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(54) **Pitch or stickies control agent**

Hilfsmittel zur Kontrolle von Harz- und klebrigen Ablagerungen

Produit pour combattre la poix ou les dépôts collants

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(56) References cited:
**DE-A- 1 546 237 US-A- 3 582 461
US-A- 5 068 279**

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Description

BACKGROUND OF THE INVENTION

The present invention relates to the use of melamine aldehyde-type polymers to inhibit and/or control pitch or stickies deposition in pulping and papermaking processes. More particularly, this invention relates to inhibiting the deposition of pitch on machinery used in pulping and papermaking processes and to the removal of pitch from machinery used in pulping and papermaking processes. This invention further relates to inhibiting the deposition of stickies on machinery used in secondary fiber pulping and papermaking processes and to the removal of stickies from machinery used in secondary fiber pulping and papermaking processes.

Pitch, stickies and tackies continue to be a problem in pulp and paper mills. It is believed that the problems caused by the build up of pitch or stickies and tackies on pulp and papermaking machinery and in the final paper cost the pulp and paper industry many millions of dollars per year in lost production. Pitch, as used herein, maybe generally defined as any resin-based deposit of widely varying composition originating in the extractive fraction of wood. The extractive fraction of wood is one of the four principal components of wood. The other three are cellulose, lignin, and hemicellulose. The extractive fraction is defined as a complex mixture of substances which are soluble in water, alcohol, benzene, ether, and/or acetone. The extractive fraction, which generally makes up from about 3% to 10% of the weight of wood, contains such components as low molecular weight carbohydrates, terpenes, aromatic and aliphatic acids, alcohols, tannins, color substances, proteins, lignins, alkaloids, and soluble lignins.

The term "stickies" and "tackies", as used herein, are interchangeable terms that primarily include synthetic contraries found in secondary fiber. For example, stickies and tackies include, but are not limited to, ink residuals, tars, latexes and heat melt contaminants found in secondary fiber. As such, stickies and tackies are distinct from pitch, which, as defined above, includes any resin-based deposit of widely varying constituency originating in the extractive fraction of wood. The constituents of pitch are naturally occurring, as opposed to the synthetic compounds that comprise stickies. While pitch and stickies cause similar problems in papermaking operations, they are distinct both in terms of their origin and their composition.

Pitch is a major problem in pulp and papermaking because it (1) agglomerates and also occludes other matter to form visible "dirt" in the final paper, (2) plates out and collects on machinery used in pulping and papermaking process such as screens, filters refining equipment, pulp washers, and paper machines, and (3) reduces pulp brightness and brightness stability. The composition and amount of pitch deposited on pulping and papermaking machinery and in the final paper vary

with the time of the year the trees are harvested, the type of wood, and the type of the pulping process used. For example, wood pulped from trees cut in the early spring and fall generally contains more pitch than wood pulped from trees cut at other times during the year. Pitch deposited in softwood Kraft mills tends to have a relatively larger abietic acid to fatty acid-ester ratio than pitch found in hardwood Kraft mills, and pitch deposit problems are generally somewhat more severe in sulfite mills. The sulfite pulping process removes only about one half of the resins and fatty esters leaving a considerable portion of these materials encapsulated within the cellulose fibers. However, these encapsulated materials are released by the shearing forces of pulping and papermaking processes and thus pitch deposits are more prevalent in the stock preparation area and on the paper machine. Pitch problems can be quite bothersome in mechanical pulp mills, including groundwood, TMP, CTMP, and semi-chemical pulping processes, particularly those that utilize softwoods. This is because there is little chemical degradation of the fatty acid esters and resin esters. Therefore, those materials are not washed out and tend to remain dispersed in the aqueous system of the pulping process.

Stickies and tackies are a major problem in secondary fiber pulp and papermaking operations because, like pitch, they (1) agglomerate and also occlude other matter to form visible "dirt" in the final paper, (2) plate out and collect on machinery used in pulping and papermaking process such as screens, filter refining equipment, pulp washers, and paper machines, and (3) reduce pulp brightness and brightness stability. The composition and amount of stickies deposited on pulping and papermaking machinery and in the final paper vary with the type of secondary fiber used in the pulping operation. As used herein, the term "secondary fiber" includes any paper fiber used for a second time in the production of a paper end-product.

