PITCH CONTROL IN PULP AND PAPERMAKING PROCESSES
Stanley A. Lipowski, Livingston, and James F. Hern, Newark, N.J., assignors to Diamond Shamrock Corporation, Cleveland, Ohio
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ABSTRACT OF THE DISCLOSURE

Water soluble dicyandiamide-formaldehyde condensates are used in controlling the pitch which forms during pulp and papermaking processes. A condensate which is the reaction product of dicyandiamide and formaldehyde is effective in controlling the pitch which is liberated during pulp and papermaking processes.

This invention relates to a method of controlling the pitch which forms in pulp and papermaking processes.

One of the frequently occurring problems in pulp and paper manufacture is caused by pitch, viz., the collection of resinous materials and gums on pulp handling equipment or paper machine parts. Pitch is liberated from the pulp during the screening, beating and refining processes and tends to accumulate as a colloidal suspension of negatively charged, insoluble sticky dark colored particles which form lumps. These particles cause trouble by collecting on mill equipment, by filling in the wires of paper machines thereby producing holes in the finished paper or by collecting on the felt or machine parts as sticky, dark colored lumps. Troublesome pitch comes mostly from resins or resinous matter in the fibers themselves. Once pitch becomes attached to the machine parts, the only way it can be removed is by scrubbing with gasoline, kerosene or special cleaning compounds. In some paper mills, special solvents are sprayed on the return side of the wire and on the felt return to remove pitch. All of these methods have proven costly and have not destroyed or prevented the formation of pitch during the pulp and papermaking processes.

In the past, it has been found that the best way to remove pitch is to prevent its formation during the papermaking or pulping processes. In the pulping process, this has been accomplished by adding various pitch control agents, e.g., chemical sequestants, dispersing agents or surface active agents to the pulp during washing, screening and/or bleaching operations. Another common practice for controlling pitch deposits in pulp and paper mill operations is to add talc (magnesium silicate) or bentonite (montmorillonite) which adheres the pitch to the fibers thereby preventing pitch deposition. The main disadvantages of this practice are (1) high amounts of these materials are required (many times in excess of 0.5% by weight of the dry pulp weight), (2) incompatibility with other additives and materials used in the papermaking processes (sizing chemicals and the like), and (3) also the pitch may remain with the fibers during the pulping operation when these materials are used and the pitch may deposit out during the refining operation in the papermaking process.

In the papermaking process, the pitch control agents are normally added at the beater or prior to the refining operation. These agents have produced a material reduction of the pitch that collects on the paper felt and machine parts during the pulp and papermaking operation. Use of these pitch control agents has resulted in very little shutdown time in the operation of paper machines and in a decided improvement in screening conditions and pulp cleanliness as well as improved quality pulps. Some effective and commonly used pitch control agents in pulp manufacture for controlling pitch include naphthalene sulfonic acid-formaldehyde condensates such as those disclosed by Dr. Poschmann in Pulp and Paper Magazine of Canada 60:T 109–114 (1959) and the xylene sulfonic acid-formaldehyde condensates such as those described in U.S. Pat. No. 3,154,466—Nothum, patented Oct. 27, 1964. While use of these anionic aryl sulfonic acid-formaldehyde condensates in pulp and paper manufacture has proven to be an effective, low cost method of dispersing pitch, in many mills there is still a need for improved pitch control agents. During the past few years, there has been a strong trend toward closing up white water systems in papermaking operations. This change entails reuse of water which has been removed from the sheets during formation rather than discharging this water into streams and adding to pollution problems. When dispersant types of pitch control agents have been used, the pitch remains dispersed in the aqueous phase and continues to build up in the system as the waters are continually reused, reaching a point eventually where pitch breakout and deposition occurs. Hence, there is now an important need for a pitch control agent which is effective in small amounts and which will allow the pitch to be carried out of the system with the fibers so that the pitch will not remain in the system where it will eventually become a problem.

It is an object of this invention to provide an improved method of controlling pitch formation during the pulp and papermaking processes. A further object is to provide a more effective pitch control agent for preventing pitch from collecting on paper felt, wires and other machine parts during the pulping and papermaking processes. Still another object is to provide an improved method of making paper pulp whereby improved cleanliness in the mill equipment, in the pulp and in the paper is achieved. Other objects of this invention will become apparent from the detailed description given herein. However, it is intended that the detailed description and specific examples do not limit this invention, but merely indicate preferred embodiments.

