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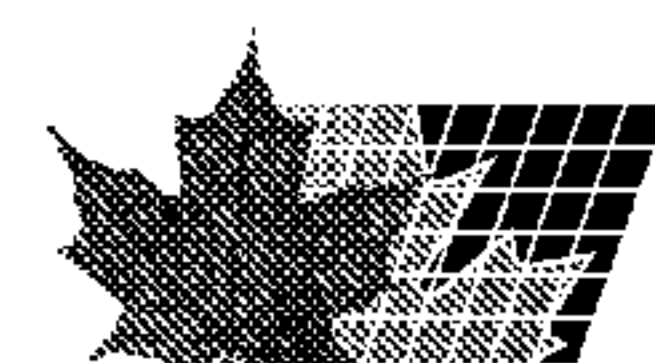
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(54) Titre : COMPOSITION STABLE ET NON TOXIQUE DE LIGNOSULFONATE ET UREE-FORMALDEHYDE ET  
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(54) Title: NON-TOXIC, STABLE LIGNOSULFONATE - UREA - FORMALDEHYDE COMPOSITION AND METHOD OF  
PREPARING THEREOF

(57) Abrégé/Abstract:

A non-toxic stable lignosulfonate - urea - formaldehyde composition. The composition is particularly useful as a binder for animal feeds. A method of making the composition is also disclosed.



Abstract of the Disclosure

A non-toxic stable lignosulfonate - urea - formaldehyde composition. The composition is particularly useful as a binder for animal feeds. A  
5 method of making the composition is also disclosed.

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NON-TOXIC, STABLE LIGNOSULFONATE - UREA - FORMALDEHYDE  
COMPOSITION AND METHOD OF PREPARATION THEREOF

Background and Summary of the Invention

5 The present invention relates to a lignosulfonate - urea - formaldehyde composition, its use and its preparation.

10 Lignosulfonate (LS) commonly is used as a generic term for spent sulfite liquor (SSL), LS purified from SSL, sulfonated alkali lignin from alkaline pulping processes, e.g. Kraft Process, and sulfonated hydrolysis lignin obtained from wood saccharification. For the purposes of this invention LS refers to SSL or LS purified from SSL.

15 LS is obtained from the sulfite pulping process in which wood is cooked with sulfite at elevated temperatures at or below pH 7. In this process the lignin, about 25% of wood, is partially hydrolyzed and sulfonated, and is rendered water soluble. Hemicelluloses are also partially hydrolyzed to reducing sugars and oligosaccharides. The  
20 cellulose, approximately the remaining 50% of wood, is left largely intact and insoluble. It is removed leaving soluble LS in solution or more specifically SSL.

25 SSL, as is, at 8-15% solids, or concentrated, or fractionated, or dried is used commercially in many application areas, for example in dispersion and binding.

30 LS is used to provide higher green and dried strengths in the manufacture of refractory shapes, face brick and ceramics. It is used in pelleting of animal feeds to give stronger pellets, less fines development during handling and improved feed consumption and conversion. LS is used to make foundry sand molds. It  
35 is used as a binder to granulate various fine

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substrates in pin mixers, Muller mixers, disk and drum granulators. It is used as a binder in briquetting. LS is coated topically to abate dusting from roads, coal, siliceous materials, other clays, fertilizers and prills.

In these applications, LS adsorbs to surfaces of the substrate, and at correct concentrations can provide tack in the system. Upon drying very strong shapes result. These shapes remain strong as long as they are dry, probably due to extensive hydrogen bonding, since LS contains sulfonic, carboxyl and hydroxyl groups. Water redissolves LS and as a result shapes bound with it will degrade with moisture.

The water solubility of LS has limited its utility. Topical treatments are impermanent, depending upon weather. As a result, various attempts have been made to improve water resistance of LS bound shapes as for example emulsification of hydrophobes in LS, U.S. Patent No. 4,666,522 by Hollis et al. While the hydrophobe inclusion substantially delays the access of moisture to LS bonds, especially in compacted shapes, the LS is eventually accessible to water and the bonds broken.

On the other hand, for many years phenol-formaldehyde resins (PF) and urea-formaldehyde resins (UF) have been used to generate highly water resistant and moderately water resistant bonds, Handbook of Adhesives by Skeist. Even moderately water resistant UF bonds far exceed resistance obtained by LS because PF and UF actually react to form covalent bonds.

Because of the economy of using LS versus UF and PF, there are reported numerous efforts at extension of resins with LS.

Homquist H.W., U.S. Patent No. 4,186,242 reports hot pressing of wood chips with UF and ammonium

lignosulfonate to get reduced formaldehyde emissions, the UF and ammonium lignosulfonate being added separately. Doronin, Yu G et al, Derevobrab Prom.-st 1983(3) 11-13 reports that addition of LS at  $\leq 20\%$  to UF did not adversely affect physico-mechanical properties of hardboard but resulted in decreased water resistance. When LS was added to the resin rather than separately, water miscibility was decreased. Svitkina MM et al, Derevobrab Prom.st. 1982(4) 4-6 report that adding 15% and 10% LS to surface and middle layers respectively, along with UF, gave good particle board. However, mixing 750 - 800 kg LS with 25 tons binder at 30 - 35°C gave increased resin viscosity and decreased miscibility to resin with water. Coyle R.P., U.S. Patent No. 3,931,972 cites alkaline methylation of LS with formaldehyde and then phenol and more formaldehyde to make a LS - PF resol resin. Bornstein, U.S. Patent No. 4,130,515 reports an LS-melamine-formaldehyde board binder made by reacting the components in-situ under alkaline conditions. Tomis B et al, Czech Patent No. 202,450 reports a water resistant binder from a two step condensation, first condensing 2:1 moles of formaldehyde : urea at pH 7 - pH 9.5, reducing pH to 5.1 with formic acid and condensing additionally with LS, LS being about 10% of the final binder solids. Morze et al, Qb. Ref - Semin Pokroky Uyroby Pouiziti Lepidiel Drevopriem 6:112-121, 1983 showed addition of Calcium LS to UF decreased formaldehyde release but caused deterioration of particle board properties. They recommended a maximum extension of UF to be 20%. In U.S. Patent No. 3,990,920 Grabowsky shows that addition of small amounts of sodium lignosulfonate improves the cold adhesion of glue UF to wood particles. Azaroy VI et al, Soviet Patent No. 1,237,678 makes an alkali lignin

