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(11) **EP 1 063 277 A2**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
27.12.2000 Bulletin 2000/52

(51) Int Cl.7: **C10L 5/14**

(21) Application number: **00305291.7**

(22) Date of filing: **22.06.2000**

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

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(30) Priority: **23.06.1999 GB 9914537**

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(54) **Fuel briquetting composition and the manufacturing of fuel briquettes using it**

(57) A fuel briquetting composition comprising a mixture of fuel particles, e.g., coal or petroleum coke, an alkaline phenol-formaldehyde resin, an esterified phenol-formaldehyde resole resin, a water-activatable green strength additive and water. Fuel briquettes can be made using this mixture by forming it into briquettes and allowing the resinous components of the mixture to

react with the result of hardening the briquettes.

The use of an esterified phenol-formaldehyde resole resin as the curing agent for the alkaline phenol-formaldehyde resin binder has the advantage that the reaction product does not result in the incorporation of unreactive by-products into the polymer matrix which would, if present, lower the water resistance of the product.

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Description

[0001] This invention relates to a fuel briquetting composition which includes fuel particles, an alkaline phenolic resin, an esterified phenolic resin, a water-activated green strength additive and water. Also, it relates to a method of making fuel briquettes using a phenolic resin composition produced from esterified phenolic resins under alkaline conditions having a reduced content of unreactive by-products.

[0002] It is known that phenolic resins may be cured under alkaline conditions through reaction with organic esters, including lactones and organic carbonates. Such ester curing of alkaline phenolic resole resins is described in DE-C-1,065,605, DE-C-1,171,606, JP-A-49-16793 and JP-A-50-130627. According to these publications, a highly alkaline phenolic resole resin in aqueous solution may be cured at ambient temperature by reaction with an organic ester by contacting the resin with the ester in the form of a liquid or a gas. Such techniques find use in the bonding of sand in refractory applications, such as in the production of foundry moulds and cores (US-A-4,426,467, US-A-4,468,359, US-A-4,474,904).

[0003] A process for agglomerating coal fines using a phenol-formaldehyde resole resin in aqueous alkaline solution, as binder, is disclosed in EP-A-0241156. According to this, a mixture of the coal fines, the aqueous alkaline resole resin binder and, as curing agent, an ester of a polyhydric alcohol, a carbonate ester or a lactone is formed into agglomerates, dried and then cured.

[0004] The hardening of alkaline phenolic resins using ester curing agents involves the saponification of the ester, but it is a disadvantage that the alcohol products of the saponification reaction are not incorporated into the final resin structure but remain in the cured mass as non-resinous compounds in the form of free alcohols. The presence of free alcohol in the cured composition is considered to be disadvantageous in the applications where there is need for high strength and water resistance.

[0005] We have found that these and other disadvantages can be avoided or, at least, substantially reduced by employing an esterified phenolic resin as curing agent for an alkaline phenolic resin binder in the preparation of a cured phenolic resin composition. By using an esterified phenolic resin as the curing agent the release of free alcohols during the saponification stage is avoided as a phenol-formaldehyde resin is the alcohol of the saponification reaction and forms part of the final phenol-formaldehyde polymer matrix.

[0006] According to the present invention, there is provided a fuel briquetting composition comprising a mixture of

- (i) fuel particles;
- (ii) an alkaline phenolic resin selected from alkaline phenol-formaldehyde novolak resin and alkaline phenol formaldehyde resole resin;
- (iii) an esterified phenolic resin selected from esterified phenol-formaldehyde resole resin and esterified phenol-formaldehyde novolak resin;
- (iv) a water-activatable green-strength additive; and
- (v) water.

with the proviso that when the alkaline phenolic resin is an alkaline phenol-formaldehyde novolak resin the esterified phenolic resin is an esterified phenol-formaldehyde resole resin.

[0007] The present invention also provides a method of making fuel briquettes comprising the steps of forming the mixture described above, shaping the mixture into briquettes and allowing the briquetted mixture to cure.

[0008] The method is applicable to the production of briquettes using particulate fuel, such as coal, e.g., anthracite, bituminous coal or coking coal, and petroleum coke. The particulate fuel may be produced by grinding lump fuel to the required particle size although fuel fines may be used that require no further particle size reduction.