A new class of pitch control agents for use in pulp and papermaking processes has been discovered. These agents are characterized as water soluble cationic amonophat resins which are dicyandiamide-formaldehyde condensates. The dicyandiamide-formaldehyde condensates are condensates of the amino resin base, dicyandiamide, and formaldehyde as well as condensates of dicyandiamide and formaldehyde along with other amino resin bases which
form water soluble cationic aminoplast resins. These agents differ from the anionic aryl sulfonic-formaldehyde condensates described above in that they are cationic in nature, i.e., they are positively charged, whereas the anionic agents are negatively charged. These cationic aminoplast resins control pitch formation during pulp and papermaking and prevent its collection on the processing equipment.

These cationic resins bring about the attachment of the pitch, in the form of discrete particles, to pulp fibers so that the pitch particles are uniformly distributed on the fibers. Paper produced from such pulp does not contain objectionable dark spots or specks of pitch and does not stick to the press rolls during manufacture. These improved pitch control agents are suitable for use in all methods of pulping, that is, sulfate, sulfite, semi-chemical, groundwood, reclaimed fibers and the like. Their use brings about substantial reductions in the amount of pitch which accumulates on the wires and other parts of the papermaking machine. This is particularly evident in that this breaks caused by press roll sticking are markedly reduced. Reduction in breaks caused by press roll sticking is particularly important because press roll sticking can cause breaks and press roll unwrapping which results in thirty minute or longer downtimes. Us of these water soluble condensates has resulted in a marked reduction in the downtime in the papermaking operation and a decrease in in-scouring losses on groundwood cleanliness as well as improved quality pulps and papers.

As indicated above, the most important advantage of the process using these water soluble condensates lies in the ability to eliminate difficulties caused by pitch in the production of paper and in the operation of the paper machine.

In the improved process of this invention, a pitch controlling quantity of a water soluble dicyandiamide-formaldehyde condensate is added to the pulp containing pulp. Generally, the pitch control agent is added to the pulp prior to the screening or refining operations so that it may be mixed with the pulp for a period of from about 30 to about 60 minutes to obtain the maximum pitch controlling effect. The optimum amount of pitch control agent which will be required varies because the process concerns itself with natural products (wood pulp) which contain various degrees of pitch. For these purposes, the condensates should be added to the pulp prior to screening or refining operations in pulp and in papermaking processes in amounts of from about 0.2% to about 100% based on the weight of the pitch present in the dry pulp to effectively reduce the amount of pitch formed during the papermaking operation. These condensates can be added in greater amounts than 100% without detracting from any of their beneficial properties as pitch control agents. Since no additional beneficial results in pitch control were noted with concentrations in excess of 100%, it is not usually practical or economical to utilize larger amounts of these agents. The condensates may be added to the system in the form of a dry powder or as about 35% to 55% by weight aqueous water solution, but preferably as a 1% to 10% by weight aqueous solution so that mixing with the pulp or papermaking furnish is rapid.

Water soluble dicyandiamide-formaldehyde condensates useful in controlling pitch are reaction products of the amino resin base, dicyandiamide, and formaldehyde as well as reaction products of dicyandiamide, at least one other amino resin base and formaldehyde. The other amino resin bases are materials such as guanidine, guanlyurea, urea, thiourea, bieture, melamine, ammeline, ammelide, cyanuric acid, guanamines as well as their mixtures and derivatives. The other amino base should contain reactive hydroxyl groups and be inorganic in nature, i.e., they are not derived from resins. Hence, by the expression dicyandiamide-formaldehyde condensate is meant those condensates obtained from dicyandiamide with or without at least one other amino resin base and formaldehyde or a formaldehyde liberating material, with or without etherification of the free methylol groups. Reactive methylol groups are those that can be etherified by reaction with an alkane such as methanol, ethanol, n-propanol, n-butanol or the like to obtain stabilized condensates. Etherified condensates have longer shelf lives and improved stability and are a preferred embodiment.