UF resin by premethylation of alkali lignin at pH 9 - 12, adds urea and condenses at pH 7.5 - 9.0 and finally adds  $\text{NH}_4\text{Cl}$  reducing pH to 5.0 - 6.5 to further condense and reduce free formaldehyde level. Resin cure was  
5 faster and storage time went from 2 - 3 months to 4 - 7 months. The highest level of alkali lignin obtained in resin was 17% of solids.

Edler F.J., U.S. Patent No. 4,194,997 and U.S. Patent No. 4,244,846 relates a significant  
10 achievement in mixing UF resins and LS. Significant is the fact that Edler reports for the first time being able to obtain UF-LS mixtures containing high levels of LS which are compatible using very low condensed UF resins. That Edler has a mixture rather than a  
15 reaction product is evident in that similar reacted formulations are not compatible and that low solids precipitates UF.

Thiel et al, U.S. Patent No. 646,448 reports a stable resin including 5% to 30% LS by reacting urea  
20 and formaldehyde in the presence of lignosulfonates. Keirn G.I., U.S. Patent No. 2,622,979 reports a high strength paper container treated with a LS modified UF resin in which the resin contains 5% to 20% LS on urea. Maier C. et al, Romanian Patent No. 89,056  
25 reports a three step condensation of formaldehyde with urea, adding 5% to 30% sodium LS in the final polycondensation step.

Krut-ko N.P. et al, Ah. Prikl. Spektr. 48(1) 95-98, 1988 studied the reaction of mixtures by infrared  
30 spectroscopy. They report evidence that reaction occurs between the sulfo and carbonyl groups of sodium LS giving crosslinking. The effect was intensified by heating.

None of the adhesive or resin work has been  
35 able to provide a reacted LS-urea-formaldehyde resin

including large amounts of LS, in fact not more than 20%. Furthermore, UF resins typically contain 40% - 45% free formaldehyde, less if diluted, which is in itself a hazardous chemical, i.e., a carcinogen. These resins must be handled and used carefully.

The invention provides a composition which is suitable for use in the manufacture of hardboard. The invention also provides a composition which is suitable for use in the preparation of high quality animal feed pellets for aquaculture wherein said pellets have extended survival time in water. Further, the invention provides a composition which can coat substrates such as siliceous materials, coal, etc. and cure at ambient temperature to eliminate dusting and provide a waterproof barrier. For example, waste sites, coal piles, etc. Still further, the invention provides a composition which can be used in the manufacture of molds and bricks or other shapes which will be resistant to moisture. The invention also provides a low cost composition which is based in large part on a very low cost waste product, spent sulfite liquor, thereby alleviating environmental problems while providing a unique economical resin composition.

According to one aspect of the invention, we provide a stable composition including in solution about 55 to 95 parts methylol lignosulfonate - urea - formaldehyde polymer, about 1 - 28 parts sugars, and about 1 - 30 parts oligosaccharides, wherein about 55 - 80% of the total solids content is sulfite liquor resulting from sequentially reacting spent sulfite liquor with formaldehyde at acidic pH to form methylol lignosulfonate containing about 0.8 methylol groups per monomeric unit of the lignosulfonate portion of the spent

sulfite liquor, thereafter reacting the methylol lignosulfonate - containing spent sulfite liquor with an excess of urea to form lignosulfonate -methylene - urea in the spent sulfite liquor, and thereafter reacting the lignosulfonate - methylene - urea material with additional formaldehyde to give a molar equivalency of formaldehyde to urea in excess of 2:1 to obtain methylol lignosulfonate - urea - formaldehyde polymer, wherein the ratios of urea to spent sulfite liquor to formaldehyde on a weight basis range from 1:3:1.4 to 1:7:2 respectively after the reaction sequence.

According to a further aspect of the invention, we provide a method of making a non-toxic stable methylol lignosulfonate - urea - formaldehyde polymer wherein about 55 - 80% of the total solids content is sulfite liquor, comprising sequentially:

(a) reacting spent sulfite liquor with formaldehyde at acidic pH to form methylol lignosulfonate containing about 0.8 methylol groups per monomeric unit of the lignosulfonate portion of the spent sulfite liquor,

(b) reacting the methylol lignosulfonate - containing spent sulfite liquor with an excess of urea to form lignosulfonate - methylene - urea in the spent sulfite liquor, and

(c) reacting the lignosulfonate - methylene - urea with additional formaldehyde to give a molar equivalency of formaldehyde to urea in excess of 2:1 to obtain methylol lignosulfonate - urea - formaldehyde polymer, wherein the ratios of urea to spent sulfite liquor to formaldehyde on a weight basis range from 1:3:1.4 to 1:7:2, respectively, after the reaction sequence.

According to yet a further aspect of the invention, we provide a lignosulfonate - based binder comprising a composition including about 55 - 95 parts methylol lignosulfonate - urea - formaldehyde polymer, about 1 - 28

part sugars, and about 1 - 30 parts oligosaccharides, wherein about 55 - 80% of the total solids content is sulfite liquor resulting from sequentially reacting spent sulfite liquor with formaldehyde at acidic pH to form methylol lignosulfonate containing about 0.8 methylol groups per monomeric unit of the lignosulfonate portion of the spent sulfite liquor, thereafter reacting the methylol lignosulfonate - containing spent sulfite liquor with an excess of urea to form lignosulfonate - methylene - urea in the spent sulfite liquor, and thereafter reacting the lignosulfonate methylene - urea material with additional formaldehyde to give a molar equivalency of formaldehyde to urea in excess of 2:1 to obtain methylol lignosulfonate - urea - formaldehyde polymer, wherein the ratios of urea to spent sulfite liquor to formaldehyde on a weight basis range from 1:3:1.4 to 1:7:2, respectively, after the reaction sequence.

