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**WO 03/085199 A2**

(54) Title: WHITE PITCH DEPOSIT TREATMENT

(57) Abstract: The present invention relates to a deposit control system, consisting of an inorganic or organic (natural or synthesized) coagulant and a microparticulate material (synthetic or naturally-occurring) such as bentonite clay, cross-linked polymer, colloidal silica, polysilicate, for pulp containing white pitch/stickies.

## White Pitch Deposit Treatment

### **Background**

Organic deposits in the papermaking system can cause losses in productivity and reduce the quality of the finished paper by forming spots, holes and breaks. These organic deposits are the result of naturally occurring pitch in the wood itself or from synthetic materials, such as adhesive, hot melt or latex, found in recycled pulps. These components are hydrophobic and accumulate in the process water. These deposits can agglomerate and stick onto papermaking machine surfaces or in the paper sheet. Deposits originating from wood are called "wood pitch" where as deposits from man-made materials are called "stickies" or "white pitch". White pitch is specific to coating binder lattices such as styrene butadiene rubber (SBR) and polyvinyl acetate.

Paper manufacture, in the simplest sense, involves producing a pulp from wood, slurring the pulp and water, and forming a pulp mat, which is pressed and dried to form paper. In the critical forming step, the pulp/water slurry (furnish) is formed as a mat on the wire web of the paper machine. Excess water and fines (white water) pass through the mat on the wire and are recycled. The formed web goes forward into the press and dryer section of the machines where the mat becomes paper.

Broke paper is the term used in the paper industry to describe the paper, which does not meet specifications, and for that reason could not be sold. This paper is usually recycled internally at the mill to recover fibers but it may also be sold to other mills as a source of fiber. The broke paper may be coated, the coating being applied to the base sheet of paper as it is manufactured. The broke paper, which is coated, is referred to as coated broke paper. Waste paper is the term used in the paper industry to describe paper, which has been utilized by a consumer. It is often termed "post consumer waste." This paper is often collected and recycled at a mill to recover fibers. The waste paper may be coated, the coating being applied to the base sheet of paper as it is manufactured. The waste paper, which is coated, is referred to as coated waste paper. Coated paper that is recycled can be broke or wastepaper. In recent

years many paper mills have experienced problems with the recycling of coated paper because the coatings introduce materials that normally would not be present in the original stock of fibers used to manufacture the base paper sheet.

The coatings normally comprise various pigments and binders. Typical pigments used include many types of clay, calcium carbonate, titanium dioxide, and other specialty fillers. The problems of white pitch are thought to be mainly caused by the binders, which include latex polymers derived from styrene-butadiene and polyvinyl acetate resins and natural binders such as starch.

White pitch problems have been known for some time in the paper producing industry. White pitch is sticky, light gray substance which is found as a deposit on metal surfaces in the wet-end, forming press, or dryer sections of the paper machine. It is termed "white" to distinguish it from the brown or black pitch, which results from materials contained in the wood. White pitch is also found in the white water system. At times the pitch deposits carbonize to give black deposits in the dryer section of the paper machine. The white pitch problem has been shown to be caused by the relatively high use of coated paper in the furnish of mills experiencing the problem. When coated paper is re-pulped, the clay or minerals and the latex in the coatings do not readily disperse into the pulp but form agglomerations, which result in white pitch. White pitch can coat the equipment or form defects in the paper if it travels into the paper machine with the pulp. High machine downtime, frequent cleaning, paper sheet defects such as holes, and increased number of sheet breaks are costly problems associated with white pitch deposits. Equipment clean up is quite involved because deposits can be found on the foils, table rolls, vacuum boxes, dryer cans and dryer felts, and throughout the press felts.

