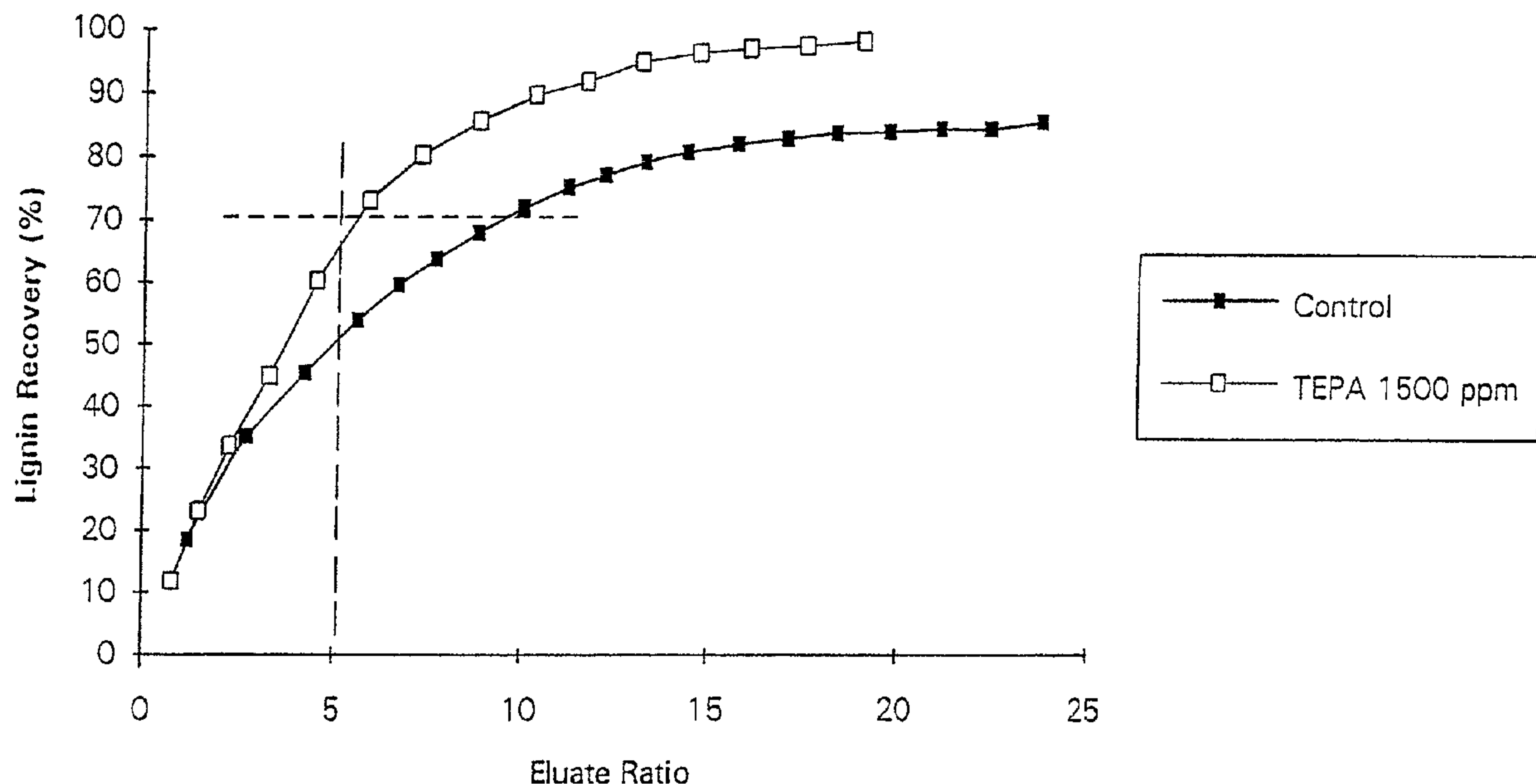




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(57) Abrégé/Abstract:

Ethyleneamines are used in washing pulp to remove lignin. A process for washing a cellulose pulp mixture containing lignin to remove at least a portion of the lignin therefrom comprises use of a washing composition with at least 100 ppm of an ethyleneamine. The process includes an improvement in a washing process for a cellulose pulp mixture containing lignin wherein a washing composition is used to remove at least a portion of the lignin, the improvement comprising use of at least 100 ppm of an ethyleneamine with the washing composition and/or using an amount of ethyleneamine at least equivalent to 100 ppm based on the washing composition with the washing composition. The washing composition is also novel and includes a washing composition for washing kraft pulp comprising water and at least 100 ppm of an ethyleneamine.

