United States Patent Office

3,303,031
Patented Feb. 7, 1967

3,303,031

CARBONACEOUS RAMMING PASTE

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No Drawing. Filed Dec. 9, 1965, Ser. No. 512,801
20 Claims. (Cl. 106—56)

This application is a continuation-in-part application of application Serial No. 271,489, entitled "Carbonaceous Ramming Paste," filed April 8, 1963, and now abandoned.

This invention relates to a unique carbonaceous ramming paste, and refers more particularly to a thermosetting cold ramming carbonaceous paste, that is, one which is plastic and rammable in its "as received" condition without having to be pre-heated.

In the metal producing industry various cements and pastes are used in the patching of and repairing of cupola linings, furnace linings, other high temperature apparatus, taphole areas, run-out throughs and the like. They are also utilized in other miscellaneous metallurgical applications which require durable refractory materials such as in the joints between structural forms of carbon. Heretofore, most conventional carbonaceous ramming pastes were thermoplastic, granular and solid-like at room temperature and had to be heated up on site to make them plastic enough to be rammed or tamped into place manually with a trowell or with an air gun. The heating of these previous type carbonaceous pastes is cumbersome and requires additional on site equipment. The temperature controls on such equipment must be precise in order to permit a high degree of thermal control since it is rather difficult to heat the prior art pastes to a desired uniform workable consistency. The equipment must also be provided with vented hoods and other fume control devices to remove any objectionable and/or toxic vapors and fumes which are formed.

Furthermore, if the standard prior type pastes are heated in a crude fashion, as is usually done in smaller establishments, i.e., in a container which is heated over an open gas torch, localized overheating usually occurs thus causing the pastes to be of variable plasticity and of inferior quality. Another disadvantage of these pastes is the difficulty in handling them while hot which invariably results in greater waste.

It is, therefore, the principal object of the invention to provide a carbonaceous ramming paste, which does not have to be preheated in order to become rammable.

Another object is to provide a cold ramming paste plastic enough to ram, yet firm enough to build monolithic walls or blocks.

A further object is to provide a cold ramming paste which can be air "gunned" in place or manually trowelled in place.

Yet a further object is to minimize the amount of waste generated when using a ramming paste.

The invention by means of which these objects are achieved comprises a dry carbonaceous blend which when mixed with a sufficient amount of water becomes plastic at room temperature. The blend is composed of relatively coarse classified carbonaceous particles, a high melting point primary binder, a water soluble secondary binder, plastic clay, and fine carbon flour. As used herein, the term "carbonaceous" refers to materials known in the art as carbon, graphite, coke and/or mixtures thereof.

Other aims and advantages of the invention will be readily apparent from the following description and appended claims.

In accordance with a preferred embodiment of the invention, the objects are accomplished by mixing together, in the proper proportions as set forth hereinafter, carbon particles and carbon flour, a plastic clay, a milled pitch having a high melting point of from about 150° C.

to about 175° C., which serves as a permanent primary binder and, as a temporary secondary binder, an aqueous solution comprising calcium lignosulfonate and water in a weight ratio of about 55:45. The calcium lignosulfonate will be referred to hereinafter as UCL, i.e., unrefined calcium lignosulfonate. The constituents of the paste should be preferably blended in a particular order as subsequently disclosed herein to preclude and minimize particle breakdown.

The paste contains, by weight percentages about 5 percent to 20 percent flour, 20 percent to 50 percent particles, 10 percent to 15 percent of the milled pitch, 12 percent to 40 percent milled plastic clay, and the remainder being the solution of UCL and water, the water being present in an amount of from about 7 percent to 14 percent, and the calcium lignosulfonate being present in an amount of from about 8 to 15 percent. The carbon particles and carbon flour are used in a weight ratio of about 2:1 to about 3:1. The particles may be constituted from anthracite coal, metallurgical or petroleum coke, preferably calcined, or graphite, and can range in size from about ½ inch to about 1/32 inch, particularly from about ¼ inch to about 1/32 inch in the case of graphite, and from about ½ inch to about 1/16 inch in the case of anthracite. The flour may be made from these same materials. The flour should be milled such that 45 percent will pass through a 200 mesh screen. The plastic clay particles are milled to pass 100 percent through a 20 mesh screen.