Sources of secondary fiber include, but are not limited to, tissue, fine paper, boxboard, linerboard, footboard and newsprint. Each of these sources generally contains unique impurities, such as inks, colors, fillers, strength resins and/or coatings, which means that the stickies composition and concentration can vary widely from one secondary fiber to another.

The presence of calcium carbonate in the pulping process exacerbates the problem of pitch and/or stickies deposition on pulp and papermaking machinery. Crystallized calcium carbonate can provide nucleation sites for precipitated metal soaps thereby producing hydrophobic particles which coalesce with other particles to form a pitch deposit.

There have been many attempts over the years to eliminate pitch or stickies problems by adding control agents to pulping and/or papermaking processes. While more thorough pulp washing may help to reduce pitch or stickies problems, the most common methods of treatment involve the addition of dispersants or adsorb-

ant fillers to the furnish. For example, treatments may involve the use of alum, talc, anionic pitch-control agents such as polynaphthalene sulfonates or modified lignosulfonates, cationic pitch control agents such as polyquaternary ammonium polymers, methylcellulose derivatives and nonionic surfactants. None of these treatments are believed to be particularly effective.

Examples of the use of poly quaternary ammonium polymers as pitch control agents can be found in US-A-3,582,461. The '461 patent discloses the use of water soluble dicyandiamide-formaldehyde condensates to prevent pitch deposition on machinery used in pulping and papermaking processes. Other amino resin bases like melamine may be used together with dicyandiamide to form the condensate. By contrast, the instant invention utilizes water insoluble acid colloids.

Examples of attempts to control pitch with other types of compounds or processes are found in US-A-3,812,055; 3,895,164; 3,896,046; 3,992,249; 4,313,790.

Zirconium chemicals have also been used to control pitch. See, for example, US-A-4,950,361.

The instant melamine formaldehyde-type polymers are widely used in water treatment, particularly in the treatment of paint spray booths. See, for example, US-A-4,656,059, 4,629,572, 4,935,149 and 5,068,279.

However, the use of melamine formaldehyde-type polymers as described in claim 1 to control pitch or stickies deposition in papermaking is not known or suggested in the art.

As indicated above, the present invention as described in claim 1 relates to the inhibition and/or control of pitch or stickies in papermaking operations. While pitch is defined as the material comprising naturally occurring resinous materials and gums liberated during the screening, heating and refining processes that occur during papermaking, stickies are defined as synthetic additives which enter into paper furnishes. More particularly, stickies are defined as adherent deposits caused by organic materials used in paper and board converting operations which are typically introduced into paper machine furnishes with recycled fibers. The word "stickies" is derived from the fact that the resultant deposits stick to wires, felts, and other parts of paper machine. Stickies are a diverse mixture of synthetic materials ranging from hot-melt and pressure-sensitive adhesives to binders and coatings for inks or wet strength resins. Polymeric examples include, for example, polyethylenes, polybutadiene-styrenes, polyvinylacetates and polyacrylates.

SUMMARY OF THE INVENTION

The instant invention is directed to the inhibition of pitch or stickies deposits on and to the removal of pitch or stickies deposits from pulping and/or papermaking machinery, particularly wet-end papermaking machinery, comprising adding to a pulp slurry or paper furnish in contact with said machinery an effective amount of a

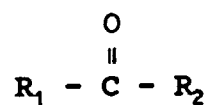
designated melamine formaldehyde-type polymer.

DETAILED DESCRIPTION OF THE INVENTION

More particularly, the present invention relates to a method for inhibiting pitch deposition on pulping and papermaking equipment or machinery, and/or for removing existing pitch deposits from such equipment or machinery, comprising adding to a furnish, stock or papermaking stream containing pitch which contacts said equipment or machinery a water-insoluble melamine formaldehyde-type polymer acid colloid.

The present invention also relates to a method for controlling and/or inhibiting stickies and/or tackies deposition on secondary fiber papermaking equipment or machinery, and/or for removing existing stickies/tackies deposits from such equipment or machinery, comprising adding to a secondary fiber furnish, stock or papermaking stream containing stickies or tackies which contacts said equipment or machinery a water-insoluble melamine formaldehyde-type polymer acid colloid.