Various solutions have been suggested for dealing with the white pitch problem. Several deposit control chemicals are currently being used or evaluated by the paper industry. By trapping and dispersing the small latex particles in the sheet, the white pitch problem can be controlled. More specifically, the latex particles should be attached to the fibers immediately passing through the re-pulper. At this point the latex particles are small and anionic, and therefore, they can exit the system as part of a sheet. Due to the anionic character of both the latex particles and the fibers, an additive having low molecular weight and high cationic charge

is best suited for this purpose. However, the additive alone may not be sufficient to contain the latex particles in the paper sheet and the use of a retention aid compatible with the additive may be important for successful control of white pitch.

Synthetic polymers are the most successful known antideposition additives for white pitch. They are highly cationic, enabling them to create a strong electrostatic bond between the fibers, the latex particles and the additive. Once bonded, the fiber will carry the latex particles through the mill, with the help of a retention aid, and the particles will become part of the finished paper. Medium molecular weight polyglycol, amine/glycol or polyethyleneimine polymers have been shown to be useful in reducing white pitch.

Some of the methods for treating white pitch problems are described in documents below.

U.S. Pat. No. 5,131,982 (Michael R. St. John) describes the use of DADMAC containing polymers and copolymers to treat cellulose fibers recycled from coated broke recovery to make them suitable for making paper.

U.S. Pat. No. 4,997,523 (Pease et al) describes the use of a tetrafunctional alkoxyated diamine in combination with a phosphate compound, phosphonate compound or phosphoric acid to minimize the deposition of white pitch on paper making equipment.

U.S. Pat. No. 4,643,800 (Maloney et al) describe the use of an oxyethylene glycol nonionic surfactant in which one end hydroxyl group has been substituted with an aliphatic or alkylaromatic group and the other end hydroxyl group has been replaced with a polyoxypropylene group or a benzyl ether group in combination with a medium molecular weight (500-50,000) polyelectrolyte dispersant to remove and disperse contaminants from secondary fiber during re-pulping.

There are several disadvantages of the use of polymers to control white pitch. Polymers are not generally cost efficient. For example, polyethyleneimine (PEI), a tertiary amine polymer, is an effective white pitch control additive yet it is quite costly to use.

There are other solutions used for control of white pitch. Talc was commonly used in the past and is still sometimes used to control deposits. As a surface-active filler, talc acts to control deposits by detackifying the area around the pitch particle so that it cannot attach to the paper making equipment. However, this offers only a temporary solution to the pitch problem that reappears as the process continues. Talc does not bind the latex particles to the fibers, and therefore when exposed to shear, new tacky areas appear causing deposits. Also, additives which react with the surface of the pitch particle to render it less tacky (detackifiers) offer temporary solution to controlling white pitch. Published U.S. Patent Application 2001/0023751 describes a process for reducing sticky contaminants using polyvinyl alcohols and bentonite. The polyvinyl alcohol acts as a masking agent for the particles. The problem relates to the need to use excess quantities of polyvinyl alcohols. The bentonite absorbs excess polyvinyl alcohol.

#### **Summary of the Invention**

The present invention is a deposit control system, consisting of an inorganic or organic (natural or synthesized) coagulant and a microparticulate material (synthetic or naturally-occurring) such as bentonite clay, cross-linked polymer, colloidal silica, polysilicate, or borosilicate for pulp containing white pitch/stickies. The order of addition of these two components is essential to secure the benefits of reduced white pitch in a papermaking process. Coagulant can be added to the pulper or thick stock chest and the microparticulate may be added at the exit of the pulper or chest prior to stock dilution.

#### **Detailed Description**

Results of a number of turbidimeter measurements are shown in Figure 1. Turbidity of the backwater (filtrate) is an indicator of colloidal retention of latex emulsion particles or cleanliness. Using polyamine as a single component, a reduction in turbidity is achieved compared to not treating the coated broke. However, the addition of microparticle material with the coagulant provides a significant reduction in water turbidity. This data indicates that more white pitch/stickies particles are staying with the stock rather than re-circulating in the papermaking system. These lab results demonstrate that the coagulant/microparticulate system significantly reduces the accumulation of white pitch/stickies in the papermaking system.