[0009] Coal briquettes produced using the process described in EP-A-0241156 have poor water repellency properties because the esters used as hardeners react to form hygroscopic free alcohol by-products, such as glycerol and glycols. On storage, the briquettes may absorb up to 15% water based on the dry product weight. The physical strength of the briquette reduces with increasing water content. A particular advantage of using an esterified resole is that the reactive resole product of the hardening reaction is incorporated into the polymer matrix of the binder and imparts a degree of humidity resistance to the briquette with the physical strength of the briquette maintained during storage in damp conditions.

[0010] The invention makes use of a binder for the particulate fuel which is an alkaline phenolic resin. This resin may be an alkaline phenol-formaldehyde novolak resin or an alkaline phenol-formaldehyde resole resin.

[0011] The terms "phenol-formaldehyde resole resin" and "phenol-formaldehyde novolak resin" are, of course, terms well known in the phenolic resin art. Resoles are thermosetting, i.e., they form an infusible three-dimensional polymer upon the application of heat and are formed by condensing a phenol with a molar excess of formaldehyde in the presence of a basic catalyst. Phenol-formaldehyde novolak resins, on the other hand, are phenol-ended chain polymers formed by the reaction of formaldehyde with a molar excess of a phenol, typically in the presence of an acidic catalyst.

These novolak resins are permanently fusible non-curing resins which are conventionally cured into an insoluble, infusible resin by reaction with a formaldehyde donor curing agent, such as hexamethylenetetramine, at elevated temperature.

[0012] For reasons of availability and reasonable cost, coupled with repeatability and freedom from strong or offensive odours, the preferred phenol-formaldehyde resins used in the present invention are based on the condensation product of formaldehyde with phenol, itself.

[0013] Such condensation products may be manufactured in known ways by reacting phenol and formaldehyde in the presence of basic or acidic catalysts, although the preparation of such materials does not form part of this invention. Where basic catalysts are employed for this purpose the resin product will possess free methylol groups in a proportion which will depend primarily on the ratio of formaldehyde to phenol. These methylol groups are attached to phenolic ring carbon atoms at ring positions which are ortho and/or para to the phenolic hydroxyl groups. Typically, in the production of a phenol-formaldehyde resole resin in the presence of alkali the molar ratio of phenol:formaldehyde used in the condensation reaction will be in the range of from 1:1.2 to 1:3.0, preferably from 1:1.5 to 1:3.0. The amount of alkali used as condensation catalyst will typically be about 0.1-2% by weight based on the weight of the phenol used, generally sufficient to maintain a pH of at least 8, but may be considerably higher. The degree of condensation of such a resole resin can conveniently be described by reference to two parameters; the residual solids on heating at 100°C to constant weight and the viscosity of the resole solution. Typically the phenol-formaldehyde resole resin will have a solids content of from 30-95% preferably 50 to 75%, by weight and a viscosity of from 0.1 to 100 poise, preferably 1 to 25 poise, at 25°C.

[0014] Typical examples of condensation catalysts useful in the preparation of resole resins include the oxides and hydroxides of sodium, potassium, lithium, barium, calcium and magnesium.

[0015] The phenol-formaldehyde novolak resin may be made in any of the known ways. In order to obtain a resin having the properties of a novolak, that is to say, in order to obtain a product which does not thermoset upon heating, it is necessary to react the phenol and the formaldehyde in a molar ratio of less than 1 mole of formaldehyde to each mole of the phenol.

[0016] The phenol used is preferably phenol itself or m-cresol or a mixture of phenol and a m-cresol. Other phenols or homologues that may be used to form all or part of the phenol component in the novolak resin include 3,5-xylene-1-ol, ethyl phenol, resorcinol, phloroglucinol, pyrogallol, mixtures of aldehyde-reactive phenols, such as mixed cresol isomers and xlenols and phenolic blends, such as those obtained from coal tar fractionation, and cashew nut shell liquid. For reasons of availability and reasonable cost, coupled with repeatability and freedom from strong or offensive odours, the preferred type of phenolic novolak is a condensation product of phenol, itself, and formaldehyde.

[0017] The novolak resin may be prepared using any of the catalysts commonly employed for this purpose. Suitable acid catalysts include the strong mineral acids, such as sulphuric, phosphoric and hydrochloric acids, and organic acids, such as oxalic and salicylic acids or anhydrides, such as maleic anhydride.