An effective amount of a melamine formaldehyde-type acid colloid polymer must be used. As used herein, the melamine formaldehyde-type polymer acid colloid is a polymer comprising: (a), melamine or a substituted melamine; and (b) a compound described by the following formula:



wherein R₁ and R₂, which may be the same or different, are selected from the group consisting of H and straight or branched C₁₋₄ alkyl groups. The preferred compounds of (b) comprise aldehydes, with methanal (formaldehyde), ethanal and propanal being especially preferred; the most preferred aldehyde is formaldehyde. Also, moderate amounts of additional moieties, including, for example, urea and/or dicyandiamide, may be present in the melamine formaldehyde-type polymers of this invention.

Irrespective of the presence of additional moieties, however, the mole ratio of component (a) to component (b) should range from about 1:1 to about 1:6, with the preferred ratio being from about 1:1 to 1:3. The most preferred mole ratio is about 1 mole of melamine or a derivative thereof to about 2 to 2.5 moles of an aldehyde. Thus, the most preferred polymer is prepared from melamine and formaldehyde with the mole ratio of melamine to formaldehyde being about 1:2 to about 1:2.5.

The instant melamine-formaldehyde polymers are insoluble in water. They are therefore best utilized in acidic solutions wherein the melamine polymer is stabilized in a fine colloidal state of suspension. Calgon's product CA-289, which has a pH of about 1.6 to about

2.1, is an example of the preferred form. This product contains 8% active melamine-formaldehyde polymer in an acidic aqueous solution. Any acid can be used to prepare the melamine aldehyde acid suspension, although hydrochloric acid is preferred. Also, other stabilizing agents, such as alcohols, can be used.

The percent by weight of active melamine polymer in a stabilized (acidic) suspension or solution should range from about 0.1% to about 20%, preferably 1% to about 15%, and most preferably about 4% to about 12%, due to cost and product stability considerations. The pH should be sufficiently low to keep the melamine aldehyde-type polymer in a fine colloidal suspension.

The molecular weight of the melamine aldehyde-type polymer is not critical. However, the preferred molecular weight ranges from about 500 to about 50,000, and the most preferred molecular weight ranges from about 500 to about 5,000. As noted above, suitable melamine aldehyde-type polymers are commercially available from Calgon Corporation, under the trade-names CA-289 and WT-2511. These products have molecular weights of about 2,200.

An effective amount of the melamine formaldehyde-type polymer should be added to or maintained in the furnish, papermaking or secondary fiber stream being treated. The melamine polymer interacts with the pitch or stickies contained in such streams, thereby inhibiting pitch or stickies deposition and/or removing existing pitch or stickies deposits from the surface of papermaking equipment. As used herein, the term "effective amount" refers to that amount of melamine formaldehyde-type polymer which achieves the desired inhibition or removal of pitch or stickies for a given system.

The melamine polymer can be applied intermittently or continuously to the papermaking stream being treated at a preferred dosage of at least about 4.54×10^{-3} kg (0.01 lb.) polymer per 9.07×10^2 kg (ton) of dry fiber, on an active polymer basis. More preferably, the dosage should be maintained between about 0.18 kg/ 9.07×10^2 kg (0.40 lb/ton) to about 4.54 kg/ 9.07×10^2 kg (10.0 lb/ton). The melamine formaldehyde-type polymer can be added at any convenient location, but is preferably added so as to allow the maximum contact between melamine formaldehyde-type polymer and the pitch or stickies. For example, the melamine formaldehyde-type polymer may be added to brown stock washers, deckers, high density chests or machine dilution chests. Also, multiple points of addition may dilution chests. Also, multiple points of addition may be used.

EXAMPLES

Example 1 - Paper Mill Trial - Pitch Control

Calgon product CA-289 was fed to a small storage chest after the outside brown stock high density chest of a bleached softwood Kraftmill. The trial used fresh wood chips. The stock, after treatment, went through the

screening room and eventually to the bleach plant. The feed rate ranged from 0.91 to 4.54 kg (2 to 10 lb) of 8%, by weight, active polymer per 9.07×10^2 kg (ton) of furnish. This equates to a feed rate of about 0.07 to 0.36 kg per 9.07×10^2 kg (0.16 to about 0.8 lb per ton), on an active polymer basis.

Visual observations during the trial of the screens room and the reject cleaner - cones in the bleach plant indicated that they were virtually free of pitch. Further, pulp staining demonstrated a significant decrease in the amount of loose pitch in the system i.e., colloidal and sheared off encapsulated pitch. The pitch plate deposition in the screened room decreased slightly (8%) after the trial.