The present invention is a deposit control system, consisting of an inorganic or organic (natural or synthesized) coagulant and a microparticulate material (synthetic or naturally-occurring) such as bentonite clay, cross-linked polymer, colloidal silica, polysilicate, or borosilicate for pulp containing white pitch/stickies.

The coagulant can be inorganic or organic (natural or synthetic) material. Examples of suitable organic coagulants are a lower molecular weight, high charge density, polymer, which is usually a homopolymer of recurring cationic groups or a copolymer of at least 80% by weight cationic monomer and 0 to 20% by weight acrylamide or other non-ionic monomer. The cationic groups can be derived from diallyl dimethyl ammonium chloride and dialkylaminoalkyl (meth) - acrylates and -acrylamides (generally as quaternary ammonium or acid addition salts). Dimethylaminoethyl acrylate or methacrylate quaternary ammonium salt is often particularly preferred. Alternatively the coagulant can be a condensation polymer such as a dicyandiamide polymer, a polyamine or a polyethyleneimine. Inorganic coagulants (such as alum, lime, ferric chloride, and ferrous sulfate) can be used.

The cationic coagulant materials, which may find use in this aspect of the invention, include well-known commercially available low-to mid molecular weight water-soluble polyalkylenepolyamines including those prepared by the reaction of an alkylene polyamine with a difunctional alkyl halide. Materials of this type include condensation polymers prepared from the reaction of ethylenedichloride and ammonia ethylene dichloride, ammonia and a secondary amine such as dimethyl amine, epichlorohydrin-dimethylamine, epichlorohydrin-dimethylamine-ammonia, polyethyleneimines, and the like. In certain cases cationic starch may be employed as the coagulant. Inorganic coagulants, e.g., alum and polyaluminum chloride, may also be used in this invention. The usage rate of inorganic coagulants is typically from 0.005 to 1% by weight based on the dry weight of fiber in the furnish.

The preferred coagulant is a cationic polyelectrolyte that is a poly(diallyl di(hydrogen or lower alkyl) ammonium salt having a number average molecular weight greater than 300,000 but less than 2,000,000.

The microparticle materials can be synthetic or naturally occurring. Examples of suitable microparticle materials are swellable clay materials, cross-linked polymer, colloidal silica, borosilicate or a suspension of microparticulate anionic material selected from bentonite, colloidal silica, polysilicate microgel, polysilicic acid microgel and crosslinked microemulsions of water soluble monomeric material.

Microparticle materials are widely used in the papermaking industry as retention aids, particularly for fine paper production. One such system employs swellable clays to provide an improved combination of retention and watering is described in U.S. Pat. Nos. 4,753,710 and 4,913,775, the disclosures of which are hereinafter incorporated by reference into this specification. In the method disclosed in Langley et al., a high molecular weight linear cationic polymer is added to the aqueous cellulosic papermaking suspension before shear is applied to the suspension, followed by the addition of a swellable clay, such as bentonite, after the shear application. Shearing is generally provided by one or more of the cleaning, mixing and pumping stages of the papermaking process, and the shear breaks down the large flocs formed by the high molecular weight polymer into microflocs. Further agglomeration then ensues with the addition of the bentonite clay particles.

Other microparticle programs are based on the use of colloidal silica as a microparticle in combination with cationic starch such as that described in U.S. Pat. Nos. 4,388,150 and 4,385,961, the disclosures of which are hereinafter incorporated by reference into this specification, or the use of a cationic starch, flocculant, and silica sol combination such as that described in both U.S. Pat. Nos. 5,098,520 and 5,185,062, the disclosures of which are also hereinafter incorporated by reference into this specification. U.S. Pat. No. 4,643,801 claims a method for the preparation of paper using a high molecular weight anionic water soluble polymer, a dispersed silica, and a cationic starch.