[0018] As stated above, to manufacture a novolak resin the phenol and the formaldehyde are reacted together in a molar ratio of less than 1 mole of formaldehyde to each mole of the phenol. In general, the formaldehyde will not be used in a molar ratio to phenol of less than 0.2:1. Typically the molar ratio of formaldehyde to phenol will be within the range of from 0.2:1 to 0.85:1 since amounts of formaldehyde in excess of this maximum involve an increased risk of premature gelation of the resin and amounts below 0.2 mole per mole of phenol are uneconomic because of the increased level of phenol that would remain unreacted. In order to obtain a good compromise of properties we prefer to use a formaldehyde to phenol molar ratio in the range of from 0.4:1 to 0.7:1.

[0019] In the case of an acid-catalysed novolak resin, it is only necessary to employ sufficient of the acidic material to obtain a satisfactory rate of resinification and the proportion required will vary with the type of acid used. In the case of the strong mineral acids, such as sulphuric acid or hydrochloric acid, this will generally be in the range of from 0.02 to 1.0%, and preferably from 0.1 to 0.6%, by weight based on the weight of the phenol employed. With organic acids, such as oxalic acid or maleic anhydride, it is typical to use amounts in the range of from 0.1 and 10%, and preferably from 1 to 5%, by weight based on the weight of the phenol employed.

[0020] Methods for the preparation of acid-catalysed novolak resins are well known and are described, for example, in GB 1,210,239 and in GB 1,391,420.

[0021] The novolak resins formed are preferably treated, when the reaction is substantially complete, to remove unreacted phenol. This is because we have found that free phenol in the novolak resin appears to inhibit the crosslinking mechanism that takes place when the esterified phenol-formaldehyde resole resin reacts with the novolak resin in the presence of alkali and, therefore, causes a loss of strength in the product. Removal of free phenol may most conveniently be accomplished by steam distillation, but other methods of removing unreacted phenol, such as precipitation of the resin from solution and washing of the precipitate prior to drying, may be employed. It will be clear that many benefits of the invention will not be achieved in full measure if substantial amounts of free phenol are left in the resin. On the other hand, it is generally uneconomic and impractical to remove all traces of free phenol from the resin. We have found, however, that a substantial improvement in strength is achieved if the free phenol content of the novolak

resin is reduced to less than 2% and, most preferably, to less than 1 %.

[0022] According to a preferred embodiment, the alkaline phenol-formaldehyde resin will be a novolak resin since phenolic novolak resins in aqueous alkaline solution are storage stable. Such a storage stable binder obviously has the advantage particularly that it can be used and stored in warm and hot climates. As a consequence of the hardening reaction that occurs between an alkaline novolak resin on the addition of an esterified resole resin the emission of formaldehyde is reduced compared to the case where an alkaline resole resin is reacted with the esterified resole resin.

[0023] The curing agent used for the phenol-formaldehyde resole resin or the phenol-formaldehyde novolak resin in accordance with the present invention is an esterified phenolic resole resin. The esterified phenolic resin will be an esterified phenol-formaldehyde resole resin or an esterified phenol-formaldehyde novolak resin except in the case when the alkaline phenolic resin binder is an alkaline phenol-formaldehyde novolak the esterified phenolic resin curing agent will be an esterified phenol-formaldehyde resole resin. Such an esterified resole resin will typically be prepared by esterifying one or more methylol groups present in a phenol-formaldehyde resole resin which has been produced as described earlier. Thus, the esterified phenol-formaldehyde resole resin will contain one or more esterified methylol groups positioned ortho and/or para to a phenolic hydroxyl group or esterified phenolic hydroxyl group. The esterified resole resins are typically organic carboxylate esters. These esters may be derivable from any aliphatic, alicyclic or aromatic mono-, di- or polybasic carboxylic acid capable of forming esters with methylol groups. It is also possible for an esterified methylol-containing resole resin to contain ester groups derived from more than one of these acids. For most purposes, however, the esters will be those formed from lower carboxylic acids, especially formic acid and acetic acid. Where reference herein is made to the acid component of the ester group, this is intended only as descriptive of the type of group and it is not intended to indicate that the acid itself need be employed for the manufacture of the methylol ester. In fact, the ester may be formed in any known way and the procedure adopted may be varied, as will be known to those skilled in the art, to suit the particular compounds being produced. Examples of some methods of esterification that may be used include:-

- (1) reaction of the methylol containing resole resin with acid anhydride, mixed anhydride or acid chloride, typically in the presence of a suitable catalyst;
- (2) ester exchange between a methylol-containing resole resin and a suitable carboxylic acid ester in the presence of a suitable catalyst or by acid interchange as described, for example, in US 2,544,3651; and
- (3) treatment of a methylol-containing resole resin with ketene, diketene or their derivatives.