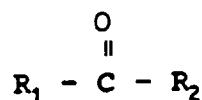
The Uhle boxes in the press section of the paper machine were cleaned one day before and one day after the colloidal melamine formaldehyde trial. No pitch or scale deposits were found in the Uhle boxes. This treatment replaced an effective AZC program.

Example 2 - Mixed Office Waste - Stickies Control

A melamine-formaldehyde acid colloid, commercially available from Calgon Corporation, was fed to a secondary fiber furnish prepared from a mixed office waste containing 3% by weight fiber, deinking chemicals, ink solids and bleach. The polymer dosage, on an active basis, was 0.30 kg/ 9.07×10^2 kg (.65 pounds/ton). Hand sheets were then prepared from the treated and untreated furnishes. The untreated hand sheets contained large tacky particle with fiber attached to them. The treated hand sheets contained smaller, non tacky particles with fewer fibers attached. These tests demonstrated the ability of the polymer to impede agglomeration of the stickies particles. These tests also demonstrated the ability of CA-289 polymer to render the surfaces of the stickies non-tacky.

Claims

1. A method for inhibiting pitch or stickies deposition on pulping and papermaking equipment or machinery, and/or for removing existing pitch or stickies deposits from such equipment or machinery, comprising adding to a furnish, stock or papermaking stream containing pitch or stickies which contacts said equipment or machinery, a water-insoluble melamine formaldehyde-type polymer acid colloid, wherein said water-insoluble melamine formaldehyde-type polymer acid colloid comprises (a), melamine or a substituted melamine; and (b) a compound described by the following formula:

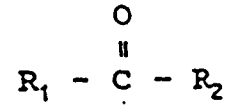


wherein R_1 and R_2 , which may be the same or different, are selected from the group consisting of H and straight or branched C_{1-4} alkyl groups.

2. A method according to claim 1 for inhibiting pitch deposition on pulping and papermaking equipment or machinery, and/or for removing existing pitch deposits from such equipment or machinery, which comprises adding to a furnish, stock, or papermaking stream containing pitch which contacts said equipment or machinery the water-insoluble melamine formaldehyde-type polymer acid colloid.
3. The method of Claim 2, wherein b) is formaldehyde.
4. The method of Claim 2, wherein the mole ratio of a):b) is about 1:1 to about 1:6.
5. The method of Claim 3, wherein the mole ratio of a):b) is about 1:1 to about 1:6.
6. A method according to claim 1 for inhibiting stickies deposition on secondary fiber pulping and papermaking equipment or machinery, and/or for removing existing stickies deposits from such equipment or machinery, comprising adding to a secondary fiber furnish, stock or papermaking stream containing stickies which contacts said equipment or machinery the water-insoluble melamine formaldehyde-type polymer acid colloid.
7. The method of Claim 6, wherein b) is formaldehyde.
8. The method of Claim 6, wherein the mole ratio of a):b) is about 1:1 to about 1:6.
9. The method of Claim 7, wherein the mole ratio of a):b) is about 1:1 to about 1:6.

Patentansprüche

1. Verfahren zur Hemmung der Harz- oder Klebstoffablagerung auf einer Pulpen- und Papiermaschine bzw. -maschinenanlage und/oder zum Entfernen vorhandener Harz- oder Klebstoffablagerungen von dieser Maschine bzw. Maschinenanlage, umfassend
das Zugeben zu einem Beschickungs-, Ausgangsstoff- oder Papierherstellungsstrom, der Harz oder Klebstoffe enthält und die Maschine bzw. die Maschinenanlage kontaktiert, eines wasserunlöslichen, sauren Kolloids eines Melamin-Formaldehyd-Polymers, wobei das wasserunlösliche, saure Kolloid des Melamin-Formaldehyd-Polymers enthält: (a) Melamin oder ein substituiertes Melamin; und (b) eine Verbindung der Formel:



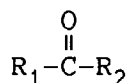
wobei R_1 und R_2 gleich oder verschieden sind und ausgewählt aus der Gruppe mit H und geraden oder verzweigten C_{1-4} -Alkylgruppen.

2. Verfahren nach Anspruch 1 zur Hemmung der Harzablagerung auf einer Pulpen- und papiermaschine bzw. -maschinenanlage und/oder zum Entfernen vorhandener Harzablagerungen von dieser Maschine bzw. Maschinenanlage, umfassend
das Zugeben zu einem Beschickungs-, Ausgangsstoff- oder Papierherstellungsstrom, der Harz enthält und die Maschine bzw. die Maschinenanlage kontaktiert, eines wasserunlöslichen, sauren Kolloids des Melamin-Formaldehyd-Polymers.
3. Verfahren nach Anspruch 2, wobei b) Formaldehyd ist.
4. Verfahren nach Anspruch 2, wobei das Molverhältnis von a) :b) etwa 1:1 bis etwa 1:6 ist.
5. Verfahren nach Anspruch 3, wobei das Molverhältnis von a) :b) etwa 1:1 bis etwa 1:6 ist.
6. Verfahren nach Anspruch 1 zur Hemmung der Klebstoffablagerung auf einer Sekundärfaserpulpen- und papiermaschine bzw. -maschinenanlage und/oder zum Entfernen vorhandener Klebstoffablagerungen von dieser Maschine bzw. Maschinenanlage, umfassend
das Zugeben zu einem Sekundärfaserbeschickungs-, -ausgangsstoff- oder -papierherstellungsstrom, der Klebstoffe enthält und die Maschine bzw. die Maschinenanlage kontaktiert, des wasserunlöslichen, sauren Kolloids des Melamin-Formaldehyd-Polymers.
7. Verfahren nach Anspruch 6, wobei b) Formaldehyd ist.
8. Verfahren nach Anspruch 6, wobei das Molverhältnis von a) :b) etwa 1:1 bis etwa 1:6 ist.
9. Verfahren nach Anspruch 7, wobei das Molverhältnis von a) :b) etwa 1:1 bis etwa 1:6 ist.

Revendications

1. Un procédé pour inhiber le dépôt de poix ou de résidus collants sur le matériel ou la machinerie de fabrication de pâte et de papier et/ou pour éliminer

les dépôts existants de poix ou de résidus collants de ce matériel ou cette machinerie, comprenant l'addition à un courant de composition de fabrication, de pâte ou de fabrication du papier contenant de la poix ou des résidus collants, qui entre en contact avec ledit matériel ou ladite machinerie, d'un colloïde acide polymère du type mélamine-formaldéhyde insoluble dans l'eau, dans lequel ledit colloïde acide polymère du type mélamine-formaldéhyde insoluble dans l'eau comprend (a) de la mélamine ou une mélamine substituée ; et (b) un composé décrit par la formule suivante :



où R₁ et R₂, qui peuvent être identiques ou différents, sont choisis dans le groupe formé par H et les radicaux alkyle en C₁-C₄ linéaires ou ramifiés.

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8. Le procédé de la revendication 6, dans lequel le rapport molaire a):b) est d'environ 1:1 à environ 1:6.
 9. Le procédé de la revendication 7, dans lequel le rapport molaire a):b) est d'environ 1:1 à environ 1:6.
2. Un procédé selon la revendication 1 pour inhiber le dépôt de poix sur le matériel ou la machinerie de fabrication de pâte et de papier et/ou pour éliminer les dépôts de poix existants de ce matériel ou cette machinerie, qui comprend l'addition à un courant de composition de fabrication, de pâte ou de fabrication du papier contenant de la poix, qui entre en contact avec ledit matériel ou ladite machinerie, du colloïde acide polymère du type mélamine-formaldéhyde insoluble dans l'eau.
 3. Le procédé de la revendication 2, dans lequel b) est le formaldéhyde.
 4. Le procédé de la revendication 2, dans lequel le rapport molaire a):b) est d'environ 1:1 à environ 1:6.
 5. Le procédé de la revendication 3, dans lequel le rapport molaire a):b) est d'environ 1:1 à environ 1:6.
 6. Un procédé selon la revendication 1 pour inhiber le dépôt de résidus collants sur le matériel ou la machinerie de fabrication de pâte et de papier à partir de fibres secondaires et/ou pour éliminer les dépôts existants de résidus collants de ce matériel ou cette machinerie, comprenant l'addition à un courant de composition de fabrication, de pâte ou de fabrication du papier à base de fibres secondaires, contenant des résidus collants, qui entre en contact avec ledit matériel ou ladite machinerie, du colloïde acide polymère du type mélamine-formaldéhyde insoluble dans l'eau.
 7. Le procédé de la revendication 6, dans lequel b) est le formaldéhyde.