impregnated twice over those impregnated once.

EXAMPLE 25

A graphite section having an apparent density of 1.7 was impregnated with a saturated solution of ortho-phosphoric acid and followed by a drying operation at 100° C. for 12 hours. The resulting piece was then impregnated with a solution of caustic soda, controlling the degree of concentration of this solution so that the resulting sodium phosphate compound deposited in the pores of the graphite had a molar ratio of $Na_2O:P_2O_5$ of 0.6:1. After drying and baking as outlined in the previous examples, this material was subjected to air oxidation at 750° C. and the rate of oxidation determined to be about one-tenth that of the untreated material.

EXAMPLE 26

The treatment described in Example 25 was repeated except that caustic potash was substituted for the caustic soda. The improvement in oxidation resistance of the treated graphite was of the same order of magnitude.

EXAMPLE 27

A saturated solution of o-phosphoric acid in water and another solution of sal soda (sodium carbonate) were used as impregnants in treating graphite sections having an apparent density of 1.67. Following the first impregnation with phosphoric acid solution and drying at 100° C. for 12 hours, the resulting piece was impregnated with sodium carbonate solution, controlling the concentration of the latter solution so that the molar ratio of $Na_2O:P_2O_5$ in the deposited impregnants was 0.6:1. Two of these cycles were employed, the pieces being dried at 100° C. after each impregnation. After heating at 250° C. to effect dehydration the treated graphite and untreated graphite were tested for resistance to oxidation at 750° C., the results being as follows.

TABLE V

	Oxidation (Percent Loss by Weight)	
	1 hr.	2 hrs.
Untreated graphite	26	39
Treated graphite	4	6

EXAMPLE 28

The procedure described in Example 27 was repeated except that sodium sulfide was substituted for the sodium carbonate. The improvement in oxidation resistance of the treated graphite over the untreated graphite was of the same order of magnitude.

It is to be understood that the above specific examples are recited merely by way of illustration and not by way of limitation. Nor is the invention limited to the specific solutions or combinations of reagents set forth. It should be understood that any combination of solutions which contain or which will form alkali phosphate compounds in the claimed ratio of $M_2O:P_2O_5$ either at atmospheric temperatures or pressures, or at elevated temperatures or pressures, will be employed within the scope of the invention. It should also be understood that volatile acids other than hydrochloric may be employed to effect substantial solution of alkali metal phosphate compound in the treating solution.

We claim:

1. A method for producing an oxidation-resistant, refractory material which comprises impregnating a carbon body with a solution comprising essentially alkali metal phosphate compound, the molar ratio of $M_2O:P_2O_5$ in said compound being between about 0.1:1 and about 2.4:1, said letter M symbolizing one atom of alkali metal, and drying the impregnated body to remove substantially all of the solvent therefrom.

2. The method according to claim 1 wherein the essential components of the impregnation solution consist essentially of sodium phosphate

(Na_3PO_4) and o-phosphoric acid in a molar ratio of $Na_2O:P_2O_5$ of between about 0.3:1 and about 0.6:1.

3. The method according to claim 1 wherein the essential components of the impregnation solution consist essentially of potassium phosphate (K_3PO_4) and o-phosphoric acid in a molar ratio of $K_2O:P_2O_5$ of between about 0.3:1 and about 0.6:1.

4. A method for producing an oxidation resistant, refractory material which comprises placing in the pores of a carbon body a solution comprising essentially alkali metal phosphate compound, the molar ratio of $M_2O:P_2O_5$ in said compound being between about 0.1:1 and about 2.4:1, said letter M symbolizing one atom of alkali metal, and drying the impregnated body to remove substantially all of the solvent therefrom.

5. The method according to claim 4 wherein the molar ratio of $M_2O:P_2O_5$ is between about 0.3:1 and about 0.6:1.

6. A method for improving the resistance to oxidation of a graphite body which comprises impregnating said body with a solution comprising essentially alkali metal phosphate compound, the molar ratio of $M_2O:P_2O_5$ in said compound being between about 0.1:1 and about 2.4:1, said letter M symbolizing one atom of alkali metal, and drying the impregnated body to remove substantially all of the solvent therefrom.

7. A method for improving the resistance to oxidation of a body of gas-baked carbon which comprises at least partially impregnating said body with a solution comprising essentially alkali metal phosphate compound, the molar ratio of $M_2O:P_2O_5$ in said compound being between about 0.1:1 and about 2.4:1, said letter M symbolizing one atom of alkali metal, and drying the impregnated body to remove substantially all of the solvent therefrom.

8. The method according to claim 7 wherein the molar ratio of $M_2O:P_2O_5$ is between about 0.3:1 and about 0.6:1.

9. A method of improving the resistance to oxidation of a carbon body which comprises impregnating said body with a solution wherein the solutes comprise essentially alkali metal hydroxide and at least one agent of the group consisting of the oxy acids of phosphorus, their anhydrides, their mono- and di-ammonium salts and mixtures thereof, the ratio of $M_2O:P_2O_5$ in said solution being between about 0.1:1 and about 2.4:1, said letter M symbolizing one atom of alkali metal, and drying the impregnated body to remove substantially all of the solvent therefrom.