The invention resin is non-toxic to rats,  $LD_{50} > 5$  gm/kg body weight, and is non-irritating to skin and eyes. The invention resin is a stable solution for at least two months. It is easily spray dried to provide a powder which can be incorporated as an adhesive or reconstituted to 50% solution.

We have discovered that acidic premethylation of LS to achieve consumption of about 3% formaldehyde on SSL, about 0.8 methylol groups per monomeric unit of the lignosulfonate portion of the SSL, is essential to produce a stable invention with good performance. Without this step we, as others, find reaction of such a high level of LS with urea and formaldehyde gives insolubles formation and gelling. Accordingly, about 2 to 8 parts formaldehyde is reacted with about 70 parts spent sulfite liquor having a range of from about 45 to 65% total solids to form the acid methylolated lignosulfonate. If more than about 8 parts formaldehyde is employed there is excess formaldehyde which, during the next

succeeding step with urea forms UF resin which reacts with the lignosulfonate to form an undesirable insoluble product. Additionally, if less than about 2 parts formaldehyde is used there is insufficient reaction with the lignosulfonate, i.e. there is insufficient methylation of a lignosulfonate.

The second step involves reaction with urea at about a 3:1 molar ratio to formaldehyde added for the methylation. The urea-rich reaction provides a chemical environment for reaction of urea with the methylol groups of the methylol-rich LS. Accordingly, about 10 to 30 parts urea on spent sulfite liquor solids is employed, e.g. about 18-22 parts of urea to one part of methylol lignosulfonate-containing spent sulfite liquor. If more than about 23 parts are utilized, an undesirable insoluble product is formed. If less than about 10 parts urea is employed, there is insufficient reaction to obtain the lignosulfonate methylene urea.

After formation of mainly lignosulfonate methylene urea, additional formaldehyde is added to give a total added formaldehyde to urea ratio of about 2.6 : 1 and further condensation is conducted. If the formaldehyde in this step is added with urea in the prior step, an insoluble gelling composition results because urea preferentially reacts with the formaldehyde rather than the methylol lignosulfonate to form UF in the presence of the lignosulfonate. The UF reacts during heating with the LS to form a high level of insolubles. Accordingly, about 16 to 25 parts formaldehyde is employed in this subsequent formaldehyde reaction with the lignosulfonate methylene urea, e.g. about 20 to 24 parts of formaldehyde to one part of lignosulfonate-methylene-urea. Less than about 16 parts results in undesirable insolubles while more than about 25 parts results in excess formaldehyde which is toxic and thus undesirable. As noted above, the total molarity of the formaldehyde to urea in the system is about 2.6 moles of formaldehyde per mole of urea. If less than about 2.4 moles of formaldehyde per mole of urea in the system is employed, the system gells up resulting in undesirable insoluble compounds. As a result, there must be at least a total molarity of about 2.4 or higher in the system in order to properly form the methylol lignosulfonate urea formaldehyde polymer.

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Finally, about 6% ammonia on total solids may be added if desired to give pH 7.5 - 9.0 for the final liquid which is stable for about two months and which can be easily spray dried to a powder. That the chosen amount of ammonia addition gives the desired pH is significant as a measure of desired completion of the final reaction of formaldehyde. If reaction is not completed, the pH will be less than the desired level due to formation of excessive hexamethylenetetramine. Accordingly, about 5 to 8 parts ammonia gives the desired pH to quench the reaction and provide stability therefore. Although ammonia is preferable, any compound or mixture of compounds that raises the pH to between 7.5 to 9.0 may be employed so long as that compound also results in tying up any excess formaldehyde in the system.

The significance of acid methylation for the solubility and stability is great. For example, as reported herein, Azarov VI et al premethylolated alkali lignin under alkaline conditions but did not achieve a product of high lignin content. In alkali or Kraft lignin about one-third of the phenolic nuclei are free in the 5-position ortho to the phenolic hydroxy, Marton J. et al Lignin Structure and Reactions, 1966 pp. 125-144. Therefore, methylation is limited to about 0.33 methylol groups per lignin monomer. In acid methylation, reaction is preferentially at the site meta to phenolic hydroxyl. There are many more of these sites available and, unlike alkaline catalyzed methylation, the significance of whether or not the phenolic group is free or involved in a linkage with another monomer disappears. A free phenolic group allows reaction to proceed more easily in alkaline

reaction with formaldehyde. That a higher level of methylation, 0.8/monomer, achieved by the invention allows essentially all of the UF condensate (polymethylene urea) to be attached to the more hydrophillic calcium lignosulfonate providing the  
5 desired solubility characteristics.

Isolation of the active resinous component of the composition shows intact sulfo groups and equivalent calcium indicating non-involvement of sulfo  
10 groups which Krut-ko et al showed to be involved in reaction when UF resin was mixed and reacted with lignosulfonate such as in the Edler mixtures of UF and SSL.

Furthermore, the composition includes  
15 essentially all of the urea reacted with the methylol lignosulfonate.