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(21) International Application Number: PCT/US95/16571 (22) International Filing Date: 20 December 1995 (20.12.95) (30) Priority Data: 08/373,354 17 January 1995 (17.01.95) US (71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventors: CROFT, Alan, P.; 325 Petunia, Lake Jackson, TX 77566 (US). SHEFFIELD, Byford, D.; Route 5, 135 Queens Court, Brazoria, TX 77422 (US). (74) Agent: ULMER, Duane, C.; The Dow Chemical Company, Patent Dept., B-1211, 2301 Brazosport Boulevard, Freeport, TX 77541 (US).		(81) Designated States: BR, CA, JP, KR, MX, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: USE OF ETHYLENEAMINES IN THE REMOVAL OF LIGNIN (57) Abstract Ethyleneamines are used in washing pulp to remove lignin. A process for washing a cellulose pulp mixture containing lignin to remove at least a portion of the lignin therefrom comprises use of a washing composition with at least 100 ppm of an ethyleneamine. The process includes an improvement in a washing process for a cellulose pulp mixture containing lignin wherein a washing composition is used to remove at least a portion of the lignin, the improvement comprising use of at least 100 ppm of an ethyleneamine with the washing composition and/or using an amount of ethyleneamine at least equivalent to 100 ppm based on the washing composition with the washing composition. The washing composition is also novel and includes a washing composition for washing kraft pulp comprising water and at least 100 ppm of an ethyleneamine.		

USE OF ETHYLENEAMINES IN THE REMOVAL OF LIGNIN

This invention relates to removal of lignin, particularly to the use of amines in such removal. In one more particular aspect, the invention relates to brownstock washing.

Removal of lignin is a common problem especially in dealing with wood pulps. Wood pulps include pulps such as chemical (for example kraft process), thermomechanical, mechanical, chemimechanical, chemithermomechanical or groundwood pulp.

The need for facile lignin removal is especially evident in kraft pulping processes. These processes are well known in the art and include digestion of pulp using an alkaline medium, preferably containing an inorganic hydroxide, to release cellulose fibers from other components such as lignin. After digestion, fibers are commonly released under pressure into a tank in a process referred to as blowing or blowdown. Then the pulp is washed to remove spent chemicals, lignin and other organic chemicals. The liquid removed from the pulp is referred to as black liquor and contains 25 percent dissolved solids, 50 percent of which are organic, primarily lignin solubilized as phenolates or carboxylates, other cellulosic material, and sodium soaps. After this washing stage, which is referred to as brownstock washing, the pulp is optionally bleached before being made into paper. The black liquor resulting from the washing stage is called "weak black liquor" and is commonly concentrated by evaporation to a desired concentration and burned to reclaim the inorganic chemicals and provide fuel value. The organic materials are advantageously incinerated. Brownstock washing is described in more detail, for instance, by Josephson et al., "Multi-component Control of Brownstock Washing," Tappi Journal, v. 76, no. 9, pp. 197-204 (1993).

Removal of lignin from the pulp is important because lignin carried over into a bleaching step results in a higher requirement for bleaching chemicals including additives and for effluent treatment. Poorly washed pulp is believed to be a source of precursors for certain dioxins and chlorinated furans during bleaching. It is also important to minimize the wash water used to

remove lignin because any water in excess of the amount desired in the black liquor requires energy for removal, for example evaporation, from the liquor and may result in a greater cooking chemical makeup requirement for reuse of a black liquor. Ineffective washing can lead to foaming in screening and papermaking operations and to high requirements for pH control chemicals in later stages. There is increasing environmental pressure to reduce effluent and have more complete recycling of all components of the process, including water; therefore, use of less water becomes more desirable.

10 In spite of the importance of optimizing lignin removal, especially brownstock washing, most additives for papermaking have addressed problems in the bleaching and papermaking steps. See, Thayer, Paper Chemicals, Chemical and Engineering News, November 1, 1993. pp. 28-42. However, Li et al, in Colloids and Surfaces, 64
15 (1992) pp. 223-234 report tests using cationic poly(diallyldimethylammonium chloride) or poly(DADMAC) to increase efficiency of the displacement of aqueous kraft lignin from a bed of glass beads designed to model the displacement washing characteristics of pulp fiber pads on kraft brownstock washers. They
20 also report earlier work on non-reacting water-soluble polymers and show some work with a lower molecular weight polyamine available from Allied Colloids under the trade designation Percol 1597, now known to be polymeric propenaminium, dimethylpropenyl chloride (CAS 26062-79-3), which was said to have a behavior little different from the
25 poly(DADMAC). These quaternary amine polymers were used in amounts of 250 to 1500 mg/L which corresponds approximately to 250 to 1,500 ppm (parts per million by weight). It was observed that performance of lower molecular weight poly(DADMAC) was significantly worse than the other polymers and that use of the cationic polymers resulted in
30 a colloidal phase in the eluate. All observations were reported to be consistent with a clotting mechanism. Dealing with a colloidal suspension in the black liquor requires extra handling and equipment.