[0024] It is also possible to produce the desired esterified resole resin by the action of an acid anhydride on mono-, di-, or tri-dialkylamino methyl substituted phenols or phenol derivatives.

[0025] Generally speaking, phenolic resole resins are acid sensitive and in most cases it will be necessary to esterify the methylol groups, and optionally the phenolic hydroxyl groups, on a phenolic resole resin by an indirect route, so as to avoid gelation of the resin. The tendency to gel may be reduced or eliminated by blocking the phenolic -OH groups by esterifying or etherifying them, as described, for example, in DE-C-474,561. Obviously, any catalyst employed to promote the esterification reaction must not be capable of entering into further reaction with the esterified methylol groups of the product of the esterification reaction under the reaction conditions used. An example of a suitable esterification catalyst is pyridine.

[0026] A preferred procedure is to form the acetate ester of methylol-containing phenolic resole resin by introducing ketene into a solution of the methylol-containing phenolic resole resin. In this case, the ketene is preferably generated immediately prior to use, typically in equipment such as that described in US 2,541,471 or 3,259,469. By reacting the resole resin with diketene in a similar way, the acetoacetate ester of the phenolic compound is obtained. Other esters may be formed by ester exchange.

[0027] Suitable ester groups include formate, acetate, acetoacetate, acrylate, propionate, lactate, crotonate, methacrylate, butyrate, isobutyrate, caproate, caprylate, benzoate, toluate, p-amino-benzoate, p-hydroxybenzoate, salicylate, cinnamate, laurate, myristate, palmitate, oleate, ricinoleate, stearate, oxalate, succinate, fumarate, maleate, adipate, phthalate, azelate and sebacate. Acetate esters form a particularly preferred class of compounds according to the present invention.

[0028] Since the esterification reaction evolves water, it may be accelerated by the use of non-aqueous conditions, as well as by the use of non-boiling solvent capable of forming an azeotrope with water.

[0029] The esters of the present invention may typically be prepared by choosing conditions which preferentially esterify the methylol (-CH₂OH) groups and not the phenolic -OH groups in the resole. However, as it is clear from the above the esterified resole resin may be one in which all of the phenolic hydroxyl groups themselves are esterified, i. e., it contains no free phenolic hydroxyl groups. This is because, in such a case, the esterified resole resin will be stable on storage due to the inactivation of the phenolic -OH group, even at relatively high ambient temperature.

[0030] Generally, when an acid is used to esterify the resole resin the preferred amount of acid used will be equal, on a molar basis, to the content of free methylol groups. However, in cases where a plurality of methylol groups is

present it is possible to esterify only a proportion of the methylol groups, so that the remaining unesterified methylol groups allow the product to be thermally polymerised at a later stage. This could, for example, be a convenient means of retaining a degree of thermoplasticity in the product.

[0031] On the other hand, an excess of acid may be required to introduce esterification at low temperature. Ideally, any residual free acid should be removed from esterified resole resin before the latter is reacted with the alkaline phenolic resin in the production of the fuel briquettes since any residual free acid present in the esterified resole resin will react with and so neutralise the alkali present.

[0032] The curing agent may, alternatively, be an esterified phenol-formaldehyde novolak resin in the case where the binder is an alkaline resole resin. Phenol-formaldehyde novolak resins do not normally contain methylol groups. For this reason, an esterified phenol-formaldehyde novolak resin contains only esterified phenolic -OH groups. Under alkaline conditions a cross-linking reaction involving an esterified novolak will only occur if free methylol groups are introduced such as are found in the form of an alkaline resole resin.

[0033] The esterified resin will be used in the performance of the present invention in an amount typically from 10-120% by weight based on the weight of the alkaline phenol-formaldehyde resin binder. Preferably, the amount of esterified resin used will be from 20 to 60% by weight of the alkaline phenol-formaldehyde resin.

[0034] The present invention also makes use of a water-activatable thickening agent. Typically, this will be a natural product or a derivative of a natural product, such as starch or a starch derivative, cellulose or a cellulose derivative or a natural gum, such as gum arabic or guar gum, and mixtures of these. It is well recognised that the hydration properties of natural gums, particularly guar gum, are pH dependent. As the pH of a guar gum solution increases above about 10.5 the rate of hydration is reduced and the final viscosity low. The use of guar gum as the thickening agent, therefore, constitutes a preferred embodiment of the invention. Preferably, the thickening agent is used at a level of from 0.1 to 1.0% by weight based on the dry fuel particulate. After mixing the components of the briquette-forming composition, the mixture is formed into briquettes typically by means of a roll press and is then allowed to cure.