Clearly there are advantages over prior art in addition to novelty. The invention is non-toxic. The invention can be used widely because there is no  
20 dangerous evolution of formaldehyde in unprotected environments. The invention gives bonding of wood particles when used at concentrations of about 1 - 5% by weight that is essentially equal to that bond quality obtained with PF resin, and a bond far more  
25 water resistant than obtainable with UF resin. The invention can be used at a concentration of about 0.5 - 4% by weight for pelleting animal feeds while PF and UF resins cannot because of toxicity and/or adverse effects on feed utilization and animal growth. The  
30 invention based upon waste sulfite liquor can be spread at a concentration of about 0.3 - 3 gal./yd.<sup>2</sup> to dry and cure as a water impervious film at ambient temperatures. Also, when used in concentrations of about 1 - 5% by weight, as an additive in the  
35 manufacture of refractory materials provides water

resistant dry shapes which are not appreciably degraded by moisture. For example, the invention is useful in the manufacture of refractory brick and/or ceramics, an underwater aquaculture feed binder and as a water impervious coating for coal.

#### Brief Description of the Drawing

Fig. 1 is a schematic illustration showing the effects of urea and formaldehyde levels and reaction temperatures on the properties of a resin from acid methylolated SSL.

#### Description of the Preferred Embodiment of the Invention

It is preferred to use calcium base hardwood spent sulfite liquor from the acid sulfite process at 55 - 60% total solids, 70 parts solids. The preferred pH is 3.0 to pH 3.5. Methylolation is preferably accomplished by adding 3.0 - 5.0 parts of formaldehyde and reacting 12 - 24 hours at 90 - 95°C. Thereafter, the temperature is reduced to 70 - 80°C. Urea, 20 parts, is thereafter added and the solution held at 70 - 80°C for two hours. Subsequently, 22.5 parts additional formaldehyde is added and the solution is reacted at 70 - 85°C for four hours to six hours. Finally, 5.8 parts of ammonia is added giving pH 8.0 - 8.5 and the solution is cooled.

Calcium base LS is preferred as ammonium LS gives rapid gelling in the reaction. Sodium based LS in the reaction gives resin formation, but the resin has inferior performance as compared to one formed from calcium base LS. It is believed that calcium may catalyze the reaction.

High solids LS is preferred because the reaction generates water and use of 37% formaldehyde causes dilution and a final resin solids of over 45% is desired for maintaining solution, lower cost spray drying and desirably viscosity.

Calcium based hardwood LS is preferred over softwood LS due to lower viscosity, greater solubility and greater stability of the resin.

#### Examples

5     Example 1

Figure 1 shows the significance of levels of formaldehyde and urea and reaction temperatures per generation of an easily handled resin solution from acid methylolated SSL.

10    Example 2

Resin was made using LS from a calcium based hardwood spent sulfite liquor. Analytical data, Table 1, are for the starting LS, the resin itself as described in the invention and fractions of that resin separated after dilution with water. All samples were vacuum dried at 60°C.

15           The spent sulfite liquor contains 57% as calcium lignosulfonate, the remainder being carbohydrate derived moieties such as sugars and  
20    oligosaccharides. All -OCH<sub>3</sub> is contributed by the lignosulfonate. All the calcium is from the SSL. Based upon these numbers we can see that the invention includes about 75% LS (SSL), on a vacuum dried basis.

25           The high OCH<sub>3</sub> content of the insolubilized resin fraction cannot mean that it is greater than 100% SSL but indicates that the lignosulfonate and not the carbohydrate components are involved with the actual resin formed. Furthermore, the data indicate that  
30    lignosulfonate from the spent sulfite liquor is 60% of the resin and that methylene urea based on nitrogen accounts for about 32% of the resinous solids isolated.

Finally, it is of note that calcium in the resinous isolate is equivalent to sulfonic sulfur indicating free sulfonate groups in the lignosulfonate.

By calculation from the data one gets an average dp of polymethylene urea on the calcium lignosulfonate of 2.7. Furthermore, calculation clearly shows that essentially all of the urea is combined as calcium lignosulfonate polymethylene urea.

Table 1

|    |                    |            |                  | Insolubilized<br>Fraction of<br>Invention | Remaining<br>Soluble<br>Fraction |
|----|--------------------|------------|------------------|-------------------------------------------|----------------------------------|
| 10 | <u>Parameter</u>   | <u>SSL</u> | <u>Invention</u> |                                           |                                  |
|    | % by Weight        | 100        | 100              | 23                                        | 77                               |
|    | % OCH <sub>3</sub> | 8.90       | 6.91             | 9.36                                      | 5.59                             |
|    | % Total N          | 0.09       | 11.98            | 12.56                                     | 11.72                            |
|    | % Total S          | 5.60       | 3.46             | 3.09                                      | 3.65                             |
| 15 | % Sulfonic S       | 5.0        | -                | 3.09                                      | -                                |
|    | % Ca               | 4.02       | 3.00             | 2.44                                      | 3.17                             |
|    | % Non-Sulfonic S   |            |                  | nil                                       |                                  |

Example 3

20                Resin made according to the preferred embodiment was spray dried at 500°F inlet and 200°F outlet temperatures. The powder was added at 1% and 2% by weight to a feed comprising 50% fish meal, 25% wheat flour and 25% ground corn. The mixture was conditioned to 200°C using live steam and pelleted through 1-1/2 x 5/32 die in a CPM CL-Type 2 mill. Retention time in the system is 30 seconds. A commercial lignosulfonate feed binder popular in aquaculture, available under the trade mark Langobin, was also tested at 2%. Results in Table 2 show the invention gives higher quality pellets in terms of pellet durability, PDI. PDI is determined by tumbling pellets according to ASAE 269.1 including four 3/4-inch hex nuts per chamber. The invention resin is also about twice as effective in reducing fines as the commercial binder.