10. The method according to claim 9 wherein the alkali metal hydroxide is sodium hydroxide and the acid of phosphorus is o-phosphoric acid.

11. The method of claim 9 wherein the alkali metal hydroxide is potassium hydroxide and the ammonium salt of the oxy acid of phosphorus is o-phosphoric acid.

12. A method for improving the resistance to oxidation of a carbon body which comprises alternately impregnating said body with a solution of at least one agent of the group consisting of the oxy acids of phosphorus, their anhydrides, their mono- and di-ammonium salts and mixtures thereof and a solution of a compound of the group consisting of the phosphates, carbonates, hydroxides and sulfides of an alkali metal, the amount of said solutions absorbed by said body being so controlled that the resulting alkali metal phosphate compound formed in said body has a molar ratio of $M_2O:P_2O_5$ of between about 0.1:1 and about 2.4:1, said letter M symbolizing one atom of alkali metal, and drying the impregnated body to remove substantially all of the solvent therefrom.

13. The method according to claim 12 wherein the impregnation solutions contain alkali metal carbonate and o-phosphoric acid in a molar ratio of $M_2O:P_2O_5$ of between about 0.3:1 and about 0.6:1.

14. The method according to claim 12 wherein the impregnation solutions contain alkali metal sulfide and o-phosphoric acid in a molar ratio of $M_2O:P_2O_5$ of between about 0.3:1 and about 0.6:1.

15. The method according to claim 12 wherein the impregnation solutions comprise essentially o-phosphoric acid and alkali metal phosphate in hydrochloric acid.

16. A method for improving the resistance to oxidation of a carbon body which comprises applying thereto a solution comprising essentially alkali metal phosphate compound, the molar ratio of $M_2O:P_2O_5$ of said compound being between about 0.1:1 and about 2.4:1 and drying said body to remove the solvent therefrom, said letter M symbolizing one atom of alkali metal.

17. The method according to claim 16 wherein the alkali metal phosphate is sodium phosphate and the molar ratio of $Na_2O:P_2O_5$ is between about 0.3:1 and about 0.6:1.

18. The method according to claim 16 wherein the alkali metal phosphate is potassium phosphate and the molar ratio of $K_2O:P_2O_5$ is between about 0.3:1 and about 0.6:1.

19. A carbon body of improved resistance to oxidation containing in the pores thereof a composition comprising essentially alkali metal phosphate compound, the molar ratio of $M_2O:P_2O_5$ in said compound being between about 0.1:1 and about 2.4:1, said letter M symbolizing one atom of alkali metal.

20. A refractory, oxidation-resistant material consisting of a body of graphite and containing in the pores of said body a composition comprising essentially alkali metal phosphate compound, the molar ratio of $M_2O:P_2O_5$ in said compound being between about 0.1:1 and about 2.4:1, said letter M symbolizing one atom of alkali metal.

21. A material according to claim 20 wherein the graphite has an apparent density in the range of 1.6 to 1.8 prior to placing alkali metal phosphate compound in the pores of the graphite body.

22. A material according to claim 20 wherein the molar ratio of $M_2O:P_2O_5$ is between about 0.3:1 and about 0.6:1.

23. A material according to claim 20 wherein the resulting graphitic body contains between about 1.0 and about 10.0% by weight of alkali metal phosphate compound.

24. A material according to claim 20 wherein the ratio of $M_2O:P_2O_5$ is between about 0.3:1 and about 0.6:1, and wherein the resulting graphitic body contains between about 1.0 and 10.0% by weight of alkali metal phosphate compound.

25. A refractory, oxidation-resistant material consisting of a body of gas-baked carbon and containing in the pores of said body a composition comprising essentially alkali metal phosphate compound, the molar ratio of $M_2O:P_2O_5$ in said compound being between about 0.1:1 and

about 2.4:1, said letter M symbolizing one atom of alkali metal.

26. A material according to claim 25 wherein the molar ratio of $M_2O:P_2O_5$ is between about 0.3:1 and about 0.6:1.

27. A carbon body containing in the pores thereof a mixture of Na_3PO_4 and an oxy acid of phosphorus in amounts so that the molar ratio of $Na_2O:P_2O_5$ is between about 0.1:1 and about 2.4:1.

28. A carbon body according to claim 27 wherein the molar ratio of $Na_2O:P_2O_5$ is between about 0.3:1 and about 0.6:1.

29. A carbon body according to claim 27 wherein the oxy acid of phosphorus is o-phosphoric acid.

30. A carbon body containing in the pores thereof a mixture of K_3PO_4 and an oxy acid of phosphorus in amounts so that the molar ratio of $K_2O:P_2O_5$ is between about 0.1:1 and about 2.4:1.

31. A carbon body according to claim 30 wherein the molar ratio of $K_2O:P_2O_5$ is between about 0.3:1 and about 0.6:1.

32. A carbon body according to claim 30 wherein the oxy acid of phosphorus is o-phosphoric acid.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
504,105	Corleis et al.	Aug. 29, 1893
1,566,409	Lavene	Dec. 22, 1925
2,626,871	Zinsger	Jan. 27, 1953