It would be desirable to have an additive to improve lignin removal which avoids formation of a colloid in the wash water.

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In the practice of the invention, ethyleneamines are used in the washing of pulp, especially brownstock washing in kraft pulp processes to improve lignin removal.

The invention includes a process for washing a
5 cellulose pulp mixture containing lignin to remove at least a portion of the lignin therefrom comprising use of a washing composition with at least 100 ppm of an ethyleneamine.

Additionally, the invention includes an improvement in a process for washing a cellulose pulp mixture containing
10 lignin wherein a washing composition is used to remove at least a portion of the lignin, the improvement comprising use of at least 100 ppm of an ethyleneamine with the washing composition.

In another aspect, the invention is an improvement in brownstock washing of cellulose pulp containing lignin with a
15 washing composition, the improvement comprising using an amount of ethyleneamine at least equivalent to 100 ppm based on the washing composition with the washing composition.

In yet another aspect, the invention includes a washing composition for washing kraft pulp comprising water and
20 at least 100 ppm of an ethyleneamine.

According to one aspect of the present invention, there is provided a process for washing a cellulose pulp mixture containing lignin to remove at least a portion of the free lignin therefrom comprising use of a washing composition
25 gwith at least 100 ppm of a soluble ethyleneamine having at least two amine groups, which groups are primary or secondary amine groups, the ethyleneamine having at least one $-(CR_2-CR_2-NH)-$ unit wherein each R is independently selected from H or alkyl or from 1 to 10 carbon atoms.

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According to another aspect of the present invention, there is provided an improvement in a process for washing a cellulose pulp mixture containing lignin wherein a washing composition is used to remove at least a portion of the lignin, the improvement comprising use of at least 100 ppm of a soluble ethyleneamine having at least two amine groups, which groups are primary or secondary amine groups, the ethyleneamine having at least one $-(CR_2-CR_2-NH-)-$ unit wherein each R is independently selected from H or alkyl of from 1 to 10 carbon atoms with the washing composition.

According to still another aspect of the present invention, there is provided an improvement in brownstock washing of cellulose pulp containing lignin with a washing composition, the improvement comprising using an amount of soluble ethyleneamine having at least two amine groups, which groups are primary or secondary amine groups, the ethyleneamine having at least one $-(CR_2-CR_2-NH-)-$ unit wherein each R is independently selected from H or alkyl of from 1 to 10 carbon atoms, at least equivalent to 100 ppm based on the washing composition with the washing composition.

Figure 1 is a graphical representation of lignin removal by amounts of eluate comparing water alone with the practice of the invention.

Washing processes for removing lignin are within the skill in the art and include brownstock washing processes as well as any other process wherein lignin is removed from a cellulose pulp mixture containing lignin, preferably cellulose fibre, using a washing composition. Brownstock washing processes are preferred in the practice of the invention because brownstock is a pulp widely produced using a chemical digestion process and requires washing to remove spent

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inorganic digestion chemicals, fatty acids, lignin, lignosulfonates, and other undesired organic chemicals to produce a desired paper. Brownstock washing is widely practiced and is under environmental pressure to achieve
5 improvements in effectiveness.

The term "cellulose pulp mixture containing lignin" is used to mean a pulp mixture wherein the cellulose and lignin are sufficiently separated that at least a portion of the lignin is soluble or dispersible in water (hereinafter free lignin) rather than so intimately adhered or chemically bound to the cellulose that it is insoluble (hereinafter bound lignin). Removal of bound lignin from the pulp is not necessary. This invention is, therefore, addressed to removal of free lignin. Any cellulose pulp mixture containing free lignin is suitably used in the practice of the invention.

Cellulose pulp mixtures containing lignin are well known in the art. Cellulose commonly occurs with lignin as the resinous adhesive that holds fibers of cellulose together. A pretreatment is advantageous to treat pulp to separate the cellulose and lignin sufficiently for the lignin to be at least partially free. Such pretreatments are within the skill in the art for instance digestion of wood or other cellulose source using an alkaline medium such as in known papermaking processes, preferably kraft paper processes. The processes are often referred to in the art as delignification.