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Table 2. PDI's and % Fines Reductions  
in Aquaculture Feed.

|   |                      |          |            |                          |
|---|----------------------|----------|------------|--------------------------|
| 5 | <u>Sample Tested</u> | <u>%</u> | <u>PDI</u> | <u>% Fines Reduction</u> |
|   | Langobin             | 2        | 82.5       | 19.0                     |
|   | Invention Resin      | 1        | 83.7       | 24.5                     |
|   | Invention Resin      | 2        | 87.0       | 39.8                     |
|   | Control              | 0        | 78.4       | 0                        |

10

Example 4

Pellets made according to Example 3 with 2% invention resin and 2% Langobin, a popular commercial binder for aquaculture, were evaluated for hydrostability. Pellets, immersed in water were placed across a 14/64-inch round hole and, via monofilament loops around the cylindrical pellets, suspended on 4.5 gram weights. Hydrostability was measured as minutes until the suspended weight dropped by pulling the monofilament through the immersed pellet. Data in Table 3 show Langobin increased hydrostability by 27% while the invention resin increased hydrostability by 62%.

25

Table 3

|    |               |                                  |
|----|---------------|----------------------------------|
|    | <u>Sample</u> | <u>* Hydrostability, minutes</u> |
|    | Control       | 63                               |
|    | 2% Langobin   | 80                               |
| 30 | 2% Invention  | 102                              |

\* Average 100 pellets for each value.

35

Example 5

This example shows effectiveness in coating a siliceous substrate. A 45° conical pile of dusty fine silica waste, surface area smooth basis 1.1 yd.<sup>2</sup>, was  
5 misted with water to dampen the surface. The invention resin was applied to the surface at 1 gal./yd.<sup>2</sup> to completely coat the surface. The coating was allowed to cure 96 hours at ambient temperature.

10 The pile was then watered by hose for a protracted period. The coating did not dissolve, nor was there any penetration of water through the coating to any sub-surface layer of silica.

Example 6

15 This example shows the effect of coating a pile of western coal received by a utility. Because of the nature of coal and its susceptibility to degradation on standing, the pile was pretreated with 0.8 gal./yd.<sup>2</sup> of solution containing 0.012 lb./gal. Aerosol OT-75\* and 0.017 lb./gal. sodium sulfate. The  
20 invention was then applied at 0.8 gal./yd.<sup>2</sup>. After cure for 72 hours at ambient temperature the coating remained impervious to water after inundations of water over a period of eight weeks.

Example 7

25 This example illustrates the use of the invention in hardboard versus a commercially used phenol-formaldehyde resin. 1040 grams fiber, 5.8% moisture was mixed 10 minutes in a Littleford\* mixer with 30 grams resin solids and 120 grams water. The  
30 treated fiber is dried at 105°C. Board is pressed for 30 seconds at 400°F and 500 PSI and then for six minutes at 250 PSI. Data in Table 4. show the invention, a methylol lignosulfonate-urea resin, performs as well as the commercial PF.

35

\*trade-mark

Table 4. Hardboard Test Results

|   |               | Density     | % Weight        | % Caliper  | % Weight        | % Caliper  |
|---|---------------|-------------|-----------------|------------|-----------------|------------|
|   | <u>Sample</u> | <u>g/cc</u> | <u>Increase</u> | <u>In.</u> | <u>Increase</u> | <u>In.</u> |
| 5 | PF Resin      | 0.880       | 17.6            | 8.2        | 72              | 34         |
|   | Invention     | 0.866       | 17.6            | 8.7        | 74              | 36         |

Example 8

10 Data in Tables 5-10 show that the composition of the present invention is not acutely toxic to rats nor a primary irritant of eyes or skin of rabbits. Weight gain in rats was unaffected.

Table 5.

CLINICAL OBSERVATIONS FOR THE ACUTE  
ORAL TOXICITY STUDY OF  
RD-0160-25 46.02% SOLIDS  
IN SPRAGUE-DAWLEY RATS

Dose 5000 mg/kg B.W.

| ANIMAL #<br>& SEX | H O U R |    |    |    | D A Y |   |   |   |   |   |    |    |    |    |    |
|-------------------|---------|----|----|----|-------|---|---|---|---|---|----|----|----|----|----|
|                   | 3       | 24 | 48 | 72 | 4     | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
| 5628M             | N       | N  | N  | N  | N     | N | N | N | N | N | N  | N  | N  | N  | N  |
| 5629M             | N       | N  | N  | N  | N     | N | N | N | N | N | N  | N  | N  | N  | N  |
| 5630M             | N       | N  | N  | N  | N     | N | N | N | N | N | N  | N  | N  | N  | N  |
| 5631M             | N       | N  | N  | N  | N     | N | N | N | N | N | N  | N  | N  | N  | N  |
| 5632M             | N       | N  | N  | N  | N     | N | N | N | N | N | N  | N  | N  | N  | N  |
| 5633F             | N       | N  | N  | N  | N     | N | N | N | N | N | N  | N  | N  | N  | N  |
| 5634F             | N       | N  | N  | N  | N     | N | N | N | N | N | N  | N  | N  | N  | N  |
| 5635F             | N       | N  | N  | N  | N     | N | N | N | N | N | N  | N  | N  | N  | N  |
| 5636F             | N       | N  | N  | N  | N     | N | N | N | N | N | N  | N  | N  | N  | N  |
| 5637F             | N       | N  | N  | N  | N     | N | N | N | N | N | N  | N  | N  | N  | N  |

N = NORMAL

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Table 6.

BODY WEIGHTS (GRAMS) FOR THE ACUTE ORAL TOXICITY STUDY OF  
RD-0160-25 46.02% SOLIDS  
IN SPRAGUE-DAWLEY RATS

Dose 5000 mg/kg B.W.

| ANIMAL #<br>& SEX | DAYS |     |     |
|-------------------|------|-----|-----|
|                   | 0    | 7   | 14  |
| 5628M             | 212  | 288 | 359 |
| 5629M             | 242  | 340 | 393 |
| 5630M             | 208  | 283 | 335 |
| 5631M             | 226  | 308 | 385 |
| 5632M             | 227  | 313 | 374 |
| MEAN =            | 223  | 306 | 369 |
| -----             |      |     |     |
| 5633F             | 191  | 233 | 260 |
| 5634F             | 190  | 237 | 262 |
| 5635F             | 189  | 228 | 250 |
| 5636F             | 194  | 228 | 250 |
| 5637F             | 184  | 214 | 228 |
| MEAN =            | 190  | 228 | 250 |

Table 7.

