

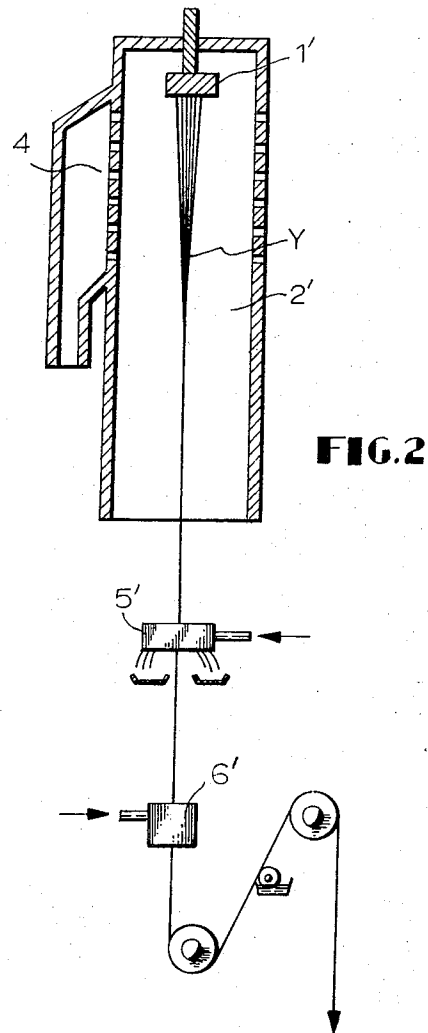
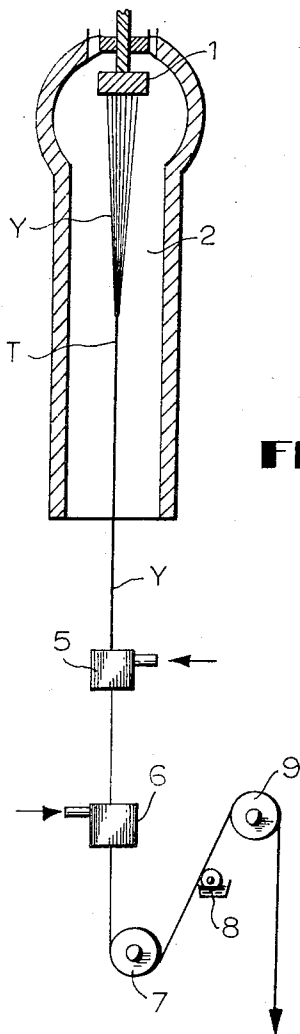
Oct. 8, 1974