Useful dicyandiamide-formaldehyde condensates include those reaction products of about one mole of dicyandiamide, about 0 to about 2 moles of one or a mixture of an additional amino resin base and about 2 to about 15 moles of formaldehyde. Formaldehyde includes formaldehyde in the form of 30 to 40% aqueous solutions, 30 to 55% alcohol solutions using alcohols such as methanol, n-butanol, i-butanol or the like, polymeric forms such as paraformaldehyde, trioxane, hexamethylene tetramine or the like as well as chemical compounds such as acetals which will liberate formaldehyde. These condensates can be prepared by any procedure which provides for reaction between formaldehyde and amino resin base such that a water soluble condensate is obtained. Reaction between the amino resin base and formaldehyde can be carried out under acid and alkaline conditions, i.e., the reaction is either acid catalyzed or alkaline catalyzed. Acid conditions usually involve a pH of from about 1.0 to about 5.5 and water soluble condensates can be etherified by using formaldehyde in excess of from about 9 to about 11 and water soluble alkaline materials are used to attain these conditions. Examples of alkaline materials are alkali metal hydroxides such as sodium hydroxide, potassium hydroxide and lithium hydroxide and other materials such as ammonium hydroxide, borax, water soluble alkali metal carbonates such as sodium carbonate, potassium carbonate or the like.

The acid catalyzed reaction is exothermic and heat is usually initially applied to initiate reaction. Reaction generally occurs at temperatures within the range of about 55°C to about 80°C.

The alkaline catalyzed reaction is endothermic and heat is applied to maintain a temperature of reflux which varies between 98°C to 102°C without pressure. Higher temperatures can be used with pressures greater than atmospheric pressure.

In etherifying the free, reactive methylol groups, the alcohol is used in equimolar amounts with respect to the methylol groups. Temperatures of about 50°C up to the reflux temperature of the mixture are used in the etherification. The number of free methylol groups are determined by the DeLong method (Rec. trav. chim. 72:653, 654 (1953)).

One particularly useful condensate is the reaction product of one mole of dicyandiamide, 0.5 mole of urea and three moles of formaldehyde in the presence of 0.2 mole of formic acid as catalyst followed by etherification with methanol of the free, reactive methylol groups in the reaction product. This condensate is an acid catalyzed condensate and is a preferred embodiment. Procedures which yield acid catalyzed condensates are described in U.S. Pat. No. 2,990,397—Fetscher et al., June 27, 1961 and in U.S. Pat. No. 3,106,541—Lipowski et al., Oct. 8, 1963, said procedures being incorporated by reference herein. Another useful acid catalyzed condensate is the reaction product of one mole of dicyandiamide, three moles of formaldehyde, one mole of urea and 0.2 mole of formic acid followed by etherification with methanol of the free reactive methylol groups of the etherification condensate is the reaction product of one mole of dicyandiamide, three moles of formaldehyde and 0.2 mole of
formic acid followed by etherification with methanol of the free reactive methylol groups. Alkaline catalyzed condensates are also useful as pitch control agents. The useful alkaline catalyzed condensate is the reaction product of one mole of dicyandiamide and four moles of formaldehyde using sodium hydroxide solution as a catalyst wherein sufficient catalyst is added to obtain a reaction mixture having a pH of about 9. These condensates are added to the pulp or papermaking furnish to control pitch formation and should not affect other properties of pulp or paper produced from the furnish.

These condensates are useful in controlling pitch formation in Kraft or sulfite bleach plants, groundwood mills, paper mills or the like. They are effective at concentrations of about 0.75 lb. per ton dry resin on dry fiber in keeping systems clean and preventing pitch deposition in a paperboard mill. Likewise they are effective at one lb. per ton dry resin on dry fiber weight in preventing press roll sticking and picking problems in a paper mill producing fine printing grades. The condensates are also effective at 0.5 lb. per ton in pitch control in a paper mill producing highly refined light weight paper grades.

For a fuller understanding of the nature and objects of this invention, reference may be made to the following examples. These examples are given merely to illustrate the invention and are not to be construed in a limiting sense. All parts, proportions, percentages and quantities are by weight unless otherwise indicated. The term g. and °C. are used to indicate grams and degrees centigrade respectively in these examples.