GROSS AUTOPSY FINDINGS FOR THE ACUTE ORAL TOXICITY STUDY OF  
RD-0160-25 46.02% SOLIDS  
IN SPRAGUE-DAWLEY RATS

Dose 5000 mg/kg B.W.

| ANIMAL #<br>& SEX | GROSS NECROPSY FINDINGS |
|-------------------|-------------------------|
| 5628M             | Normal                  |
| 5629M             | Normal                  |
| 5630M             | Normal                  |
| 5631M             | Normal                  |
| 5632M             | Normal                  |
| 5633F             | Normal                  |
| 5634F             | Normal                  |
| 5635F             | Normal                  |
| 5636F             | Normal                  |
| 5637F             | Normal                  |

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Table 8.

INDIVIDUAL SCORES FOR THE EVALUATION OF  
THE PRIMARY SKIN IRRITATION OF  
RD-0160-25 46.02% SOLIDS  
IN RABBITS

| ANIMAL<br>NUMBER | 1 HR. |    | 24 HRS. |    | 48 HRS. |    | 72 HRS. |    |
|------------------|-------|----|---------|----|---------|----|---------|----|
|                  | ER    | ED | ER      | ED | ER      | ED | ER      | ED |
| 8140M            | 0     | 0  | 0       | 0  | 0       | 0  | 0       | 0  |
| 8141M            | 0     | 0  | 0       | 0  | 0       | 0  | 0       | 0  |
| 8142M            | 0     | 0  | 0       | 0  | 0       | 0  | 0       | 0  |
| 8143F            | 0     | 0  | 0       | 0  | 0       | 0  | 0       | 0  |
| 8144F            | 0     | 0  | 0       | 0  | 0       | 0  | 0       | 0  |
| 8145F            | 0     | 0  | 0       | 0  | 0       | 0  | 0       | 0  |

ER - ERYTHEMA

ED - EDEMA

Table 9.

OCULAR RESULTS IN RABBITS RECEIVING  
RD-0160-25 46.02% SOLIDS

| ANIMAL<br>NUMBER | PARAMETER      | H O U R S |   |    |    |    |
|------------------|----------------|-----------|---|----|----|----|
|                  |                | 0         | 1 | 24 | 48 | 72 |
| 8134M            | Cornea-Opacity | 0         | 1 | 0  | 0  | 0  |
|                  | Area           | 0         | 1 | 0  | 0  | 0  |
|                  | Iris-value     | 0         | 0 | 0  | 0  | 0  |
|                  | Conjunctivae   |           |   |    |    |    |
|                  | A. Redness     | 0         | 1 | 0  | 0  | 0  |
|                  | B. Chemosis    | 0         | 1 | 0  | 0  | 0  |
|                  | C. Discharge   | 0         | 1 | 0  | 0  | 0  |
| 8135M            | Cornea-Opacity | 0         | 1 | 0  | 0  | 0  |
|                  | Area           | 0         | 3 | 0  | 0  | 0  |
|                  | Iris-value     | 0         | 0 | 0  | 0  | 0  |
|                  | Conjunctivae   |           |   |    |    |    |
|                  | A. Redness     | 0         | 1 | 0  | 0  | 0  |
|                  | B. Chemosis    | 0         | 1 | 0  | 0  | 0  |
|                  | C. Discharge   | 0         | 1 | 0  | 0  | 0  |
| 8136M            | Cornea-Opacity | 0         | 0 | 0  | 0  | 0  |
|                  | Area           | 0         | 0 | 0  | 0  | 0  |
|                  | Iris-value     | 0         | 0 | 0  | 0  | 0  |
|                  | Conjunctivae   |           |   |    |    |    |
|                  | A. Redness     | 0         | 1 | 0  | 0  | 0  |
|                  | B. Chemosis    | 0         | 1 | 0  | 0  | 0  |
|                  | C. Discharge   | 0         | 1 | 0  | 0  | 0  |

Table 10.

OCULAR RESULTS IN RABBITS RECEIVING  
RD-0160-25 46.02% SOLIDS

| ANIMAL<br>NUMBER | PARAMETER      | H O U R S |   |    |    |    |
|------------------|----------------|-----------|---|----|----|----|
|                  |                | 0         | 1 | 24 | 48 | 72 |
| 8137F            | Cornea-Opacity | 0         | 0 | 0  | 0  | 0  |
|                  | Area           | 0         | 0 | 0  | 0  | 0  |
|                  | Iris-value     | 0         | 0 | 0  | 0  | 0  |
|                  | Conjunctivae   |           |   |    |    |    |
|                  | A. Redness     | 0         | 1 | 0  | 0  | 0  |
|                  | B. Chemosis    | 0         | 0 | 0  | 0  | 0  |
|                  | C. Discharge   | 0         | 0 | 0  | 0  | 0  |
| 8138F            | Cornea-Opacity | 0         | 0 | 0  | 0  | 0  |
|                  | Area           | 0         | 0 | 0  | 0  | 0  |
|                  | Iris-value     | 0         | 0 | 0  | 0  | 0  |
|                  | Conjunctivae   |           |   |    |    |    |
|                  | A. Redness     | 0         | 1 | 0  | 0  | 0  |
|                  | B. Chemosis    | 0         | 1 | 0  | 0  | 0  |
|                  | C. Discharge   | 0         | 1 | 0  | 0  | 0  |
| 8139F            | Cornea-Opacity | 0         | 0 | 0  | 0  | 0  |
|                  | Area           | 0         | 0 | 0  | 0  | 0  |
|                  | Iris-value     | 0         | 0 | 0  | 0  | 0  |
|                  | Conjunctivae   |           |   |    |    |    |
|                  | A. Redness     | 0         | 1 | 0  | 0  | 0  |
|                  | B. Chemosis    | 0         | 1 | 0  | 0  | 0  |
|                  | C. Discharge   | 0         | 2 | 0  | 0  | 0  |

**THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE  
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:**

1. A stable composition including in solution about 55 to 95 parts methylol lignosulfonate - urea - formaldehyde polymer, about 1 - 28 parts sugars, and about 1 - 30 parts oligosaccharides, wherein about 55 - 80% of the total solids content is sulfite liquor resulting from sequentially reacting spent sulfite liquor with formaldehyde at acidic pH to form methylol lignosulfonate containing about 0.8 methylol groups per monomeric unit of the lignosulfonate portion of the spent sulfite liquor, thereafter reacting the methylol lignosulfonate - containing spent sulfite liquor with an excess of urea to form lignosulfonate -methylene - urea in the spent sulfite liquor, and thereafter reacting the lignosulfonate methylene - urea material with additional formaldehyde to give a molar equivalency of formaldehyde to urea in excess of 2:1 to obtain methylol lignosulfonate - urea - formaldehyde polymer, wherein the ratios of urea to spent sulfite liquor to formaldehyde on a weight basis range from 1:3:1.4 to 1:7:2 respectively after the reaction sequence.
2. A composition according to claim 1 in which the methylol lignosulfonate is calcium base.
3. A composition according to claim 1 in which the methylol lignosulfonate is sodium base.
4. A composition according to claim 1 in which the methylol lignosulfonate is derived from spent sulfite liquor from acid sulfite pulping of softwood.
5. A composition according to claim 1 in which the methylol lignosulfonate is derived from spent sulfite liquor from acid sulfite pulping of hardwood.
6. A composition according to claim 1 in which the composition is in spray dried powder form.
7. A method of making a non-toxic stable methylol lignosulfonate - urea - formaldehyde polymer wherein about 55 - 80% of the total solids content is sulfite liquor, comprising sequentially:

- (a) reacting spent sulfite liquor with formaldehyde at acidic pH to form methylol lignosulfonate containing about 0.8 methylol groups per monomeric unit of the lignosulfonate portion of the spent sulfite liquor,
  - (b) reacting the methylol lignosulfonate - containing spent sulfite liquor with an excess of urea to form lignosulfonate - methylene - urea in the spent sulfite liquor, and
  - (c) reacting the lignosulfonate - methylene - urea with additional formaldehyde to give a molar equivalency of formaldehyde to urea in excess of 2:1 to obtain methylol lignosulfonate - urea - formaldehyde polymer, wherein the ratios of urea to spent sulfite liquor to formaldehyde on a weight basis range from 1:3:1.4 to 1:7:2, respectively, after the reaction sequence.
8. A method according to claim 7 in which the spent sulfite liquor is calcium base from acid sulfite pulping of hardwood.
9. A method according to claim 7 in which the spent sulfite liquor is calcium base from acid sulfite pulping of softwood.
10. A method according to claim 7 in which the spent sulfite liquor is sodium base from acid sulfite pulping of hardwood.
11. A method according to claim 7 in which the spent sulfite liquor is sodium base from the acid sulfite pulping of softwood.
12. A method according to claim 7 in which the spent sulfite liquor solids concentration is about 55 - 62%.
13. A method according to claim 7 in which the spent sulfite liquor is treated in step (a) with about 3.0 - 5.0 parts formaldehyde to one part of spent sulfite liquor.
14. A method according to claim 7 in which the reaction of spent sulfite liquor with formaldehyde in step (a) is performed at about 90 - 95°C for about 12 - 24 hours.