L. H. BROWN ET AL
FURFURAL PITCH COMPOSITION

3,840,485

Filed Sept. 10, 1971

2 Sheets-Sheet 1



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2 Sheets-Sheet 2

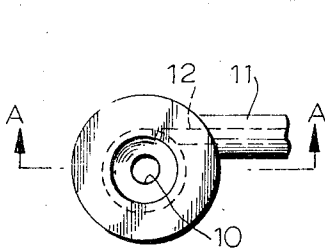


FIG. 3a

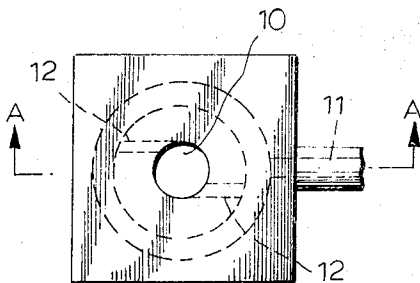


FIG. 4a

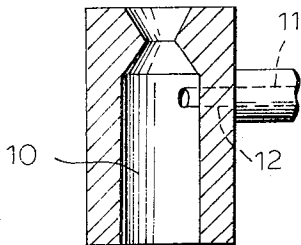


FIG. 3b

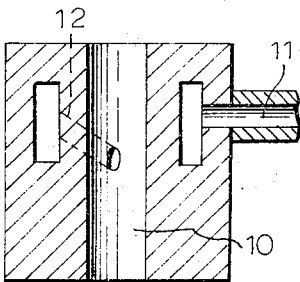


FIG. 4b

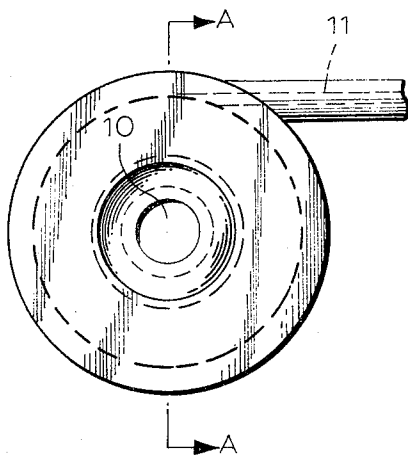


FIG. 5a

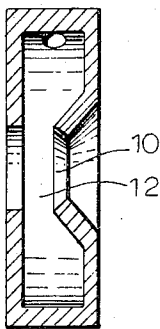


FIG. 5b

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FURFURAL PITCH COMPOSITION

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Continuation-in-part of abandoned application Ser. No. 847,385, Aug. 4, 1969. This application Sept. 10, 1971, Ser. No. 179,525

Int. Cl. C08g 51/52; C08h 9/00, 13/00; C08k 1/62, 1/64
U.S. Cl. 260—28 2 Claims

ABSTRACT OF THE DISCLOSURE

This invention provides a thermosetting binder for refractory aggregate which is relatively fluid at room temperature and which consists of between 50 and 75 percent by weight of coal tar pitch and 50 to 25 percent by weight of monomeric dispersants consisting of furfural and a member selected from the group consisting of phenol, cyclohexanone, and compounds of the formula $\text{CH}_3\text{—CO—R}$.

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 847,385, filed Aug. 4, 1969, now abandoned.

BACKGROUND OF THE INVENTION

Because of the widespread commercial availability and attractive chemical properties of coal tar pitch, particularly high melting coal tar pitch, i.e., those softening or melting above 100° C. particularly in the range 300–320° F., are highly attractive materials for use as refractory binders. Such coal tar pitches are also known as core pitches, tap hole pitches, or blast furnace pitches. However, these pitches are solids at room temperature and at most temperatures at which they can be worked conveniently. Consequently, use of these coal tar pitches as a binder for refractories e.g., basic refractory in the manufacture of refractory brick is difficult, since use of the unmodified pitches requires that the materials used with the coal tar pitch be heated to relatively high temperatures before effective coating of the materials by the pitch will take place.

It is highly desirable to provide a coal tar pitch based composition which is relatively fluid at temperatures at or near room temperatures, which composition utilizes relatively fluid monomeric materials which are highly effective as a coal tar pitch solvent or dispersant, and which convert the coal tar pitch containing composition to a thermosetting material.

Refractory articles, e.g., bricks bound by high melting coal tar pitch described hereinbefore, are conventionally employed in fabrication of a refractory lining wall, e.g., in the manufacture of a furnace lining. These constructed walls are generally heated from room temperature to high temperatures prior to initial actual use of the furnace. Use of thermoplastic materials such as unmodified high melting coal tar pitch as the binder has been found somewhat undesirable inasmuch as the binder becomes plastic and becomes subject to pressure generated distortion upon heating to elevated temperatures. It has been proposed to use a liquid polymerizable resin to render high melting pitches plastic at room temperature and thermosetting when cured. However, satisfactory use of polymerizable monomeric modifying agents has been difficult to achieve. One difficulty is the tendency of monomeric materials to vaporize at relatively low temperatures often causing blistering. Another problem encountered is internal defect development on heating.

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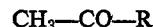
SUMMARY OF THE INVENTION

It is an object of this invention to provide a coal tar pitch based binder, which though employing so called high melting coal tar pitch is plastic and workable at room temperatures, which can be used as a binder for refractory aggregate e.g., carbon, and which is converted to a thermoset condition either at room temperature or at elevated temperatures.

It is a further object of this invention to provide such a coal tar pitch based binder from a novel combination of relatively inexpensive, widely available monomeric materials and coal tar pitch, rather than from thermosetting resins, which binder is not subject to blistering and defect development usually associated with use of monomeric additives and coal tar pitch.

It is still a further object of this invention to provide a novel combination of monomeric materials and catalysts which achieve unexpected carbon yields on thermal decomposition.

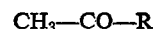
These objects are accomplished by a thermosetting binder for refractory aggregate which is relatively fluid at room temperature and which has a Conradson carbon yield of at least 50 percent by weight consisting essentially of between 50 and 75 percent by weight of coal tar pitch having a softening point above 100° C. and between 50 and 25 percent by weight of monomeric polymerizable thermosetting dispersants consisting of furfural and a member selected from the group consisting of phenol, cyclohexanone, and compounds having the formula:



wherein R is a hydrocarbon group having between 2 and 4 carbon atoms, inclusive. The hydrocarbon group in the above formula may be saturated or unsaturated and straight or branched chain.