The use of the temporary binder in conjunction with the plastic clay serves a two-fold purpose. Initially it gives green strength to the paste and makes the paste plastic and rammable and it also provides a temporary preset to the paste after drying at room temperature. The temporary binder should not dissolve the permanent binder and with the clay should harden at a temperature substantially below the melting point of the permanent binder.

Although, either an organic material or an inorganic material or mixtures thereof may be used as the temporary binder, it must harden at a temperature substantially below the melting point of the pitch (permanent binder) and it must also provide sufficient plasticity to render the paste rammable. Examples of materials that have been found to be suitable in the practice of the invention are sodium silicate, colloidal clay, starch (wheat), methoxy cellulose, dextrine, aluminum phosphate and styrene polymers.

UCL is a paper mill by product which may be obtained in dry powder form or in an aqueous solution. An analysis of the ash residue of calcium lignosoulfonate obtained from two available sources is as follows [a more extensive description of this constituent is found on pages 83–89 of the February 11, 1963, issue of Chemical and Engineering News published by the American Chemical Society]:

	Source I	Source II
	Percent	*Percent*
CaO	5.58	4.9
MgO	0.36	1.5
Na_2O	1.71	0.3
Fe_2O_3	0.69	0.02
Organic matter by difference	91.66	93.8

If desired, the oxidation resistance of the cold ramming paste can be improved by the incorporation of boric oxide in the liquid phase (UCL and water) of the paste prior to mixing. The boric oxide presumably as boric acid minimizes the evaporation of the water from the paste, thus prolongs the shelf life thereof, prevents fermentation of the UCL constituent and also forms a boro silicate glass with the silica constituent of the clay. Using 0.5

percent boric oxide by weight of the final mix, test samples were formed and baked to 950° C. in a protective cover. These samples and identically baked "cold ramming paste" samples containing no boric oxide were then heated to 600° C. in air in order to determine their relative resistance to oxidation. More specifically, the 0.5% boric oxide samples lost only .12 percent per hour per square centimeter of its weight whereas in the same units the control samples (no B_2O_3) lost .27 percent. The crushing strength of the 0.5% B_2O_3 test samples exhibited a strength of 1359 pounds per square inch as compared to 1072 pounds per square inch for the control samples. No additional benefits are achieved with amounts of the boric oxide in about excess of about 3 percent. The addition of boric oxide as an oxidation inhibitor to the cold ramming paste does not impair its excellent alkali resistance.

A preferred blend of the cold ramming paste was prepared with the following compositions by weight: The process for making the cold ramming paste of the invention follows: The particle sizes are all given in terms of the Tyler standard screen scale.

Material:	Lbs
45% [1] calcined anthracite base flour	15.64
Milled pitch [2] (M.P. of about 150° C.–175° C.)	12.49
UCL	9.92
Plastic fire clay (all through 20 Tyler mesh)	15.64
1400° C. calcined anthracite particles (through 10 on 20 Tyler mesh)	12.70
1400° C. calcined anthracite particles (through ½" on 3 Tyler mesh)	25.49
Total	91.88

[1] 45% through a 200 mesh.
[2] 100% through a 35 mesh.

The materials are dispensed into a conventional mixer in the order listed, first the calcined anthracite base flour and last the larger particles. In accordance with the invention, it is important to charge the particles to the mixer after the flour in order to minimize the particle breakdown during blending and mixing. The mixture is blended for about ten minutes at room temperature. Thereafter the resulting blend (91.88 lbs.) is mixed with 8.12 pounds of water for thirty minutes at room temperature.

This mixture or paste can be packaged in polyethylene lined bags or boxes for shipment. Of course, the package should be sealed to preclude stiffening of the paste by moisture loss due to the evaporation of the water constituent. However, if the loss of water constituent is not too high, one can replace the water to the mixture in order to maintain the desired plasticity. The paste should be plastic enough to be workable and yet sufficiently stiff to support itself in place.

The paste is now ready for use by trowelling, ramming, extruding, air-gunning or the like. When the paste is first applied, an initial setting action forms a hard carbon mass which when further heated, permits the permanent binder to soften and flow throughout the mass but precludes its exudation or bleeding out therefrom and at no time does the applied paste slump or lose form. Upon subsequent heating, the permanent binder is carbonized thus forming a strong carbon bond. Of course, any size batch can be made if desired by using the same relative proportions.