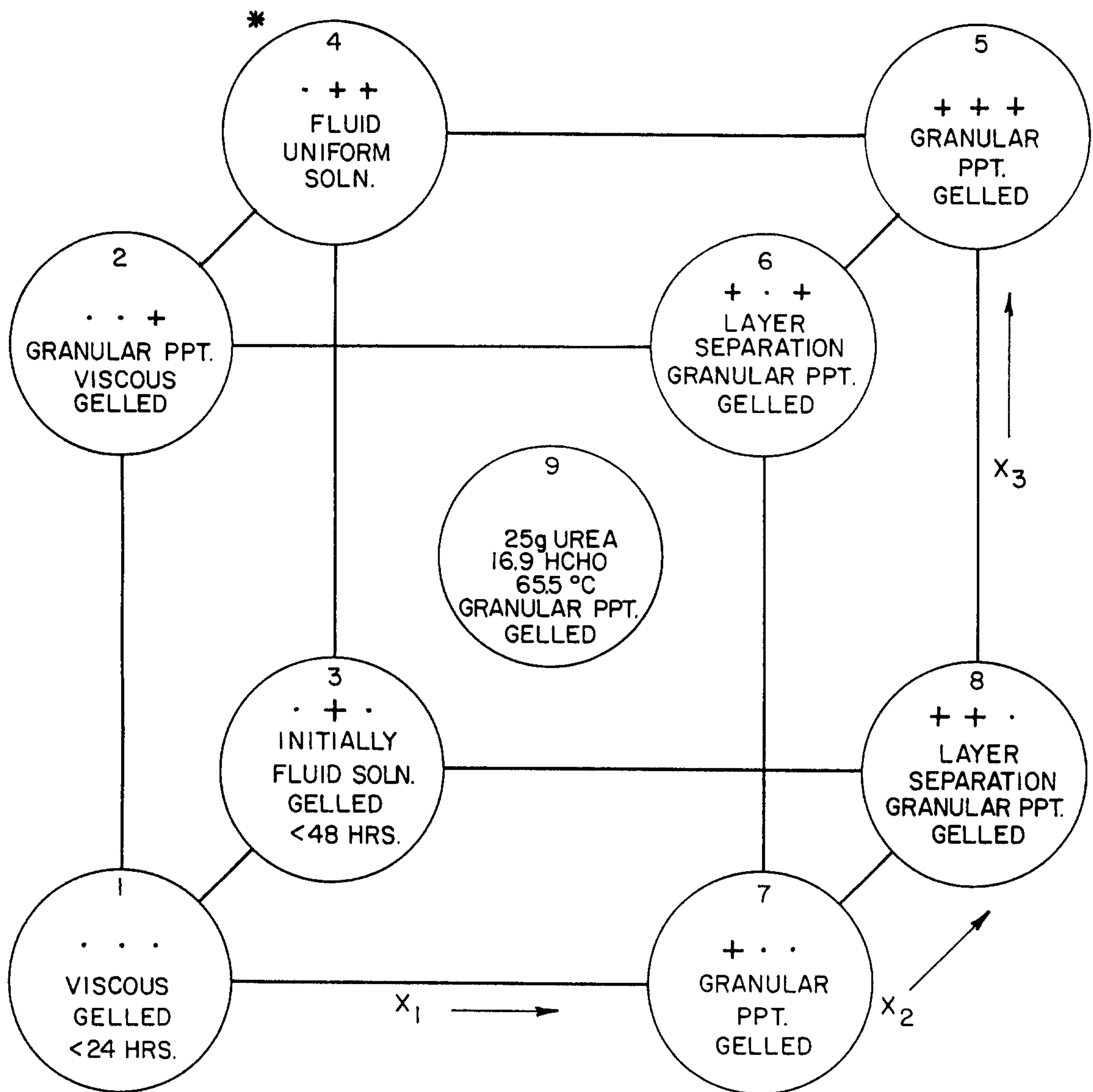
5. A method according to claim 7 in which about 18 - 22 parts of urea to one part of methylol lignosulfonate-containing spent sulfite liquor are added in step (b).
16. A method according to claim 7 wherein the reaction of the methylol lignosulfonate-containing spent sulfite liquor with an excess of urea in step (b) is performed at about 70 - 80°C for about 1 - 3 hours.
17. A method according to claim 7 in which about 20 - 24 parts of formaldehyde to one part lignosulfonate-methylene-urea are added in step (c).
18. A method according to claim 17 in which the formaldehyde addition is for about 4 - 6 hours at about 70 - 80°C.
19. A method according to claim 7 further including the step of raising the pH of the formaldehyde reaction in step (c) to about 7.5 - 9.0 to quench the reaction and provide stability therefor.
20. A method according to claim 19 wherein said pH raising step comprises adding about 5 - 8 parts ammonia.
21. A lignosulfonate - based binder comprising a composition including about 55 - 95 parts methylol lignosulfonate - urea - formaldehyde polymer, about 1 - 28 part sugars, and about 1 - 30 parts oligosaccharides, wherein about 55 - 80% of the total solids content is sulfite liquor resulting from sequentially reacting spent sulfite liquor with formaldehyde at acidic pH to form methylol lignosulfonate containing about 0.8 methylol groups per monomeric unit of the lignosulfonate portion of the spent sulfite liquor, thereafter reacting the methylol lignosulfonate - containing spent sulfite liquor with an excess of urea to form lignosulfonate -methylene - urea in the spent sulfite liquor, and thereafter reacting the lignosulfonate methylene - urea material with additional formaldehyde to give a molar equivalency of formaldehyde to urea in excess of 2:1 to obtain methylol lignosulfonate - urea - formaldehyde polymer, wherein the ratios of urea to spent sulfite liquor to

formaldehyde on a weight basis range from 1:3:1.4 to 1:7:2, respectively, after the reaction sequence.

22. A binder according to claim 21 in which the methylol lignosulfonate is calcium base.
23. A binder according to claim 21 in which the methylol lignosulfonate is sodium base.
24. A binder according to claim 21 in which the methylol lignosulfonate is derived from spent sulfite liquor from acid sulfite pulping of softwood.
25. A binder according to claim 21 in which the methylol lignosulfonate is derived from spent sulfite liquor from acid sulfite pulping of hardwood.
26. Use of a binder according to claim 21 as an animal feed binder.
27. Use of a binder according to claim 21 as an underwater aquaculture feed binder.
28. Use of a binder according to claim 21 in bonding wood in the manufacture of hardboard.
29. Use of a binder according to claim 21 in bonding refractory materials.
30. Use of a binder according to claim 29 in bonding face brick or ceramics.
31. Use of a binder according to claim 21 as a water impervious coating.
32. Use of a binder according to claim 31 as a water impervious coating for coal.

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**FIG. 1** BOX WILSON STUDY OF EFFECTS OF UREA AND FORMALDEHYDE LEVELS AND REACTION TEMPERATURES ON THE CROSS PROPERTIES OF RESIN MADE FROM 70 GRAMS METHYLOLATED HARDWOOD SPENT SULFITE LIQUOR.



VARIABLES:

- $X_1$  = GRAMS OF UREA/70g HARDWOOD CALCIUM LIGNOSULFONATE  
 $X_2$  = GRAMS OF FORMALDEHYDE/70g HARDWOOD CALCIUM LIGNOSULFATE  
 $X_3$  = REACTION TEMPERATURES, °C, OF UREA REACTION AND SUBSEQUENT FORMALDEHYDE REACTION

|       |        |       |
|-------|--------|-------|
| $X_1$ | 20g    | 30g   |
| $X_2$ | 11.25g | 22.5g |
| $X_3$ | 50°C   | 80°C  |

\* 4. REPRESENTS THE INVENTION

Scott & Appleton