[0035] The fuel briquetting composition of the present invention also, preferably, contains, as diluent, at least one ester selected from monomethyl esters of an aliphatic carboxylic acid, dimethyl esters of an aliphatic dicarboxylic acid and diethyl esters of an aliphatic dicarboxylic acid. Examples of such ester diluents include the methyl and ethyl esters of formic acid, acetic acid, propionic acid, lactic acid, stearic acid and oleic acid and the dimethyl and diethyl esters of oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid and maleic acid.

[0036] The following examples illustrate the principles and the benefits of the invention. In these examples the materials used are phenol-formaldehyde resole acetate, an alkaline phenol-formaldehyde resole resin (Resin A), an alkaline phenol-formaldehyde novolak resin (Resin B) and triacetin. The powder thickener referred to in all examples is guar gum.

Preparation of phenol-formaldehyde resole acetate

[0037] Phenol (1 mol) and sodium hydroxide (0.004 mol) were charged to a reaction vessel and the temperature maintained at 50°C whilst 50% formalin (0.6 mol) was added. The temperature was then raised to 80°C. The temperature was maintained at 80°C as a second charge of 50% formalin (1.0 mol) was added slowly over 30 minutes. The mixture was then held at 80°C for a further 45 minutes. The pH was adjusted with p-toluene sulphonic acid solution to 4.0±0.2. The resin was cooled to 60°C and then pyridine (7.9 g) and acetic anhydride (1.0 mol) were cautiously added while controlling the exotherm by immersing the reaction vessel in an ice/water bath. The mixture was then allowed to stand overnight at room temperature. Ethyl acetate was then added to the mixture, and the product extracted. The extract was washed several times with water, then with dilute acid and finally with water again and the organic phase was dried, filtered and evaporated to dryness. A viscous, straw-coloured liquid was obtained. The viscosity was reduced to <300 cp by adding a mixture of 15% dimethyl adipate, 62% dimethyl glutarate and 23% dimethyl succinate.

Preparation of an alkaline phenol-formaldehyde resole resin (Resin A)

[0038] Resin A is an alkaline phenol-formaldehyde resin with a formaldehyde to phenol molar ratio of 1.9:1 and a sodium hydroxide to phenol molar ratio of 0.6:1. Phenol (1 mol) and sodium hydroxide (0.004 mol) were charged to a reaction vessel and the temperature maintained at 60°C whilst 50% formalin (0.6 mol) was added. The temperature was allowed to be raised to 80°C and maintained at 80°C while a second charge of 50% formalin (1.0 mol) was added slowly over 30 minutes. The mixture was then held at 80°C for 60 minutes before 50% sodium hydroxide solution (0.596 mol) was charged maintaining temperature at 80°C. The resin was condensed at 80°C to a viscosity of 300cP.

Preparation of alkaline phenol-formaldehyde novolak resin solution (Resin B)

[0039] Phenol (1.0 mol) was charged to a flask fitted with reflux and condensing facilities and vacuum and heated

to 80°C. Sulphuric acid and salicylic acid were added and stirred until dissolved. The phenol and acids were then heated to 110°C and 50% formalin (0.5 mol) was added of 90 minutes. Reflux was continued for 90 minutes. The 0.88 ammonia was then added and water distilled off under atmospheric pressure until the temperature rose to 150-155°C. Steam was passed into the resin to remove free phenol. Viscosity was measured at intervals after removal of all the residual water by vacuum distillation up to 150°C under 26-27 inches Hg. Steam distillation was continued until viscosity rose to 10-13 Poise at 125°C using a 40 Poise cone on an ICI melt viscometer (available from Research Equipment Ltd). The novolak was cooled to 90°C whereupon 50% sodium hydroxide was added (3.6 mol). The alkaline novolak was then cooled to room temperature and the viscosity was lowered by water addition until a figure of between 5-10 Poise was reached.

Example 1

[0040] Using a Kenwood laboratory mixer and bowl, 1 kg of anthracite was mixed with 3g of powder thickener and 100g water. After 60 seconds mixing, 50g of Resin A and 6g of resole acetate were added to the wet anthracite. After commencement of mixing a 100g sample was removed every 60 seconds whilst continuing mixing. Each sample was placed into a 2" compression tube and compacted using a hydraulic press at a fixed pressure. The first specimen was tested immediately for green strength indication. The compressive strengths of the 3rd and 7th specimens were measured after 20 minutes from the time of release from the press to give an indication of pre-cure. The compression strengths of the 2nd, 4th and 5th specimens were measured after 1, 2 and 24 hours respectively. After 23 hours specimen 6 was completely immersed in water for 60 minutes and the compressive strength of the saturated specimen recorded. The results are shown in the table below.