The above paste when mechanically formed and then baked to 950° C. exhibited the following properties:

Bulk density (g./cc.)	1.367
Real density (g./cc.)	2.030
Compressive strength (lbs./in.^{2}) (baked to 950° C.)	796
Percent porosity	32.66

The carbon particles and flour are used as filler material and the quantity of such ingredients may vary widely depending on the size of the particles and flour and the particular properties desired in the final paste; amounts ranging from about 32 percent to about 58 percent (combined carbonaceous material) have been successfully employed in the practice of the invention. It is interesting to note that the clay acts primarily as a plasticizer and not as a binder, and the amount thereof in the paste is not as narrowly critical as the milled pitch. If too little clay is utilized, the paste develops the characteristic of poor plasticity whereas if an excess of clay is used, the shrinkage becomes too excessive and intolerable. It has been further found that the amount of the temporary binder (UCL) is somewhat critical and that it is related to and dependent upon the fineness of the particles and flour, and the amount of clay used. The higher the clay content, the greater the amount of UCL required for a paste which is workable and has good plasticity. The finer the carbon filler, the more UCL is required. Furthermore, if too little UCL is used, the paste becomes dry whereas if an excess is utilized the paste becomes somewhat wet and sticky. If the pitch content is too low (probably not less than about 7 percent), the final product strength will be very poor and with more than about 20 percent pitch, the paste will become mushy on curing.

It will of course be understood that the above described invention is susceptible to numerous modifications. For example, if a paste of high thermal conductivity is desired, the calcined anthracite base flour can be replaced by graphite flour. The following composition is an example of a paste having high thermal conductivity.

Material:	Lbs.
45%[1] graphite flour	15.6
Milled pitch (M.P. of about 150° C.–175° C.)	12.5
UCL	10.0
Plastic fire clay (all through 20 Tyler mesh)	15.6
Graphite particles (through 3 mesh on 6 mesh)	19.1
Graphite particles (through 10 mesh on 20 mesh)	19.1
Total	91.9

[1] 45% through a 200 Tyler mesh.

These ingredients are blended and mixed together in a mixer for about ten minutes at room temperature. Then, 8.1 pounds of water is added to the resulting blend and mixed at room temperature for thirty minutes. This paste also exhibits good workability and plasticity for most applications. Indeed, it is interesting to note that paste mixtures containing both graphite and carbon particles can be made to achieve any desired thermal conductivity within practical limits.

Another embodiment of the invention is a slightly modified formulation which is particularly useful in such applications as cupola patching where it is preferable to air-gun the paste in place. The composition of the paste for such a mix which is either coarse or fine is as follows:

Material	Fine Mix	Coarse Mix
1,400° C. Calcined antractie particles (through 20 on 35 Tyler mesh)	35.0	13.0
1,400° C. Clacined antracite particles (through 10 on 20 Tyler mesh)		26.0
45%* Calcined anthracite base flour	17.5	15.5
Plastic fire clay	17.5	15.5
Milled pitch (M.P. of about 150° C.–175° C.)	15.0	15.0
UCL	15.0	15.0
	100.0	100.0

*45% through a 200 mesh.

As is ordinarily done with ceramic refractories, the water is mixed with the air-blown mix (coarse or fine) at the nozzle of a conventional air-gun and gunned onto the

walls of a cupola which is to be patched-up. The paste adhered very successfully to all inclined walls and even to a vertical wall.

Ramming pastes esepcially adherent to vertical or inclined walls can be prepared from compositions containing a high percentage of clay and a low percentage of carbon particles and flour. Such compositions, while still plastic enough to ram, are at the same time stiffer and more adherent than compositions containing a lesser amount of clay and a higher amount of carbon particles and flour, and will remain in place completely free of any support if applied against a vertical or inclined wall. The self-supporting qualities of such pastes makes them especially suitabe for repairing carbon block cupola and furnace linings as they can be applied against a vertical wall of a cupola or furnace needing repair and the wall restored to its original shape without the necessity of erecting a retaining wall for support. The following compositions are illustrative of self-supporting pastes especially useful for such application:

Material:	Weight percent
45%[1] calcined anthracite base flour	8
Milled pitch[2] (M.P. of about 150° C.–175° C.)	13
UCL	11
Plastic fire clay (all through 20 Tyler mesh)	35
1400° C. calcined anthracite particles (73% through 3/16" mesh on 3/32" mesh)	24
Water	9
Total	100.0

[1] 45% through a 200 mesh.
[2] 100% through a 20 mesh.