The coal tar pitch useful in this invention has a softening point above 100° C. as measured by the ring and ball method of ASTM Test D36–64T. Coal tar pitches softening in the range 300–320° F. are preferred. These coal tar pitches are commonly known as core pitch, tap hole pitch, or blast furnace pitch.

The thermosetting binder of this invention is prepared by a method which comprises (a) blending 50 to 75 percent by weight of coal tar pitch having a softening point above 100° C. and 50 to 25 percent by weight of monomeric polymerizable dispersants consisting of furfural and a member selected from the group consisting of phenol, cyclohexanone, and compounds having the formula:



wherein R is a hydrocarbon group having between 2 and 4 carbon atoms inclusive; and (b) heating the blended mixture to solubilize the coal tar pitch in the monomeric polymerizable dispersants. It is essential that the blend be heated for a time and at a temperature sufficient to solubilize the coal tar pitch in the dispersants to produce a homogeneous binder. The time and temperature necessary to solubilize the coal tar pitch in the dispersants will vary with the softening point of the coal tar pitch, the total amount of dispersants, and the relative amounts of the several dispersants. Excessive heats should be avoided to prevent premature polymerization of the binder. While the parameters of time and temperature necessary to solubilize the coal tar pitch in the dispersants cannot be generally stated, they are easily determined by one skilled in the art. For example, we have found that solubilization of the pitch in the dispersants can be achieved by gradually raising the temperature of the blend from 70° to 90° C. over a period of several hours, for example, 4 hours.

Generally speaking molar ratios of furfural to phenol between 1.5 and 2 moles of furfural to 1 mole of phenol are preferred when phenol is the second ingredient of the dispersant component; and molar ratios between 1 and 2 moles of furfural to 1 mole of cyclohexanone, methylaliphatic ketone of the above formula, or mixtures thereof are preferred when cyclohexanone, methylaliphatic ketone, or mixtures thereof is the second ingredient of the dispersant component.

The thermosetting binder produced herein along with a catalyst is admixed with refractory aggregate. While the order of mixing is not critical, it is preferred to mix the aggregate and catalyst first. To this mixture the thermosetting binder is added. Another method is to mix catalyst, thermosetting binder, and aggregate all at once.

The refractory aggregate selected can be carbon or non-combustible materials such as metal oxides. These oxides, in turn, may include alumina, zirconia, magnesia, zircon, chrome ore, chromium oxide, and dead-burned dolomite.

The amount of thermosetting binder used on the aggregate depends in well-known ways on the surface area, porosity, shape, etc., of the refractory aggregate particles. For economical reasons, no more binder need be used than to dampen the aggregate and to effectively bind the aggregate particles together. For example, if the aggregate is finely divided graphite or carbon, the amount of thermosetting binder may be as high as 40 percent by weight based on the weight of the aggregate. If the aggregate is dead-burned dolomite for example, we have found that only 4-8 percent by weight thermosetting binder is necessary to effectively bind the aggregate particles together.

Acids and bases commonly used in the art are used as catalysts in this invention. Suitable acid catalysts include inorganic and organic acids such as hydrochloric acid, sulfuric acid, nitric acid, orthophosphoric acid, benzene sulfonic acid, toluene sulfonic acid, naphthalene sulfonic acid, maleic acid, oxalic acid, malonic acid, phthalic acid, lactic acid, and citric acid. Suitable acid catalysts also include Friedel-Crafts type catalyst such as ferric chloride, aluminum chloride, and zinc chloride. Suitable acid catalysts include organic anhydrides such as maleic anhydride and phthalic anhydride. Examples of further satisfactory conventional acid catalysts include mineral acid salts of urea, thiourea, substituted ureas such as methyl urea and phenyl thiourea; mineral salts of ethanol amines such as mono-, di-, and triethanolamine; and mineral acid salts of amines such as methyl amine, trimethyl amine, aniline, benzyl amine, morpholine, etc. Preferred acid catalysts have a K_a of at least 10^{-3} .