A still further microparticle is derived from borosilicates, preferably aqueous solutions of colloidal particles of borosilicate have a molar ratio of boron to silicon of from 1:1000 to 100:1 and generally from 1:100 to 2:5. The microparticle retention aid can be a colloid of borosilicate having a chemistry similar to that of borosilicate glass. This colloid is generally prepared by reacting an alkali metal salt of a boron-containing compound with silicic acid under conditions

resulting in the formation of a colloid. The borosilicate particles may have a particle size over a wide range, for example from 1 nm (nanometer) to 2 microns (2000 nm), and preferably from 1 nm to 1 micron.

The microparticle may be inorganic, for instance colloidal silica (such as described in U.S. Pat. No. 4,643,801), polysilicate microgel (such as described in EP-A-359,552), polysilicic acid microgel (such as described in EP-A-348,366), aluminum modified versions thereof. In particular systems can be used as described in U.S. Pat. Nos. 4,927,498, 4,954,220, 5,176,891 and 5,279,807 and commercialized under the trade name Particol by Ciba Specialty Chemicals and Dupont.

Anionic organic microparticulate materials can be used also. For instance, anionic organic polymeric emulsions are suitable. The emulsified polymer particles may be insoluble due to being formed of a copolymer of, for instance, a water-soluble anionic monomer and one or more insoluble monomers such as ethyl acrylate, but preferably the polymeric emulsion is a cross-linked microemulsion of water-soluble monomeric material, for instance as described in U.S. Pat. Nos. 5,167,766 and 5,274,055 and commercialized under the trade name Polyflex by Ciba Specialty Chemicals.

The particle size of the microparticulate material is generally below 2  $\mu$ m, preferably below 1  $\mu$ m and most preferably below 0.1  $\mu$ m.

The amount of microparticle material (dry weight based on the dry weight of the cellulosic suspension) is generally at least 0.03% and usually at least 0.1%. It can be up to for instance 1.6 or 2% but is generally below 1%.

The preferred microparticle material is a swellable clay, particularly a swellable clay from the smectite family. Preferred members of the smectite family of clays include bentonite, montmorillonite, saponite, hectorite, beidilite, nontronite, fullers' earth and mixtures thereof. A swellable clay component containing primarily bentonite is particularly preferred. It is necessary that the bentonite should be in a highly swollen, activated, form and in practice this means that it should be in the form of a monovalent salt of bentonite such as sodium bentonite. Although

there are some naturally occurring sources of sodium bentonite, most natural bentonites are alkaline earth bentonites, generally calcium or magnesium bentonites. The normal practice is to activate the alkaline earth bentonite by ion exchanging the calcium or magnesium for sodium or other alkali metal or ammonium ion. Generally this is done by exposing the bentonite to an aqueous solution of sodium carbonate, although some other activating materials are known. Swellable clays are naturally occurring substances and commercially available.

Suitable fibers for the production of the pulps are all qualities conventionally used for this purpose, for example mechanical pulp, bleached and unbleached chemical pulp and paper stocks from all annual plants. Mechanical pulp includes, for example groundwood, thermomechanical pulp (TMP), chemothermomechanical pulp (CTMP), pressure groundwood, semichemical pulp, high-yield chemical pulp and refiner mechanical pulp (RMP). Examples of suitable chemical pulps are sulfate, sulfite and soda pulps. The unbleached chemical pulps, which are also referred to as unbleached kraft carrier pulp, are preferably used. Suitable annual plants for the production of paper stocks are, for example, rice, wheat, sugarcane and kenaf. Pulps are produced using waste paper alone or as a mixture with other fibers. Waste paper includes coated waste, which owing to the content of binders for coatings and printing inks, gives rise to white pitch. The stated fibers and pulps can be used alone or as a mixture with one another. The adhesives originating from pressure-sensitive adhesive labels and envelopes and adhesives from the gluing of book spines as well as hotmelts give rise to the formation of stickies.