This invention is applicable to any cellulosic pulp. Such pulps include wood pulps such as chemical (for example kraft process), thermomechanical, mechanical, chemimechanical, chemithermomechanical or ground pulp and fibers contained therein. Processes of preparing such pulps are within the skill in the art for instance as discussed in Casey, Pulp and Paper; Chemistry and Chemical Technology, 3rd ed., vol. 1, (1980) especially pages 291-491 and 504-567. In chemical pulps, the wood or other cellulose source is advantageously separated into pulp with the help of sulfate or sulfite materials, preferably for the practice of the invention sulfates and hydroxides. In mechanical and thermomechanical processes, pulp is separated by grinding or otherwise disintegrating the cellulose source. While lignin is not commonly removed from mechanical pulps, presence of large amounts of lignin can result in poor light stability, permanence and strength; therefore, removal can be desirable. Hardwood and softwood pulps and mixtures thereof are suitable for the practice of the invention as are pulps obtained from cotton, bagasse, esparto, hemp, kenaf. Wood pulps are preferred

because of their higher lignin content. Pulps obtained by alkaline processes are preferred because the process produces large quantities of undesired by products that must be removed from the pulp before further processing of the pulp into paper is possible.

5 Use of a washing composition in a process for removing lignin from a cellulose pulp mixture is within the skill in the art such as is discussed in Casey, Pulp and Paper; Chemistry and Chemical Technology, 3rd ed., vol. 1, (1980) especially pages 442-452. Commonly, the pulp mixtures containing lignin are filtered such as by
10 pouring or blowing the mixture on a screen or other perforated surface. Liquid separates and is preferably collected; then the material remaining on the filter is washed, for instance, by pouring, pulling or spraying a washing composition through or otherwise contacting it with the material on the filter. Those skilled in the
15 art will recognize that there are many variations in washing processes. For instance, countercurrent washing is sometimes used. Methods of washing commonly include dilution, extraction, and/or displacement. Most washing processes in the art use an aqueous composition, commonly water, for some type of contact (for example
20 admixing, spraying, pouring) with a pulp mixture containing lignin. The washing composition and materials soluble or suspended therein are advantageously removed by any method within the skill in the art, preferably by being flowed, forced or drawn through the pulp mixture, but optionally by other means of separation of liquids from solids
25 such as by centrifugation. A rotary vacuum filter is commonly used and is a drum partially immersed in a vat that is fed with a slurry of the stock to be washed; a mat of pulp forms on the outer surface of the drum where it is sprayed with washing composition, preferably water. Repulping optionally occurs between such drums in a series.
30 Alternatively, washing at least partially takes place inside batch digesters. Other washing processes include the use of batch diffusers.

 Washing processes such as brownstock washing are known to remove inorganic compounds as well as lignin. The inorganic
35 compounds include those introduced, for instance in a chemical digestion process. In the practice of the invention, these inorganic

materials are also advantageously removed. The inorganic materials are believed to be bound or associated with the lignin in most situations where they are present, particularly in brownstock washing.

5 Composition of a washing composition depends on the washing process used. Such compositions are within the skill in the art. For instance, in brownstock washing, water is commonly used as the washing composition, but additives within the skill in the art are optionally present, preferably additives which do not undesirably
10 interfere with the action of the ethyleneamine. Such washing compositions include for instance defoaming additives (defoamers) within the skill in the art, including for instance hydrocarbons, oils, fatty alcohols, fatty esters, fatty acids, poly(alkylene oxides) especially poly(ethylene oxide) or poly(propylene
15 oxide) derivatives and copolymers, organic phosphates, hydrophobic silica especially in hydrocarbon oils, and especially silicone compounds. While aqueous washing compositions are preferred in the practice of the invention, washing compositions alternatively comprise other solvents, suitably any solvents which remove lignin
20 and/or other black liquor components, preferably in which lignin, preferably with any associated inorganic materials, is at least partially soluble or dispersible. Such solvents include alcohols, ketones, heterocyclic compounds, polyethers and mixtures thereof. Additives are also optionally present in solvent washing
25 compositions. Water and other solvents are optionally used together in washing compositions.

 The term "ethyleneamine" is used to mean an amine having at least one ethyleneamine unit or repeating ethyleneamine units. An ethyleneamine unit is $-(CR_2-CR_2-NH)-$ where R is H or an alkyl
30 (straight, branched or cyclic) group, preferably H, but if alkyl of from 1 to 10 carbon atoms. Ethyleneamines have at least two amine groups, which groups are primary or secondary amine groups; tertiary amine groups are optionally also present. Thus, ethyleneamines include ethylenediamine, diethylenetriamine, triethylenetetramine,
35 tetraethylenepentamine, piperazine, aminoethylpiperazine, ethyleneamine mixtures such as mixtures of ethyleneamine oligomers

having an average molecular weight of 250-300 commercially available from The Dow Chemical Company under the trade designation Ethyleneamine E-100, and other mixtures thereof. In the case of ethyleneamines having isomers, one isomer or a mixture of isomers is suitably used in the practice of the invention. Amines rather than their salts or quaternary compounds are used to interact with the lignin. It is preferred that the ethyleneamine be soluble in the washing composition; therefore, the molecular weight or average molecular weight in the case of a mixture of the ethyleneamines is preferably sufficiently low to retain solubility in the washing composition, preferably in water. More preferably, the molecular weight or average molecular weight is less than 500, more preferably less than 450, most preferably less than 400. It is noted that among ethyleneamines having an (average) molecular weight less than 500, that heavier amines are often more effective. Therefore, amines having a molecular weight of at least 150 are preferred, with at least 170 more preferred and at least 200 most preferred. Among ethyleneamines, triethylenetetramine, tetraethylenepentamine, piperazine, aminoethylpiperazine, and mixtures of ethyleneamine oligomers having an average molecular weight of 200-500 are preferred with tetraethylenepentamine, piperazine, aminoethylpiperazine, and mixtures of ethyleneamine oligomers having an average molecular weight of 250-500 more preferred and piperazine, aminoethylpiperazine, and mixtures of ethyleneamine oligomers having an average molecular weight of 250-450 most preferred.

Conditions of use are not critical to the invention. However, washing is expected within the art to be more efficient at elevated temperatures than at temperatures at or below room temperature. It is, however, preferred that the solvents in the washing composition do not boil away in the washing step. Thus, temperatures of from room temperature (25° C) to the boiling point of the solvent, 100° C, in the case of water are preferred, with from 40 to 85° C more preferred and from 60 to 80° C most preferred. A temperature of 170° F (77° C) is conveniently used in brownstock washing because that is a common temperature of water coming from evaporators.

The ethyleneamines are used with the washing compositions in any amount effective to remove lignin more effectively than the same composition used in the same manner without the amine; however, it is found that amounts of ethyleneamine equivalent to at least 100 or 200 ppm by weight based on washing composition are generally preferably for observable improvements from the washing composition without the ethyleneamine. At room temperature, at least 500 ppm is preferred. More preferably, at room temperature at least 1000 ppm is used, most preferably at least 1500 ppm is used, but less is preferred at higher temperatures, advantageously at least 500, more preferably at least 1000 ppm. To avoid wasting amine and to avoid disposing of excess amine, preferably the ethyleneamine is used in an amount insufficient to reduce effectiveness and more preferably no greater than that above which no significant improvement in removal of lignin or other component, particularly black liquor components, is observed. In brownstock washing, it is found at room temperature that above 2000 ppm effectiveness is reduced and above 1500 ppm very little significant improvement is observed at concentrations; therefore, amounts preferably not greater than 2000, more preferably 2000 ppm is used at room temperature. At higher temperatures, less amine is needed, therefore, advantageously less than 1500 ppm, preferably less than 1200 ppm, more preferably less than 1000 ppm ethyleneamine is used.

The ethyleneamine is used with the washing composition. Preferably, the ethyleneamine is used in (as a component of) the washing composition, more preferably in the washing composition at the concentrations discussed previously. Alternatively, the ethyleneamine is contacted with the pulp such that it increases the effectiveness of the washing composition. For instance, the ethyleneamine is advantageously contacted with pulp, for example on a screen or filter, for example by being sprayed or poured thereon, before the washing composition is contacted with the pulp. It is expected that use in the washing composition is most efficient, and that other methods use more amine. Thus, the preferred amounts of amine for contact other than as a part of the washing composition, are somewhat greater than the preferred amounts previously discussed.

Those skilled in the art can determine optimum amounts of amine to be used in alternative methods given the data herein.

Improvement in lignin removal is noted in at least two ways. First, at a constant amount of eluate (water or other composition used to wash the cellulose pulp mixture containing lignin) an increase in lignin removal is noted. Second, and alternatively, less eluate is required to achieve a given percentage of lignin removal. The relative importance of the two methods depends on the conditions of a particular washing process. In a process designed for the use of a given amount of washing composition, for instance with distillation or evaporation apparatus sufficient for a given amount of eluate, it is important to remove as much lignin as possible with the amount of washing composition for which the process is designed because there will be less lignin going to the next stage, usually a bleaching stage, where lignin can interfere and results in disposal problems as discussed previously. Alternatively, when a predetermined amount or percentage of lignin needs to be removed, it is useful to do so using the least volume of washing composition to avoid excessive energy and equipment requirements for evaporation, distillation or other treatment of the excess water and other washing composition components.

These two types of improvement in lignin removal are illustrated in Figure 1 where the line marked by shaded squares represents washing with water alone and the line marked by open squares represents washing with water containing an ethyleneamine, in this case tetraethylenepentamine, according to the practice of the invention. The vertical dashed line starts at 5 volumes of eluate for each volume of added black liquor and shows by its intersection of the shaded squares line that 50 percent by weight of the lignin is removed by washing with water, while the intersection of the open square line shows that 65 percent by weight of the lignin is removed by washing with water containing tetraethylenepentamine according to the practice of the invention. Similarly, the horizontal dashed line at 70 percent by weight lignin removal shows that washing with water containing tetraethylenepentamine requires 6 volumes per volume of added black liquor according to the practice of the invention; while

the water alone requires 10 volumes per volume of added black liquor by the intersection with the shaded squares line. In graphs of eluate ratio against lignin removal such as in Figure 1, a plateau is noted. This plateau represents total lignin removal because use of more washing composition does not result in removal of significantly more lignin. (At best only very slight amounts are removed with additional washing such that a plateau is observed.) Preferably, in the practice of the invention one observes higher total lignin removal than is observed for pure water or washing compositions corresponding to those used in the practice of the invention except for the ethyleneamine.

Improvement in washing cellulose pulps containing lignin according to the practice of the invention can also be shown using the parameters DF(dilution factor) and, especially, DR (displacement ratio) as known in the art and explained by Josephson et al., "Multi-component Control of Brownstock Washing," Tappi Journal, v. 76, no. 9, pp. 197-204 (1993) at page 198.

The following examples are offered to illustrate but not limit the invention. All ratios, percentages and parts are by weight unless otherwise indicated. Examples (Ex.) of the invention are designated numerically, while the comparative sample (C.S.) which is not an example of the invention is designated alphabetically.

EXAMPLES 1-20 and Comparative Sample A: Effectiveness of Various Ethyleneamines Compared to Water

For each Example and Comparative Sample, a model washing bed was constructed using a 50 mm diameter cylindrical glass funnel containing a compressed mat of kraft pulp. A measured portion of black liquor was placed on the pulp mat and then water or other solutions of the test additives were used to wash the test bed. The wash liquid was added to the top of the bed by a small pump. Fractions of eluate were collected from the outlet of the test bed using a fraction collector. The eluate fractions were weighed and then analyzed for lignin concentration using UV spectroscopy. Eluate volumes and lignin concentrations were determined for each of the collected fractions. Washing efficiencies for solutions containing the test additives were

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compared to the washing efficiency for distilled water in the washing experiments.

A solution at each of the concentrations indicated in Table 1 of each of the following additives was tested and compared to a control (C.S. A) where distilled water was substituted for the test solution: ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA) (isomer mixture), tetraethylenepentamine (TEPA) (isomer mixture), Ethyleneamine E-100 (E-100), piperazine (PIP), Piperazine Amine Mix containing principally piperazine, with a minor amount of DETA, and water (about 30 percent by weight) (PIP Amine), aminoethylpiperazine (AEP), and aminoethylethanolamine (AEEA). The washing efficiencies were calculated for two different lignin recovery levels (70 percent and 80 percent). The eluate ratios, washing efficiency improvements at 70 percent and 80 percent lignin recovery, and the total lignin recovery for the series of test additives were tabulated in Table 1.

The washing apparatus consists of the following major pieces of equipment: a glass funnel made in two parts, the upper cylindrical part and the lower conical part joined with flange joints and O-ring seals, sandwiching a 70 micron (70×10^{-6} m) mesh fluorocarbon filter screen and a perforated fluorocarbon polymer support plate. (The upper portion of the glass funnel was fitted with a side arm in order to control the level of wash solution in the test bed; the bed contains a mat of prepared kraft brownstock pulp); a peristaltic pump to deliver the wash solution to the test bed using tubing; a controller to maintain a constant level in the wash bed; and a fraction collector loaded with 13 x 100 mm test tubes to collect the wash eluate.

Ultraviolet absorbance analyses of the wash eluate were performed with a spectrophotometer using a quartz cuvette with a path length of 1.0 cm. Synthetic lignin solution (614.5 g) was prepared by mixing 12.5 g of Indulin C (lignin, sodium salt) commercially available from WESTVACO Chemical Company, 100.0 g sucrose, 2.0 g sodium hydroxide pellets, and 500 g of distilled water in a flask. Analytical standards were prepared by filling five 100 ml volumetric flasks to the 100 ml mark with pH 10.0 buffer, then adding 25, 50, 75,

100, and 125 microliters of synthetic lignin solution, respectively, to each of the five volumetric flasks. The solutions were mixed completely by shaking. The UV spectrometer was calibrated using the five standards using 280 nm for the analytical wavelength. The
5 concentration of lignin in the black liquor was determined by UV spectroscopy.

The wash solutions were prepared by weighing out the desired amount (one gram for Examples 2, 6, 10, 14, and 18 where a 1000 ppm concentration was used) of additive and adding
10 distilled water to the mark in a 1000 ml volumetric flask. The concentration of the active ethyleneamine additive in the solution was given in Table 1.

The model wash bed was assembled by locking the support plate (bottom) and the 70 micron (70×10^{-6} m) mesh filter (top)
15 between the flange faces of the two parts (cylindrical top and conical bottom) of the glass funnel with a flange clamp. The assembled funnel was suspended above a vacuum flask with a ring stand and clamps. A vacuum line was attached to the outlet of the wash bed.

20 The kraft brownstock mat was prepared by placing 19.06 g of 23.09 percent consistency pulp (equivalent to 4.40 g of oven-dried pulp) in a 600 ml beaker. To the beaker was added 200.0 g of distilled water and a magnetic stir bar. The beaker was placed on a magnetic stirrer and the slurry stirred at high speed
25 for 5 minutes. The beaker was taken from the stirrer and the stir bar removed. The pulp slurry was transferred from the beaker to the wash bed. Following transfer, vacuum was applied to the outlet of the bed for 2 minutes to remove the water and form a pulp mat. Then the vacuum line was removed and the model
30 washing device containing the prepared pulp was suspended above the fraction collector using a ring stand and clamps. The sensor for the level controller was attached to the side arm to maintain the liquid level in the bed.

Eight wash solution delivery lines were passed between the wash solution reservoir (flask), the peristaltic pump, and the test bed using plastic tubing. The inlet ends of the wash solution delivery tubing were inserted into the flask containing the amine wash solution, and primed using the peristaltic pump. A 5.0 ml aliquot of the black liquor solution (density 1.0147 g/ml) was added to the kraft pulp bed using a pipette. Care was taken to insure a uniform loading. The loaded bed was then covered with a piece of filter paper (Whatman No. 1) to prevent disturbance of the bed by the addition of the wash solution. The outlet ends of the delivery lines from the pump were then inserted into the top of the glass funnel above the pulp bed, with the tubing ends 2.0 cm above the level to be maintained by the wash solution. The sample collector was loaded with clean tubes. The level controller, pump, and sample collector were turned on and the correct liquid level was obtained above the bed. Normal operation was then maintained until the end of the wash cycle. Sampling interval was controlled manually by the operator. Samples were collected until all visible color was gone from the eluate. The sample collector, level controller, and pump were then turned off.

The test tubes containing the eluate samples from the collector were then weighed. As many 100 ml volumetric flasks as there were collected samples were filled to the 100 ml mark with pH 10.0 buffer. The flasks were numbered, corresponding to the numbers of the test tubes in the fraction collector tray. To the first of the numbered volumetric flasks containing the buffer was added 100 microliters of eluate from the first test tube. The flask was then shaken to facilitate mixing. This procedure was repeated for all the remaining samples. All the samples were then analyzed by UV spectroscopy and the lignin concentrations were determined. The eluate ratio at 70 and 80 weight percent removal and the total lignin recovery were recorded in Table 1. When the 70 and 80 percent removal points were not exactly represented by experimental data points, they were extrapolated from the data points before and after the recorded lignin removal

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levels by computer. Computer results were believed to allow reporting in more precision than would reading the same points from a graph similar to that of Figure 1 for each washing composition.

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Table 1. Eluate Ratios and Washing Efficiencies for Selected Washing Additive Candidates at 70 percent and 80 percent Lignin Recovery

Ex. or C.S.	Additive Identity	Additive Conc. (ppm)	Eluate Ratio @ 70% Lignin Recovery	Eluate Ratio @ 80% Lignin Recovery	Washing Efficiency Improvement (%) @ 70% Lignin Recovery	Washing Efficiency Improvement (%) @ 80% Lignin Recovery	Total Lignin Recovery (%)
C.S. A*	None	0	9.37	13.78	0.0	0.0	85.7
Ex. 1	Ethylenediamine	500	9.11		2.8		76.1
Ex. 2	Ethylenediamine	1000	8.82	12.35	5.9	10.4	87.7
Ex. 3	Ethylenediamine	1500	8.21	12.52	12.4	9.1	84.2
Ex. 4	Ethylenediamine	2000	9.66		-3.1		80.8
Ex. 5	Diethylenetriamine	500	8.66		7.6		79.6
Ex. 6	Diethylenetriamine	1000	8.70	14.11	7.2	-2.4	85.4
Ex. 7	Diethylenetriamine	1500	7.40	10.80	21.0	21.6	87.1
Ex. 8	Diethylenetriamine	2000	8.32	12.01	11.2	12.9	84.9
Ex. 9	Triethylenetetramine	500	7.77	13.1	17.1	4.9	80.8
Ex. 10	Triethylenetetramine	1000	8.18	11.54	12.7	16.3	88.0
Ex. 11	Triethylenetetramine	1500	7.79	12.17	16.9	11.7	85.0
Ex. 12	Triethylenetetramine	2000	7.42	10.78	20.8	21.8	86.3
Ex. 13	Tetraethylenepentamine	500	8.08	12.17	13.8	11.7	83.7