Suitable base catalysts include alkali hydroxides such as lithium hydroxide, sodium hydroxide, potassium hydroxide, and the like; and alkaline earth hydroxides such as magnesium hydroxide, calcium hydroxide, and the like. Other satisfactory base catalysts include for example, amine catalysts such as primary amines like ethyl amine, propyl amine, etc.; secondary amines like diisopropyl amine, dimethyl amine, etc.; and tertiary amines like triisobutylamine, triethylamine, etc. Examples of other satisfactory base catalysts are mixtures of alkali hydroxides and alkaline earth hydroxides such as mixtures of sodium hydroxide and calcium hydroxide. We have discovered that a mixture of alkali hydroxides and alkaline earth hydroxides provides a thermosetting binder giving unexpectedly high carbon yields which approximate the carbon yield of coal tar pitch alone. Preferred basic catalysts have a K_b of at least 10^{-4} .

The amount of catalyst will vary with the type of aggregate, strength of catalyst, and the curing time desired. For example, when the catalyst is an alkali hydroxide, 0.5 percent to 5 percent based on the weight of the thermosetting binder is generally used but when the catalyst is an alkaline earth hydroxide or an amine, 5 percent to 25 percent is used.

The binder of this invention may be cured at room temperature (25° C.). However, articles produced by the process of this invention which are cured by gradually raising the temperature from room temperature to 250° C. over several hours have greater strength. The optimum rate of temperature increase is largely a function of the size of the bound article to be cured. Large articles must be heated at a slower rate of temperature increase than small articles in order that the temperature be uniform throughout the article and thus harmful internal stresses caused by uneven heating of the article be avoided.

The process of this invention can further comprise pyrolyzing or graphitizing the binder by heating the bound article to higher temperatures according to well understood procedures. For example, the thermosetting binder may be pyrolyzed by heating the cured admixture of thermosetting binder, aggregate, and catalyst in a non-oxidizing atmosphere to a temperature of at least 800° C. to pyrolyze the binder and form a carbon bonded refractory product suitable for example, when the aggregate is carbon for carbon electrodes. The thermosetting binder of this invention when pyrolyzed gives good carbon yields. These yields are in the range of about 50 to 75 percent by weight as determined by ASTM D-189-62 (Conradson carbon test). The pyrolyzed admixture may then be heated in a non-oxidizing atmosphere to a temperature of at least 2600° C. to graphitize the binder and form a graphitized refractory product.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following embodiments are shown for the purpose of illustrating this invention. It will be apparent to those skilled in the art that various changes and modifications may be made therein without departing from the spirit and scope of the invention as it is more precisely defined in the subjoined claims.

Through the Examples the terms "percent" or "parts" refers to percent by weight and parts by weight, respectively, and all temperatures are given in degrees centigrade unless otherwise indicated.

Example 1

The purpose of this example is to illustrate and demonstrate the totally unexpected results which are achieved as a consequence of the utilization of this invention. In this example three sets of binders are employed, each set utilizing blast furnace pitch having a softening point in the range 300-320° F. In each of the binders a monomeric dispersant admixture is utilized in an amount of 32.6 percent of the binder, the balance being the pitch referred to immediately hereinbefore. The monomeric dispersant included 1 percent sodium hydroxide catalyst in the form of a 50-50 sodium hydroxide-water admixture dispersed on an equal weight of carbon powder. In the preparation of each of the three binders, monomeric dispersant is thoroughly admixed with the pitch and the individual admixtures were tested as described hereinafter. The binders, "A," "B," and "C" which are utilized in this example utilized different ingredients, as follows: in binder "A," the liquid monomeric dispersant consists of two moles furfural and one mole cyclohexanone; in binder "B" the monomeric dispersant is pure furfural; in binder "C" the monomeric dispersant is pure cyclohexanone. The binders were tested neat, that is, without the addition of filler or refractory thereto, and were also tested in a basic refractory brick formula. The brick formula includes 2,000 parts by weight of periclase; 1,565 parts of catalyst (3 parts carbon, 1.5 parts sodium hydroxide, 1.5 parts water); 120 parts of binder ("A," "B," or "C," same as above). The brick formula was mixed at room temperature, shaped into one inch by one inch by six inch test bars under ten thousand p.s.i. compression.

The neat binder, that is the dispersant-pitch admixture, is subjected to a weight loss test as follows: a five gram sample, accurately weighed, is heated at 135° C. for 17 hours, 150° C. for 1 hour, 180° C. for 4 hours. After the same is returned to room temperature it is reweighed and the weight loss based on the initial weight of the monomeric mixture of the sample is calculated.

The brick bars are accurately weighed and the "density, raw brick" is calculated as grams per cubic centimeter. After the bars are accurately weighed, they are then tempered for 8 hours at 100° C., 2 hours to 140° C. and 2 additional hours to 250° C. The bars are then reweighed and the "weight loss" is determined and expressed as percent of the initial weight of the monomeric mixture of the bar. The bars are again measured and the "tempered density" of the tempered bar, or brick, is calculated as grams per cubic centimeter.