**EXAMPLE I**

84 g. (1 mole) of dicyandiamide, 243 g. (3 moles) of 37% by weight inhibited aqueous formaldehyde solution, 10.2 g. (0.2 mole) of formic acid 90% active were charged to a 1-liter four neck glass reaction flask equipped with an agitator, thermometer and condenser. The inhibited formaldehyde solution contained 8% by weight of the methanol as an inhibitor. The resulting reaction mixture was agitated and heated gradually over 30 minutes to 60° C. Agitation was continued for one hour while the temperature was maintained constant at 60° C. Then the temperature of the mixture was gradually raised to its boiling point. The exothermic reaction, which occurred when the temperature was raised above 60° C., was controlled by intermittent cooling. The boiling point of the reaction mixture was reached after about 45 minutes of heating and the mixture was boiled for two hours. The reaction mixture was then cooled to 70° C, 30 g. (0.5 mole) of urea was added to the reaction mixture and the mixture was boiled for 30 minutes and then cooled to 50° C. 33 g. of methanol was added to the reaction mixture to etherify free methylol groups and the mixture was agitated for 30 minutes at 50° C. and then cooled to room temperature. The resulting reaction product was a dicyandiamide-formaldehyde condensate, that is, a catalytic aminoplast resin in the form of a water white syrup containing 45% by weight solids. The product was soluble in water at all dilutions. The pH of a 5% by weight solution of the product was 7.2.

**EXAMPLE II**

84 g. (1 mole) of dicyandiamide, 243 g. (3 moles) of a 37% by weight uninhibited aqueous formaldehyde solution, 10.2 g. (0.2 mole) of formic acid 90% active were charged to a 1-liter four neck glass reaction flask equipped with an agitator, thermometer and condenser. The reaction mixture was agitated and gradually heated over 30 minutes to 60° C. Agitation was continued for one hour while the reaction temperature was maintained constant at 60° C. Then the temperature was gradually raised from 60° C. to the boiling point of the reaction mixture. The exothermic reaction, which occurred when the temperature was raised above 60° C., was controlled by intermittent cooling. The boiling point of the reaction mixture was reached after about 45 minutes of heating and the mixture was boiled for 30 minutes. Then the reaction mixture was reheated to its boiling point where the viscosity of the reaction mixture dropped rapidly and substantially. The reaction mixture was then boiled for 15 minutes and cooled to 60° C. 40 g. of methanol was added to etherify the free methylol groups present in the dicyandiamide-formaldehyde condensate and the reaction mixture was agitated for 30 minutes to complete etherification of the free methylol groups. The reaction mixture was then cooled to room temperature. The reaction product was a dicyandiamide-formaldehyde condensate, that is, a catalytic aminoplast resin in the form of a water white syrup containing 55% by weight solids and had a higher viscosity than the condensate obtained in Example I above. The product was soluble in water at all dilutions. The pH of a 5% by weight solution of the product was 7.0. The product had a free formaldehyde content of about 0.2% by weight and had an unlimited shelf life.

**EXAMPLE III**

84 g. (1 mole) of dicyandiamide, 243 (3 moles) of 37% by weight uninhibited aqueous formaldehyde solution, 12 g. (0.233 mole) of formic acid 90% active were added to a 1-liter four neck glass reaction flask equipped with an agitator, thermometer and condenser. The mixture was agitated for 1.5 hours at room temperature. External heat was applied to the reaction mixture and the mixture was heated to 60° C. over a one hour period. The reaction temperature was gradually raised from 60° C. to the boiling point of the mixture. The exothermic reaction, which occurred when the temperature was raised above 60° C., was controlled by intermittent cooling. The boiling point of the reaction mixture was reached after 1.33 hours of heating. The mixture was boiled for 10 minutes and then cooled rapidly to 55° C. 50 g. of methanol was added to etherify free methylol groups and the mixture was agitated without external heating or cooling until the temperature of the mixture dropped to 25° C. The resulting reaction product was a water soluble dicyandiamide-formaldehyde condensate in the form of a clear water soluble syrup containing 41% by weight solids.

**EXAMPLE IV**

84 g. (1 mole) of dicyandiamide, 324 g. (4 moles) of 37% by weight uninhibited aqueous formaldehyde solution were charged into a 1-liter four neck flask equipped with an agitator, thermometer and condenser. The pH of the mixture was adjusted to 9.0 by the addition of two drops of 50% by weight aqueous sodium hydroxide solution. The alkaline reaction mixture was then heated over 15 minutes to its reflux temperature (102° C.). The reaction mixture was refluxed for 3 additional hours. At the end of this period, the reaction mixture had become very viscous and was cooled to 80° C. 60 g. (1 mole) of urea, 100 g. of methanol and 150 g. of water were added to the mixture and the mixture was stirred without external cooling or heating until the reaction temperature was 25° C. The resulting product was a water soluble dicyandiamide-formaldehyde condensate. The pH of the product was adjusted to 6.8 by the addition of 4.5 g. of 50% by weight sulfuric acid. The resulting product was a clear, water soluble syrup containing 32% by weight solid.