Example 2

[0041] The method used in Example 1 was repeated except that 46.5g of Resin A and 9.5g of resole acetate were added as binder. The results are shown in the table below.

Example 3 (comparative)

[0042] The method used in Example 1 was repeated except that 50g of Resin A and 6g of triacetin were added as binder. The results are shown in the table below.

Table 1

Time after press	Specimen	Compressive Strength/kN		
		1	2	3
Immediate	1	0.89	0.97	0.84
20 min	3	3.41	3.92	3.63
	7	2.32	2.66	2.47
1 hour	2	5.11	6.16	5.84
2 hours	4	6.17	6.54	5.94
24 hours	5	8.95	9.78	7.72
24 hours (saturated)	6	6.99	7.35	5.41
Weight increase after 60 minutes immersed		4.76%	4.34%	10.73%
Loss in strength		21.9%	24.8%	29.9%

[0043] The results from Examples 1-3 show a steady improvement in strength development over a 24 hour period when resole acetate is used as hardener in Examples 1 and 2. The weight of water absorbed when the sample specimens are immersed in water for 60 minutes is significantly reduced in Examples 1 and 2. The reduction in compressive strength due to water saturation is most severe in Example 3 in which triacetin was used as the curing agent for Resin A.

Example 4

[0044] Formaldehyde emission measurements by the Draeger method.

Resin	Hardener	Formaldehyde (ppm)
Resin A	resole acetate	5.0
Resin B	resole acetate	0.5

[0045] Resin A, 50g, was added to a polypropylene jar with screw on lid and hardened by the addition of resole acetate 7.5g. The lid was placed on the polythene jar and the formaldehyde concentration was measured after 20 minutes, using a Draeger. Formaldehyde 0.2/a detection tube (part no. 6733081) which was inserted through a hole drilled in the polypropylene lid. The manufacturer's instructions for use procedure 234-33081e were followed. The procedure was repeated using Resin B. A reading was taken after 3 strokes of the Draeger pump.

[0046] The reaction between an alkaline novolak resin (Resin B) and a resole acetate produces significantly lower formaldehyde emissions than measured from the reaction between an alkaline resole (Resin A) and a resole acetate.

Claims

1. A fuel briquetting composition comprising a mixture of

- (i) fuel particles;
- (ii) an alkaline phenolic resin selected from alkaline phenol-formaldehyde novolak resin and alkaline phenol formaldehyde resole resin;
- (iii) an esterified phenolic resin selected from esterified phenol-formaldehyde resole resin and esterified phenol-formaldehyde novolak resin;
- (iv) a water-activatable green-strength additive; and
- (v) water.

with the proviso that when the alkaline phenolic resin is an alkaline phenol-formaldehyde novolak resin the esterified phenolic resin is an esterified phenol-formaldehyde resole resin.

2. A composition according to claim 1, wherein the composition additionally contains at least one ester selected from monomethyl esters of an aliphatic carboxylic acid, monoethyl esters of an aliphatic carboxylic acid, dimethyl esters of an aliphatic dicarboxylic acid and diethyl esters of an aliphatic dicarboxylic acid.

3. A composition according to claim 2, wherein the ester is a monomethyl or monoethyl ester of an aliphatic carboxylic acid selected from formic acid, acetic acid, propionic acid, lactic acid, stearic acid and oleic acid or is a dimethyl or diethyl ester of an aliphatic dicarboxylic acid selected from oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid and maleic acid.

4. A composition according to any one of claims 1 to 3, wherein the esterified phenolic resin is a phenol-formaldehyde resole acetate.

5. A composition according to any one of claims 1 to 4, wherein the alkaline phenolic resin is a phenol-formaldehyde resole resin in aqueous alkaline solution.

6. A composition according to any one of claims 1 to 5, wherein the alkaline phenolic resin is a phenol-formaldehyde novolak resin in aqueous alkaline solution.

7. A method of manufacturing fuel briquettes comprising the steps of forming a mixture according to any one of claims 1 to 6, shaping the mixture into briquettes and allowing the briquettes to harden.