The tempered bars, or brick, are tested in accordance with customary procedure and the flexural strength (p.s.i.) is calculated. Test results are summarized in Table I.

TABLE I

Composition of "binder"	Weight loss ("binder" only)	Raw density (brick)	Tempered weight loss, percent	Density tempered (brick)	P.s.i. flexural tempered (brick)
A.....	24.4	2.93	33.5	2.90	1,672
B.....	47.8	2.91	71.9	2.87	1,303
C.....	56.2	2.92	63.7	2.88	1,354

From a consideration of the data of Table I it is apparent that the weight loss of the neat binder is far less in the case of the binder utilizing the mixture of furfural and cyclohexanone in accordance with this invention (binder "A"). It was also noted that the viscosity of binder "A" was 75,000 c.p.s. at room temperature whereas the viscosity of binders "B" and "C" were above the limit of the testing device employed, namely, above 100,000 c.p.s. at room temperature. For a more valid comparison of viscosity a different test sample was prepared in which the dispersant was used at a 40 percent by weight level, the remainder being high melting pitch utilized in this example. In this special viscosity test the sample utilizing the two mole furfural-one mole cyclohexanone dispersant gave a 17,000 c.p.s. viscosity at room temperature, while the sample utilizing cyclohexanone alone showed viscosity of 29,000 c.p.s. at room temperature. However, at the 40 percent level, furfural diluent appears to dissolve the pitch at elevated temperatures resulting in a solid mass upon cooling. This is an anomalous situation, inasmuch as the 32.6 percent furfural in pitch results in a molasses-like viscous mixture. It is noted that the density of raw brick produced in accordance with this invention was as high as the density achieved using the monomer as a sole diluent. It is particularly significant that the weight loss upon tempering was far less in the case of the brick of this invention. It is noted that the weight loss of the brick utilizing furfural, or cyclohexanone as the pitch diluent was above 63 percent of the diluent in each instance, whereas the weight loss evidenced upon tempering by the brick produced in accordance with this invention was about one third of the diluent weight. It is also particularly significant that the p.s.i. flexural strength of the tempered brick produced in accordance with this invention was substantially higher than that of tempered brick produced utilizing binders consisting of furfural or cyclohexanone alone.

Example 2

This example illustrates another procedure by which the invention is utilized. A premix is formed by admixing ingredients in the following proportions: taphole pitch 67.4 parts; furfural 21.7 parts; cyclohexanone 10.9 parts. The admixture was heated to 100° C. to disperse the pitch in the admixture. The following ingredients were admixed in a sigma blade mixer: Periclase, 2,000 parts; premix, 120 parts; 50 percent sodium hydroxide solution in water, 1.56 parts. The ingredients were blended approximately one hour and the resulting mixture was molded at room temperature under a pressure of about 10,000 p.s.i. Portions of the composition hardened at room temperature, but it was preferred that the molded shapes be tempered at temperatures gradually increasing to 250° C. over a period of about twelve hours. The binder provided carbon yields of 50-60 percent and coke strength of 2,000 p.s.i. The carbon yield was determined by the ASTM D-189-62 (Conradson Carbon Test).

Example 3

The purpose of this example is to illustrate the fact that, even with sodium hydroxide catalyst the carbon level of the severely diluted pitch binder is surprisingly high (a diluted high M.P. pitch gives carbon yield as high as a low M.P. pitch). Moreover it also illustrates that using a combined strong base-weak base catalyst mix provides astoundingly high carbon yields (a diluted high M.P. pitch binder gives as high a carbon yield as the undiluted high M.P. pitch).

In this example, two series of tests are run; one series utilizing 1 percent sodium hydroxide (based on diluent weight) the other series utilizing a mixture of 1 percent sodium hydroxide and 23.0 percent lime (on the same basis) as catalyst mix. The sodium hydroxide is incorporated in the binder by means of a carbon carrier composition prepared from equal weights of carbon powder and an aqueous 50-50 sodium hydroxide solution.