**EXAMPLE V**

The procedure given below was used to evaluate the
pitch control properties of the following Pitch Control Agents (Compound Nos.):

I—Xylene sulfonic acid-formaldehyde condensate described in Example I of U.S. Patent 3,154,466—Notham.

II—Naphthalene sulfonic acid-formaldehyde condensate described in Example III of U.S. Patent 3,154,466, Notham.

III—Naphthalene sulfonic acid-formaldehyde condensate described in Example I of U.S. Patent 3,154,466, Notham.

IV—Dicyandiamide-formaldehyde condensate described in Example I above.

V—Dicyandiamide-formaldehyde condensate described in Example II above.

VI—Dicyandiamide-formaldehyde condensate described in Example III above.

VII—Dicyandiamide-formaldehyde condensate described in Example IV above.

15 g. of alpha cellulose shreds is charged to 600 cc. of hot water at about 50° C. in a 1-liter beaker placed on a heated water bath. The alpha cellulose is chosen as the pulp source because it is so easily available that the pitch, alpha cellulose sheets are shredded and charged to the form of shreds. The mixture is agitated with a high speed agitator equipped with cutting blades until the shreds of alpha cellulose are converted to pulp. Then the compound to be tested as a pitch control agent is added in the desired quantity to the pulp mixture and the mixture agitated for 5 minutes. The pitch, which is the sap from the Balsam Fir tree, is dispersed in acetone. Usually about 0.7 to about 0.8 gram of the pitch is dispersed in 30 ml. of acetone. The sap dispersion is added to the agitated heated pulp mixture and the pitch remains in the pulp mixture in the form of a dispersion. The pulp mixture is then heated to 75° to 80° C. with agitation and agitated for one hour. After one hour at 75° to 80° C. agitation is discontinued. The agitator is removed, rinsed with warm water, dried for about 30 minutes in an oven at 120° C., cooled and weighed to determine the quantity of pitch remaining on the agitator, that is, the increase in weight of the agitator. The percent of pitch remaining on the agitator is determined by the following formula:

\[ \text{Pitch Percent By Wt. Deposited on agitator} = \frac{\text{Increase in weight of agitator}}{\text{weight of known pitch added}} \times 100 \]

Results obtained with each of the compounds as well as the blank in accordance with the above procedure are set forth in Table I below. The small differences in the amounts of pitch and pitch control agent in Table I which were used in the tests and which are reproduced therein are considered to be statistically insignificant in that they present minor variations within experimental limits.

The pitch control agents shown in Table I are those listed above as Material No. I through VII. The term “Blank” means that a pitch control agent was not used. Pitch g. represents the weight of pitch added to 15 g. of alpha cellulose. Pitch control agent g. represents the weight of the particular agent which was added to the pulp mixture. Pitch control agent percent weight based on pitch represents the weight percent of pitch control agent based on the weight of pitch used. Pitch g. deposited on agitator represents the weight of pitch which remained on the agitator after rinsing, drying, and cooling. Pitch percent by wt. deposited on agitator represents the percent of pitch remaining on the agitator as determined by the formula given above.

It is clear from the data in Table I that the dicyandiamide-formaldehyde condensates (Material Nos. IV through VII) are effective pitch control agents. These dicyandiamide-formaldehyde condensates bring about the attachment of pitch to pulp so that the pitch particles are uniformly distributed on the fibers as evidenced by clear beaker walls and little if any pitch deposited on the agitator.

The efficacy of the pitch control agents of the present invention was further demonstrated on a full plant scale in several successive pulping and papermaking operations. These demonstrations appear as follows:

**EXAMPLE VI**

A paperboard mill producing bleached paperboard grades using bleached sulfate fiber and a furnish containing rosin size and alum was plagued with pitch problems for many years. Immediately before the trial with the pitch control agents disclosed in this invention, this mill had been adding a surfactant, sequestran type pitch control agent at the rate of about 2 lbs. per ton of dry fiber at the stock chest prior to refining and another 2 lbs. per ton after refining. Pitch control with this application had been sporadic with intermittent control and deposition problems on mill equipment, Fourdriner wires, press rolls, etc.