According to the invention, where it is desired to build up block-shaped monolithic walls of the cold ramming paste, a somewhat modified composition is preferred. It has been found that by adding about 10 percent by weight of comminuted and sized petroleum or metallurgical coke particles to the composition heretofore given (slightly modified in weight percentages) provided a satisfactory cold ramming paste for such use. The following composition is illustrative:

Material:	Weight percent
45% calcined anthracite base flour	14.3
Milled pitch (M.P. of about 150° C.–175° C.)	11.6
UCL	8.9
Plastic fire clay	14.4
1400° C. calcined anthracite particles (through 6 mesh on 10 Tyler mesh)	11.6
1400° C. calcined anthracite particles (through ½" mesh on 3 Tyler mesh)	23.2
Water	7.1
Petroleum coke[1] or regular metallurgical coke particles[2]	8.9

[1] Through 20 on 35 Tyler mesh.
[2] 100% (through 6 Tyler mesh, at least 80% on 65 Tyler mesh).

Several test sample mixes were made as previously described herein; the coke particles being mixed at the time the anthracite particles are mixed. The resultant mixtures were separately cold pressed in a 3" diameter x 12" long mold using a conventional press. The density of the test samples were measured and then they were cured in air for 5 to 7 hours with a 4000 gram weight on top of each mold. Subsequently, all samples were heated to 850° C. at a fast rate (150–200° C./hr.) while free standing, and then their densities were measured again. All of the sample molds held their shape and maintained about a 3" diameter (minimum slump and shrinkage) and they also exhibited little or no cracking.

It should be noted that one of the advantages of the cold ramming paste of the invention is its ease of handling since it need not be heated prior to application. Even further advantages are realized when the paste is packaged in moisture-proof containers such as those discussed hereinbefore.

While various specific forms of the invention have been illustrated and described herein, it is not intended to limit the invention to any of the details herein shown.

What is claimed is:

1. A cold ramming paste consisting essentially in weight percents, water in an amount of about 7% to about 14%, carbonaceous flour in an amount of about 5% to about 20%, about 10% to about 15% of a milled pitch having a melting point of from between about 150° C. and about 175° C., a temporary binder insoluble in said pitch and capable of stiffening at a temperature substantially below the melting point of said pitch, said temporary binder being calcium lignosulfonate consisting of an amount by weight of said paste of about 8% to about 15%, plastic clay in an amount by weight of said paste of about 12% to about 40%, and carbonaceous particles in an amount by weight of about 20% to about 50%, said carbonaceous flour being fine enough so that about 45% of same passes through a 200 Tyler mesh screen and said carbonaceous particles ranging in size from about ½ inch to about 1/32 inch.

2. The cold ramming paste of claim **1** wherein said carbonaceous flour comprises at least one ingredient selected from the group consisting of carbon flour, calcined anthracite base flour and graphite flour.

3. The cold ramming paste of claim **2** wherein said carbonaceous particles comprise at least one ingredient selected from the group consisting of anthracite coal, metallurgical coke, petroleum coke and graphite.

4. The cold ramming paste of claim **3** wherein said carbonaceous particles are anthracite coal.

5. The cold ramming paste of claim **4** wherein said anthracite coal is calcined.

6. The cold ramming paste of claim **5** wherein said particles comprise 1400° C. calcined anthracite particles (through ½" on 3 Tyler mesh) and 1400° C. calcined anthracite particles (through 10 on 20 Tyler mesh) in a weight ratio of about 2:1 respectively.

7. The cold ramming paste of claim **1** wherein boric oxide is added to the final mixture of said paste in an amount between about 0.5 and about 3.0 weight percent.