In this series of tests binders were prepared as in Example 1 above, and diluents "A," "B," and "C" were utilized as in that example. In addition, two binders consisting of high melting point pitch, and low melting point pitch respectively to which catalyst was added were tested for control purposes. Weight loss was determined on "neat" samples after "tempering" weighed samples in a cycle of 8 hours at 100° C. 2 hours gradually increasing up to 140° C. and 2 hours gradually increasing up to 250° C., and a percent weight loss after tempering was calculated and expressed on the basis of initial green binder weight and is reported in Table II. Other portions of the binders were tempered, as above and subjected to the coking conditions set forth in ASTM designation D-189-62 (Conradson Carbon) and weight remaining after coking, was determined and the retained weight is expressed as percent of the initial (green) binder weight. It is noted that the same amounts of catalyst were used in the diluent-

free controls (based on binder weight) as were used in the diluent-containing binders.

and between 50 and 25 percent by weight of monomeric polymerizable thermosetting dispersants consisting of fur-

TABLE II

Pitch in binder	Diluent in binder	Percent weight loss after tempering		Conradson carbon test (retained weight) green to coked	
		Na oil catalyst	Mixed catalyst	Na OH catalyst	Mixed catalyst
High M.P. (300-320° F.)	A*	15.46	4.49	57.1	65.55
Do	B	25.03	21.68	55.08	57.1
Do	C	24.03	24.4	53.15	51.7
Do	None	0.00	0.0	67.8	65.4
Lower M.P. (207° F.)	do	0.59	1.40	57.6	57.4

* Use of "A" is in accordance with invention; "B" and "C" are for purpose of comparison; no-diluent tests are "controls."

From the above data it is clear that the carbon yields from the binder of this invention (see test using diluent "A") are higher than those achieved by use of pitch and diluent ingredients alone (i.e. not in combination, see tests using "B" and "C") regardless of whether sodium hydroxide is used, or whether the mixed caustic-lime catalyst is employed. It is clear that the caustic catalyst embodiment provides the same carbon yield as the low melting point pitch without diluent, and that with the mixed catalyst, the carbon yield of the diluted binder of this invention is comparable to that achieved with solid, undiluted high melting point pitch (65.55 percent v. 65.4 percent).

Example 4

This example illustrates the use of the binder of this invention in a ramming mix.

A mixture was prepared as follows: anthracite aggregate, 1,600 parts; blast furnace pitch, 160 parts (10 percent of aggregate); mixture of 2 moles furfural and one mole of cyclohexanone, 76 parts (32.6 percent of neat binder i.e. pitch plus diluent); 3.9 parts of sodium hydroxide (in a mixture prepared from equal weights of carbon powder and 50-50 aqueous sodium hydroxide); and 9.8 parts of calcium hydroxide. These ingredients were hand mixed and mixed for ½ hour at room temperature in a laboratory mixer of the ribbon-blender type having intermeshing blades.

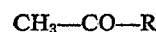
The resulting blend had a work life of about ½ hour, and was rammed into a 4" x 4" x 3.75" cavity using an electric hammer. The density of the resulting rammed material was found to be 1.57. The "green" hardness was 30 (Shore D) and after standing overnight at room temperature a hardness was observed to be 65 (Shore D).

The binder of this invention is highly useful as a binder for carbon-based ramming mixes, and is suitable for working shaped carbon articles, such as aluminum anodes, and cathode blocks, and for joining carbon cathode blocks in aluminum cells. These mixes harden themselves at room temperature, and can be used, also, with a rapid baking cycle. Moreover, as illustrated in a numbered Example 3, herein, the combination of the special diluent of this invention with the catalyst made up of weak and strong bases mixed, provides as high a carbon level as that provided by high M.P. pitch alone, upon thermal decomposition.

We claim:

1. A thermosetting binder for refractory aggregate consisting essentially of between 50 and 75 percent by weight of coal tar pitch having a softening point above 100° C.

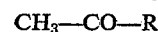
fural and a member selected from the group consisting of phenol, cyclohexanone, and compounds having the formula:



wherein R is a hydrocarbon group having between 2 and 4 carbon atoms, inclusive.

2. A process for preparing a thermosetting binder for refractory aggregate comprising:

(A) blending 50 to 75 percent by weight of coal tar pitch having a softening point above 100° C. and 50 to 25 percent by weight of monomeric polymerizable dispersants consisting of furfural and a member selected from the group consisting of phenol, cyclohexanone, and compounds having the formula:



wherein R is a hydrocarbon group having between 2 and 4 carbon atoms, inclusive; and

(B) heating the blended mixture at a temperature between 70° C. and 90° C. to solubilize the coal tar pitch in the monomeric polymerizable dispersant.

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U.S. Cl. X.R.

106—56, 273 R, 284; 208—22, 44; 260—28.5 R, 28.5 AS, 67 F; 264—29