The present invention is particularly suited for papermaking systems that utilize a pulp derived from a significant amount of recycled or broke paper. The meaning of a significant amount will vary by system and by the type of recycled or broke paper utilized but will be characterized by the presence of sufficient white pitch in the process streams to materially effect operating conditions. In general, at least 10% of the pulp must be derived from recycled or broke paper products to generate material amounts of white pitch.

The deposit control system is introduced into a papermaking system by addition to the thick or thin stock system of the papermaking process. An important aspect of this process is the timing

of addition for each component. The process requires the addition of cationic coagulant, followed by the anionic microparticle. Without being bound by theory, it is believed that the prior addition of cationic coagulant improves the adsorption of white pitch by the anionic microparticle. It is further believed that the cationic coagulant is absorbed onto the pitch (wood, white and stickies), which are predominantly anionic or non-ionic, rendering them at least partially cationic. The bentonite now having adsorbed increased amounts of pitch is retained in the paper during formation. The result is reduced amounts of white pitch in the effluent. In a preferred embodiment, coagulant is added to the pulper or thick stock chest, while the microparticulate material is added at the exit of the pulper or chest prior to stock dilution.

The invention is further described by the following non-limiting example(s). The examples illustrate the invention, which is defined solely by the accompanying claims.

#### **Example 1**

Coated paper sheets are re-pulped in a laboratory disintegrator. A 400 ml aliquot of the 1% consistency stock is mixed at 1000 rpm. A polyamine coagulant and bentonite microparticle is added in one-minute intervals during mixing. Polyamine is added at 1, 1.5 or 2 pounds per ton as received with bentonite following at 4, 6 or 8 pounds per ton. After treatment, the stock is filtered through a 100-mesh screen and the filtrate is measured for turbidity. Each filtrate sample is prepared to a 1:14 dilution with deionized water. A portable turbidimeter Hach 2100P is used in testing and the results recorded in NTUs (Nephelometric Turbidity Units). The results are shown in Figure 1.

#### **Example 2**

Coated paper sheets are re-pulped in a laboratory disintegrator. A 400 ml aliquot of the 2.5% consistency stock is mixed at 1000 rpm. Either a polyamine, polyDADMAC or polyaluminum chloride (PAC) coagulant and bentonite microparticle are added in one-minute intervals during mixing. Coagulant is added at 1 pound per ton as received with bentonite following at 4, 6 or 8 pounds per ton. Coagulant is also added as a single component at 1 or 2 pounds per ton as received. After treatment, the stock is filtered through a 100-mesh screen and the filtrate is measured for turbidity. Each filtrate sample is prepared to a 1:14 dilution with deionized water.

A portable turbidimeter is used in testing and the results recorded in NTUs (Nephelometric Turbidity Units).

### **Results**

The results of the turbidimeter measurements for each treatment are shown in Figure 2. Turbidity of the backwater (filtrate) can be an indicator of colloidal retention of latex emulsion particles or cleanliness. By using polyamine or polyDADMAC as a single component at 1 or 2 pounds per ton, a reduction in turbidity is achieved compared to not treating the coated broke. However, the addition of bentonite with the various coagulants provides a reduction in water turbidity. A significant reduction in turbidity is noted when comparing 1 pound per ton as received polyamine or PAC coagulant plus bentonite to 2 pounds per ton as received coagulant.