8. A cold ramming paste comprising in weight percents, water in an amount of about 8%, graphite flour in an amount of about 16%, about 12% of a milled pitch having a melting point of from between about 150° C. and about 175° C., a temporary binder insoluble in said pitch and capable of stiffening at a temperature substantially below the melting point of said pitch, said temporary binder consisting of about 10% of calcium lignosulfonate, plastic clay in an amount by weight of said paste of about 16% and graphite particles in an amount by weight of about 38%, said graphite flour being fine enough so that about 45% of same passes through a 200 Tyler mesh screen and said graphite particles ranging in size from about ¼ inch to about 1/32 inch.

9. The cold ramming paste as defined in claim **8** in which said graphite particles comprise large particles which pass through a 3 mesh but not a 6 mesh and small particles which pass through a 10 mesh but not a 20 mesh in a weight ratio of 1:1.

10. The cold ramming paste of claim **8** wherein said clay is plastic fire clay and all passes through a 20 Tyler screen mesh.

11. A cold ramming paste for use in building monolithic blocks therefrom comprising in weight percents, water in an amount of about 7%, about 14% calcined anthracite base flour, about 12% milled pitch having a melting point of from between about 150° C. and about 175° C., a temporary binder insoluble in said pitch and capable of stiffening at a temperature substantially below the melting point of said pitch, said binder consisting of about 9% of calcium lignosulfonate, plastic clay in an amount by weight of said paste of about 14%, calcined

anthracite particles in an amount by weight of said paste of about 35%, and the remainder of said paste being comminuted coke particles selected from the group consisting of petroleum coke and regular metallurgical coke, said calcined anthracite base flour being fine enough so that about 45% of same passes through a 200 Tyler mesh screen and said calcined anthracite particles ranging in size from about ½ to about 3/16 inch.

12. The cold ramming paste as defined in claim 11 in which said particles comprise 1400° C. calcined anthracite particles (through 6 on 10 Tyler mesh) and 1400° C. calcined anthracite particles (through ½" mesh on 3 Tyler mesh) in a weight ratio of about 1:2 respectively.

13. The cold ramming paste as defined in claim 12 wherein said remainder of said paste is petroleum coke particles, all of which will pass through a 20 Tyler mesh but not a 35 Tyler mesh.

14. The cold ramming paste as defined in claim 12 wherein said remainder of said paste is regular metallurgical coke particles, all of which pass through a 6 Tyler mesh and at least 80% of them do not pass through a 65 Tyler mesh.

15. A cold ramming paste comprising in weight percents, water in an amount of about 8%, anthracite flour in an amount of about 16%, about 12% of a milled pitch having a melting point of from between about 150° C. and about 175° C., a temporary binder insoluble in said pitch and capable of stiffening at a temperature substantially below the melting point of said pitch, said temporary binder consisting of about 10% of calcium lignosulfonate, plastic fire clay in an amount by weight of said paste of about 16% and anthracite particles in an amount by weight of about 38%, said anthracite flour being fine enough so that about 45% of same passes through a 200 Tyler mesh screen and said anthracite particles ranging in size from about ½ inch to about 1/32 inch.

16. The cold ramming paste of claim 15 wherein said anthracite base particles and flour are calcined.

17. The cold ramming paste of claim 16 wherein said particles comprise 1400° C. calcined anthracite base particles (through 10 on 20 Tyler mesh) and 1400° C. calcined anthracite base particles (through ½" on 3 Tyler mesh) in a weight ratio of about 1:2 respectively.

18. A cold ramming paste comprising in weight percents, water in an amount of about 9%, anthracite flour in an amount of about 8%, about 13% of a milled pitch having a melting point of from between about 150° C. and about 175° C., a temporary binder insoluble in said pitch and capable of stiffening at a temperature substantially below the melting point of said pitch, said temporary binder consisting of about 11% of calcium lignosulfonate, plastic fire clay in an amount by weight of said paste of about 35% and anthracite particles in an amount by weight of about 24%, said anthracite flour being fine enough so that about 45% of same passes through a 200 Tyler mesh screen and said anthracite particles ranging in size from about ½ inch to about 1/32 inch.

19. The cold ramming paste of claim 18 wherein said anthracite base particles and flour are calcined.

20. The cold ramming paste of claim 19 wherein said particles comprise 1400° C. calcined anthracite base particles of a size such that 73% pass through a 3/16" mesh but not a 3/32" mesh.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,303,031 Dated February 7, 1967

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 64, under Source II, "93.8" should read --93.28--.

Signed and Sealed this

sixteenth Day of September 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks