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3,748,220

## PITCH STABILIZATION IN PAPERMAKING

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No Drawing. Continuation of abandoned application Ser.  
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Ser. No. 242,259

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2 Claims

### ABSTRACT OF THE DISCLOSURE

A method of stabilizing pitch in paper pulp by adding to the pulp an aqueous solution of nitrilotriacetic acid sodium salt and a water soluble acrylic polymer.

This is a continuation of application Ser. No. 1,329, filed Jan. 7, 1970, now abandoned.

### BACKGROUND OF THE INVENTION

#### Field of the invention

The present invention contemplates a novel resin stabilizing composition for the stabilization of pitch or resinous matter in chemical and mechanical pulps used in paper-making.

#### Description of the prior art

In general, numerous dispersants have been used to disperse the resinous matter in paper pulps to prevent tacky deposits of pitch and fibers on papermaking equipment, especially, the Fourdrinier wire where pitch spots result in holes in the finished paper and this paper is then classified as waste or "broke." This means a loss in production and also in production time (downtime) for cleaning the wire with kerosene to remove the pitch spots.

With the advent of disc refiners, modern type jordan and pulp blenders, the tolerance of pitch in the refining and repulping cycles of chemical and mechanical pulps is reduced to levels of 50-100 parts per million of agglomerated resinous matter. The use of polyelectrolytes, such as polyphosphates, cationic starches, amines and the naphthalene sulfonates, have proven to be ineffective in stabilizing "pitch" or resinous matter of paper furnishes.

Investigations and testing with various chelating agents and polyelectrolytes showed little promise. In a recent investigation, the effectiveness of chelating agents and polyelectrolytes have been screened, particularly the sodium salt of ethylenediaminetetracetic acid

 $(\text{Na}_4\text{EDTA})$ 

the sodium salt of nitrilotriacetic acid ( $\text{Na}_3\text{NTA}$ ) tri-polyphosphate and aminotrialkylphosphates, namely "Dequest." A sodium based sulfite pulp was used and by the test method of Gustafson the order of efficiency of preventing pitch from adhering to a copper metal surface (section of a Fourdrinier wire) revealed 85% prevention for tripolyphosphate; 65% for  $\text{Na}_3\text{NTA}$ ; 37% for  $\text{Na}_4\text{EDTA}$  and 27% for "Dequest." The problem with polyphosphates is their instability in an acid medium such as the white water system of any paper mill. The reversion to orthophosphate is accelerated by heavy metal ions which predominate in a white water medium so the efficiency of polyphosphates is of a transitory nature plus the fact that they interfere with retention of "size" and fillers or the performance of papermaker's alum and the orthophosphate acts as an excellent nutrient for slime producing bacteria.

It is, therefore, apparent that there is a need for a material to stabilize these resinous materials in paper-making pulps to prevent them from depositing on the papermaking apparatus, such as Fourdrinier wire, etc.

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### SUMMARY OF THE INVENTION

It is accordingly one object of the present invention to provide a new composition for stabilizing resinous material in papermaking pulps.

Another object of the invention is to produce a composition which when added to papermaking pulps will not only reduce but prevent deposition of resinous matter on papermaking apparatus.

Yet another object of the invention is to set forth a new composition containing a polyacrylic acid compound and a chelating agent which when added to papermaking pulp, will stabilize resinous material and prevent its deposition.

These and other advantages of the present invention will become apparent from the following description and examples.

In accordance with the above objects, it has been found that a composition containing water soluble alkenecarboxylic acid polymers and certain chelating agents will prevent the deposition of resinous matter from paper pulps. The polymer should have a molecular size of from 750 to 200,000 units. The ratio of chelating of chelating agents per 1 part by weight of polymer. The agent to polymer should be from 1 to 6 parts by weight chelating agent solution and the polymer solution should have a combined concentration of 50% active ingredients.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the present invention, there has been found a new composition for stabilizing resins in paper pulp. This composition is a mixture of polyacrylates and certain chelates.

The present invention was made as a result of an investigation based on stabilizing pitch by increasing the zeta potential or negative charge of the pitch particles. This approach was reported by Dr. Rudolf Schmut in his paper "Zeta Potential Measurement—Applications in the Paper Industry," appearing in the October 1964 issue of Industrial and Engineering Chemistry.

Initially, certain chelating agents and polyelectrolytes were investigated. Among these were the sodium salts of ethylenediaminetetracetic acid ( $\text{Na}_4\text{EDTA}$ ), the sodium salt of nitrilotriacetic acid ( $\text{Na}_3\text{NTA}$ ), tripolyphosphate and aminotrialkylphosphates, namely "Dequest." Tests revealed 85% prevention for tripolyphosphate; 65% for  $\text{Na}_3\text{NTA}$ ; 37% for  $\text{Na}_4\text{EDTA}$  and 27% for "Dequest." Actual plant trials showed the chelating agent  $\text{Na}_3\text{NTA}$  was ineffective at two pounds per ton of oven dried pulp on either kraft or sulfite pulps. The combination of  $\text{Na}_3\text{NTA}$  with tripolyphosphate in a ratio of 1 to 1 proved to be ineffective even at four pounds per ton of oven dried pulp.

The next compounds tested were polyacrylates and it was found that they did have effectiveness in stabilizing a colloidal pitch particle of a lyophobic sol as occurs in papermaking pulp slurries. It was then discovered that a combination of certain chelating agents with a polyacrylate dispersant would give the highest zeta potential value, greater than that attained by either agent alone. Dr. Schmut's work showed that negative charge leading to mutual repulsion occurs at zeta potential values of -20 millivolts. Experiences with paper pulp products revealed complete repulsion occurs above -40 millivolts and this is a prerequisite in stabilization of resinous matter in any finish containing kraft sulfite, ground wood or bleached versions of the pulp.

The following mill trials demonstrated the effectiveness of the combination of a chelating agent; namely, the trisodium salt of nitrilotriacetic acid, and a polyacrylate polymer.

## EXAMPLE I

The above combination was first introduced into a bleached kraft pulp system of a mill using bleached kraft, bleached and unbleached ground wood pulps in their furnish. The bleached kraft was purchased market pulp having its origin from three separate regions of the northern hemisphere and bleached by different bleaching sequents and the resinous matter varied from 0.6% to 1.2% on oven dried pulp. Using a zeta meter the zeta potential at the slusher; equipment for repulping baled market bleached kraft pulp was -7 millivolts. Upon the addition of one pound per ton of oven dried pulp of a composition of 4.7 pounds of a 40% aqueous solution of  $\text{Na}_3\text{NTA}$  and one pound of a 33% aqueous solution of an acrylic acid polymer (Calnox 214), the zeta potential was -25 millivolts. The addition of another pound per ton at the soak chest ahead of the refiners the zeta potential was -40 millivolts and after refining the pulp the introduction of another pound per ton at the kraft storage chest showed the zeta potential was -42 to -48 millivolts or in the range of complete repulsion or stability. Another test confirmed these findings.

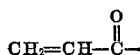
## EXAMPLE II

A pair of stainless steel plates 4" on edge were mounted in the consistency regulator box after the kraft storage chest to ascertain the tacky nature of the pitch in the pulp slurry going to the paper machines. The pitch adhering to the plates was exerted and weighed and then converted to a meaningful value or rate as milligrams per square foot per day. Prior to the use of the  $\text{Na}_3\text{NTA}$ -polyacrylate combination all the various agents previously mentioned resulted in values of 400-500 mgs./sq.ft./day. Upon the introduction of the composition of Example I, the deposition rate dropped immediately to less than 150 mgs./sq.ft./day. The pitch spots on the Fourdrinier had been completely eliminated. The composition of the instant invention does not interfere with "size" or filler retention. The mill has established production records never possible with the "downtimes" and high percentage of "broke" prior to the use of the formulated composition of  $\text{Na}_3\text{NTA}$  and a polymer of the acrylic family.

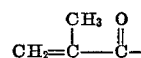
The unique features of the instant invention are obvious when the chelating agent; namely, the trisodium salt of nitrilotriacetic acid is inspected. This chelating agent does not defloc clays or inorganic pigments nor does it complex alkaline earth metal ions below a pH of 7.5. Since the aqueous medium of a white water system is always on the acid side—pH of 3.8 to 6.5—the role of chelation of calcium or magnesium ions from a high molecular weight resin acid is unlikely to be evident. Chelation of heavy metal ions cannot account for its performance since a range of 10 p.p.m. to 40 p.p.m. of  $\text{Na}_3\text{NTA}$  is present in any given white water system with the economic levels employed in mill trials. A surface phenomenon must prevail and this is enhanced by the presence of the "acrylic" polymer. Other chelates capable of the same performances are the alkyl derivatives of 3-butene 1,2,3-tricarboxylic acid and their sodium salts. It has been found that these chelates in combination with an acrylic polymer will give similar results.

The acrylic polymers employed in the instant invention are the water soluble low molecular weight "acrylics," which include polyacrylic acid, polymethacrylic acid and the alkali metal salts thereof and/or copolymers of such compounds. These polymers may be defined as water soluble alkenecarboxylic acid polymers having the structures so defined as follows:

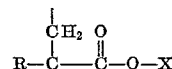
Acrylyl:



Methacrylyl:



Accordingly, the acrylic polymer preferably employed in the instant invention is the one whose polymer chain structure comprises units having the following formula:



where R is H or  $\text{CH}_3$  and X is H, Na or K.

It has also been found that a molecular size of 750 to 200,000 units will perform as a stabilizing agent for a lyophobic sol.

In practice of the invention, it is preferable to admix the chelating agent solution with the polymer solution to a concentration of 50% active ingredient. Concentrations of the chelating agent greater than 40% tend to salt out the chelating agent. In our preferable composition, we used a ratio of 4 parts of a 40% active aqueous solution of the trisodium salt of nitrilotriacetic acid to 1 part of a 25% aqueous solution of the sodium salt of a carboxylated polyelectrolyte; namely "Daxad 30." Of the lower molecular weight polymer, such as "Calnox 214," we used a ratio of 4.7 parts of the 40% aqueous solution of  $\text{Na}_3\text{NTA}$  to 1 part of the 33% active aqueous solution of the acrylic acid polymer. The liquid composition of the instant invention provides an active ingredient content of 31.0% to 32% of the  $\text{Na}_3\text{NTA}$  and 5% to 5.5% of the respective polymer solutions. On an active solid basis, this means a ratio of 6 parts of the chelating agent to 1 part of the polymer. A powder material may be used combining the dry forms of  $\text{Na}_3\text{NTA}$  with that of a dry form of the polymer; namely, "Daxad 40." The ratio of 6 parts of the chelating agent to one part of the polymer should be practiced.

Certain areas in papermaking may require a different ratio of the chelating agent to the polymer. In the repulping of coated "broke," which contains a high percentage of ash (pigments from coating of the paper) and latex; which is used as a binder in coating of paper, the latex must be stabilized in the same manner as the pitch or resinous matter of pulps. This application calls for a 1 to 1 ratio of the chelating agent to the polymer and its introduction ahead of the jordan used to repulp the "broke" is imperative. This composition is used where mills have a "broke" percentage of over 10% and as high as 35% in their paper furnish.

Mill practice has shown that one pound per ton of oven dried pulp of the preferable composition is adequate in stabilizing the resinous matter of chemical and mechanical pulps. It is imperative that where the pulp slurry is diluted to a lower consistency with fresh water or mill white water that further additions of the preferable compositions be made. In any stabilized system the optimum concentration is usually from 5 p.p.m. to 100 p.p.m. of the preferable composition and should dilution of the system occur, such as lowering the pulp consistency from the slusher at the soak chest ahead of refining or after refining requires a further addition of the preferable composition of the instant invention. Such dilutions would show a drop in the zeta potential of the pulp slurry system.

Having thus described the compositions of the invention in terms of their preferred embodiments which are set forth in the description and the examples of the aforesaid specification, it is apparent to those skilled in the art that various changes and modifications can be made in the composition without departing from the scope of the invention.

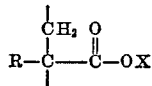
I claim:

1. A method of stabilizing naturally occurring pitch in papermaking pulp comprising adding to unbleached or bleached chemical or mechanical pulps an aqueous solution of nitrilotriacetic acid sodium salt and a water

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soluble acrylic polymer, having 750-200,000 monomer units therein wherein the nitrilotriacetic acid sodium salt is present in an amount of 1 to 6 parts by weight solids per 1 part by weight solids of acrylic polymer, and the aqueous solution is added to the pulp slurry in an amount of one pound per ton to four pounds per ton based on weight of oven dried pulp in the pulp slurry.

2. The method of claim 1 wherein the nitrilotriacetic acid sodium salt and the water soluble acrylic polymer, which has a polymer chain structure having monomer units of:



wherein R is selected from the group consisting of H and CH<sub>3</sub> and wherein X is selected from the group consisting of H, Na and K, is added as the aqueous solution in an amount sufficient to produce an active concentration of from 5 parts per million to 100 parts per mil-

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lion of nitrilotriacetic acid sodium salt and polymer in the pulp.

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