## Claims

1. A process for making paper comprising adding to a paper stock an effective amount for reducing the deposition of white pitch of at least one cationic coagulant polymer or an inorganic coagulant and followed by the addition of a microparticle material, wherein the paper stock contains pulp derived at least in part from recycled paper products.
2. A process according to Claim 1 wherein the microparticle material is selected from the group consisting of swellable clay materials, cross-linked polymer, colloidal silica, borosilicate or a suspension of microparticulate anionic material selected from bentonite, colloidal silica, polysilicate microgel, polysilicic acid microgel and crosslinked microemulsions of water soluble monomeric material and mixtures thereof.
3. A process according to Claim 2 wherein the microparticle material is an anionic material.
4. A process according to Claim 2 or Claim 3 wherein the microparticle material is a swellable clay from the smectite family.
5. A process according to any of Claims 2 to 4 wherein the microparticle material is a mineral consisting essentially of bentonite, montmorillonite, saponite, hectorite, beidilite, nontronite, fullers' earth and mixtures thereof.
6. A process according to any preceding Claim wherein the microparticle material is a mineral composed primarily of bentonite.
7. A process according to any preceding Claim wherein the cationic coagulant polymer is a homopolymer containing recurring cationic groups or a copolymer of at least 80% by weight cationic monomer and 0 to 20% by weight acrylamide or other non-ionic monomer.

8. A process according to Claim 7 wherein the cationic groups are derived from diallyl dimethyl ammonium chloride and dialkylaminoalkyl (meth)-acrylates and -acrylamides or quaternary ammonium salts thereof.
9. A process according to Claim 8 wherein the cationic groups are dimethylaminoethyl acrylate or methacrylate quaternary ammonium salt.
10. A process according to any of Claims 1 to 7 wherein the coagulant is a dicyandiamide polymer, a polyamine or a polyethyleneimine.
11. A process according to any of Claims 1 to 6 wherein the coagulant is selected from the group consisting of alum, lime, ferric chloride, polyaluminum chloride, ferrous sulfate and mixtures thereof.
12. A process according to any of Claims 1 to 7 wherein the coagulant is a polyalkylenepolyamine prepared by the reaction of an alkylene polyamine with a difunctional alkyl halide.
13. A process according to any of Claims 1 to 7 wherein the coagulant is a cationic polyelectrolyte that is a poly(diallyl di (hydrogen or lower alkyl) ammonium salt having a number average molecular weight greater than 300,000 but less than 2,000,000.
14. A process according to Claim 13 wherein the microparticle material is a mineral composed primarily of bentonite.
15. A paper product made according to the process of any of Claims 1 to 5 or 7 to 13.
16. A paper product made according to the process of Claim 6.
17. A paper product made according to the process of Claim 14.

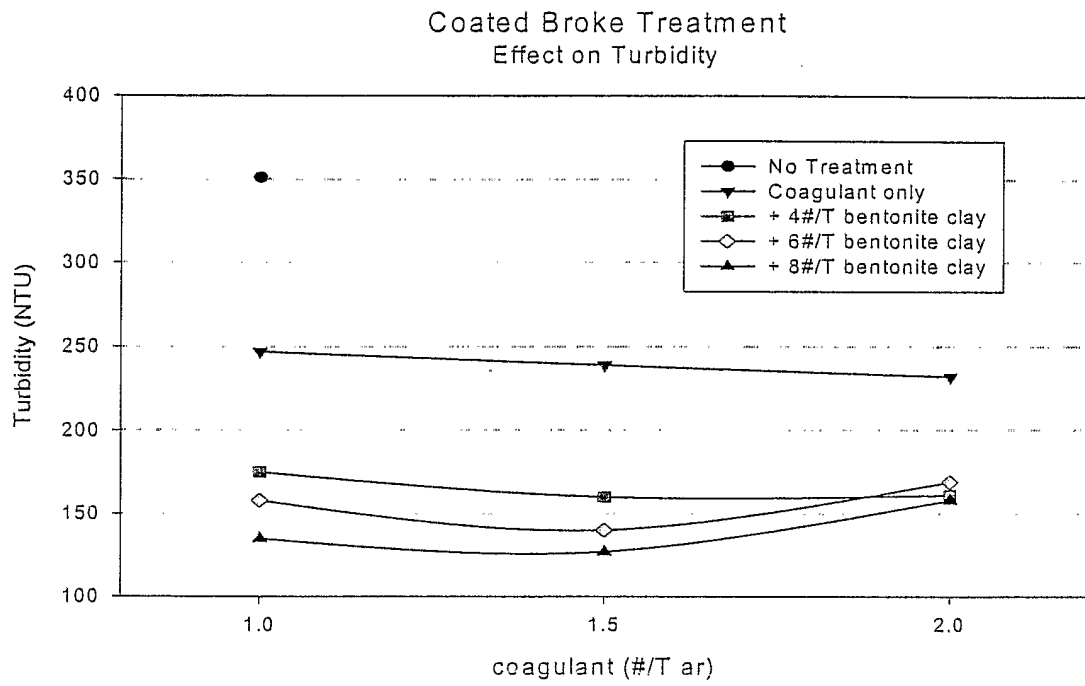


Figure 1

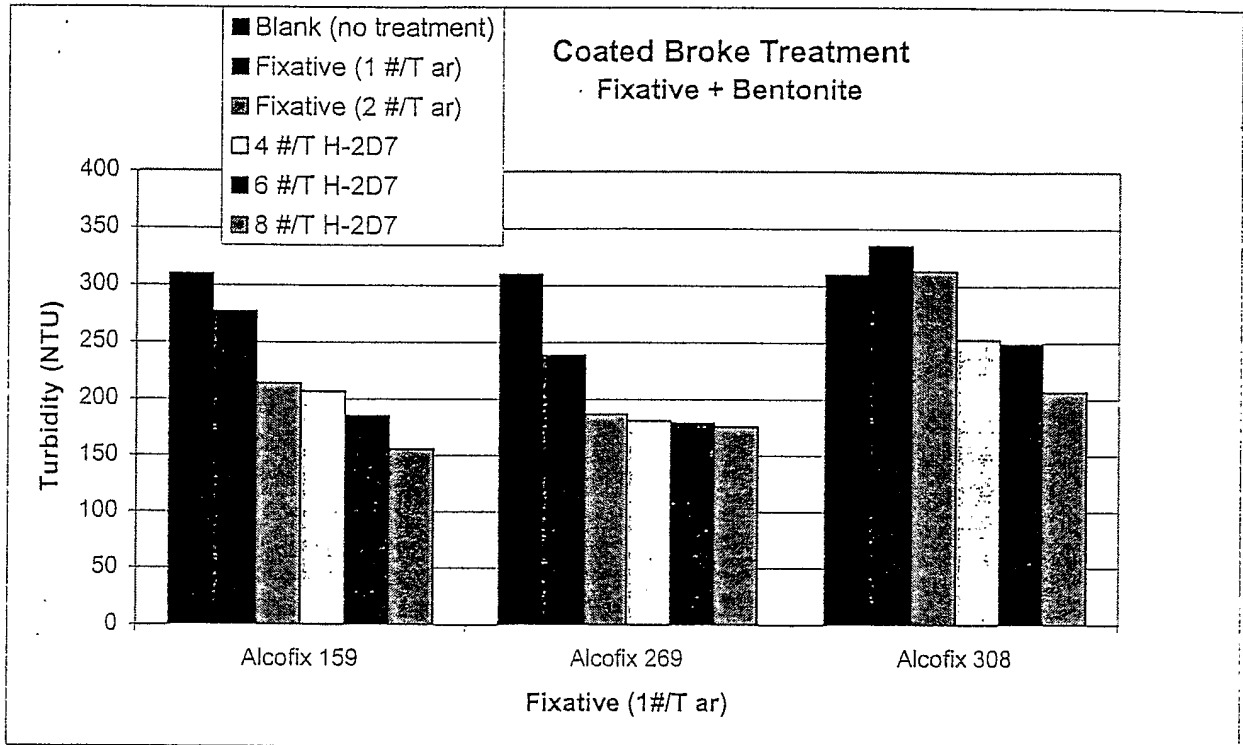


Figure 2