The sporadic results were believed to be the result of white water reuse at this mill and build up of dispersed pitch in the system until periodic cleaning was required. The pitch control agent described in Example I of the present invention was diluted to 5% solids with water and introduced into the system at the rate of 0.75 lb./ton dry resin on dry fiber, one half being added at the stock chest prior to refining and the remainder immediately after refining. This application rate was continued immediately after refining. This application rate was continued over a three month period with the system remaining clean and no deposition of pitch occurring at any point in the system subsequent to the application.

**EXAMPLE VII**

A paper mill producing various grades of fine printing papers had a long history of press roll sticking and picking problems resulting in considerable lost production time because of paper breaks and shut downs for clean up of sticking materials at the first press section of their Fourdriner paper machine. Immediately prior to a trial with the condensates and process of this invention, the mill was using up to 5 lbs. per ton of dry fiber of a naphthalene sulfonic acid-formaldehyde condensate which was added to the pulper prior to refining. This condensate permitted the mill to operate their machines for longer durations between shut downs (1 to 2 days), but did not prevent press roll build up and sticking. Furnish here was a blend of bleached sulfate and sulfate pulps, rosin size, alum and titanium dioxide. The pitch control agent described in Example I of the present invention was introduced into the pulper at the rate of 1 lb. per ton (dry resin on dry fiber weight) and has been used continuously for a 5 month period with no press roll sticking or picking problems.

**EXAMPLE VIII**

A paper mill producing highly refined light weight paper grades using a furnish containing sulfate, sulfate and groundwood pulps along with rosin size, alum and filler pigments had a continuing pitch problem. During the past few years this mill has been maintaining pitch control using surfactant type pitch control agents. The pitch control agent described in Example I of the present invention was introduced into the stock chest prior to refining at the rate of 0.5 lb. per ton (dry resin on dry fiber weight) which represented a cost reduction of 50% over normal surfactant use. This pitch control agent has been used at this application level continuously for a 4 month period with no pitch deposits anywhere in the system.
TABLE I

<table>
<thead>
<tr>
<th>Pitch control agent (Compound No.)</th>
<th>Pitch, g.</th>
<th>Pitch control agent, percent by wt., based on pitch</th>
<th>Pitch, g., percent by wt., deposited on agitator</th>
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<tr>
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<td>I</td>
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<td>II</td>
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<td>0.760</td>
<td>0.002</td>
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</table>

What is claimed is:

1. In pulp and papermaking processes, the improvement which comprises adding to the pulp from about 0.2% to about 100% of a water soluble cationic dicyandiamide formaldehyde condensate based on the weight of pitch present in the pulp to prevent deposition of pitch on machinery used in said processes.

2. The process of claim 1 wherein said improvement comprises

(a) adding said condensate to said pulp, and thereafter

(b) screening said pulp, said screening taking place at least thirty minutes after said condensate is added to said pulp.

3. The process of claim 1 wherein said condensate is the reaction product of from about one mole of the amino resin base, dicyandiamide, from about 0.1 to about 2 moles of at least one other amino resin base and from about 2 to about 15 moles of formaldehyde.

4. The process of claim 3 wherein said condensate is etherified by reaction with an alkanol.

5. The process of claim 3 wherein said condensate is the reaction product of one mole of dicyandiamide, 0.5 mole of urea and three moles of formaldehyde in the presence of 0.2 mole of formic acid as catalyst followed by etherification with methanol of the free, reactive methylol groups in the reaction product.

6. The process of claim 3 wherein said condensate is the reaction product of one mole of dicyandiamide and three moles of formaldehyde in the presence of 0.2 mole of formic acid as catalyst followed by etherification with methanol of the free, reactive methylol groups in the reaction product.

7. The process of claim 3 wherein said condensate is the reaction product of one mole of dicyandiamide, one mole of urea and four moles of formaldehyde in the presence of aqueous sodium hydroxide solution as catalyst.

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<th>Inventor(s)</th>
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S. LEON BASHORE, Primary Examiner

F. FREI, Assistant Examiner

U.S. Cl. X.R.

106—15; 162—166, 167, 190; 252—357