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Ex. 14	Tetraethylenepentamin e	1000	7.06	10.04	24.7	27.1	89.4
Ex. 15	Tetraethylenepentamin e	1500	5.55	7.22	40.8	47.6	98.6
Ex. 16	Tetraethylenepentamin e	2000	6.57	9.05	29.9	34.3	88.6
Ex. 17	Ethyleneamine E-100**	500	7.50	11.90	20.0	13.6	86.4
Ex. 18	Ethyleneamine E-100**	1000	6.69	9.54	28.6	30.8	88.7
Ex. 19	Ethyleneamine E-100**	1500	6.96	9.11	25.7	33.9	95.6
Ex. 20	Ethyleneamine E-100**	2000	9.31	13.2	0.6	4.2	88.0

* is percent by weight

* Not an example of the invention.

** A mixture of ethyleneamines having an average molecular weight of 150-300 commercially available from the Dow Chemical Company.

Examination of the entries in Table 1 shows that all the tested materials demonstrate improvement in washing efficiency at 70 percent lignin recovery (5.9-28.6 percent) in amounts of ethyleneamine less than 2000 ppm. At 80 percent lignin recovery, all additive candidates except DETA in amounts of ethyleneamine less than 2000 ppm show improvement in washing efficiency (1.2-30.8 percent). DETA shows improvement when used in amounts of 1500 and 2000 ppm. Of the additives tested, TEPA and E-100 were the most effective at improving washing efficiency. These ethyleneamines also show consistent improvement in total lignin recovery when used in amounts greater than 500 ppm. In general there was some trend toward increased performance with increasing molecular weight of the homologs in the ethyleneamine series. The variation in effectiveness with amount of ethyleneamine indicates that optimum amounts of ethyleneamine vary with the specific amine but can be determined by these procedures.

No colloids were observed in the eluates.

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CLAIMS:

1. A process for washing a cellulose pulp mixture containing lignin to remove at least a portion of the free lignin therefrom comprising use of a washing composition with
5 at least 100 ppm of a soluble ethyleneamine having at least two amine groups, which groups are primary or secondary amine groups, the ethyleneamine having at least one $-(CR_2-CR_2-NH)-$ unit wherein each R is independently selected from H or alkyl or from 1 to 10 carbon atoms.
- 10 2. The process of claim 1 wherein R is H.
3. The process of claim 1 or 2 wherein the cellulose pulp is a kraft pulp.
4. The process of any one of claims 1 to 3 wherein the ethyleneamine has a molecular weight of less than 500.
- 15 5. The process of any one of claims 1 to 4, wherein the ethyleneamine is selected from ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, piperazine, aminoethylpiperazine, mixtures of ethyleneamine oligomers having an average molecular
20 weight of 250-300, and mixtures thereof.
6. The process of claim 1 wherein the ethyleneamine is selected from triethylenetetramine, tetraethylenepentamine, piperazine, aminoethylpiperazine, and mixtures of ethyleneamine oligomers having an average molecular weight of 200-500.
- 25 7. The process of claim 1 wherein the ethyleneamine is selected from tetraethylenepentamine, piperazine, aminoethylpiperazine, and mixtures of ethyleneamine oligomers having an average molecular weight of 250-500.

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8. The process of claim 1 wherein ethyleneamine is selected from piperazine, aminoethylpiperazine, and mixtures of ethyleneamine oligomers having an average molecular weight of 250-450.

5 9. An improvement in a process for washing a cellulose pulp mixture containing lignin wherein a washing composition is used to remove at least a portion of the lignin, the improvement comprising use of at least 100 ppm of a soluble ethyleneamine having at least two amine groups, which groups
10 are primary or secondary amine groups, the ethyleneamine having at least one $-(CR_2-CR_2-NH)-$ unit wherein each R is independently selected from H or alkyl of from 1 to 10 carbon atoms with the washing composition.

10. An improvement in brownstock washing of cellulose
15 pulp containing lignin with a washing composition, the improvement comprising using an amount of soluble ethyleneamine having at least two amine groups, which groups are primary or secondary amine groups, the ethyleneamine having at least one $-(CR_2-CR_2-NH)-$ unit wherein each R is independently selected
20 from H or alkyl of from 1 to 10 carbon atoms, at least equivalent to 100 ppm based on the washing composition with the washing composition.

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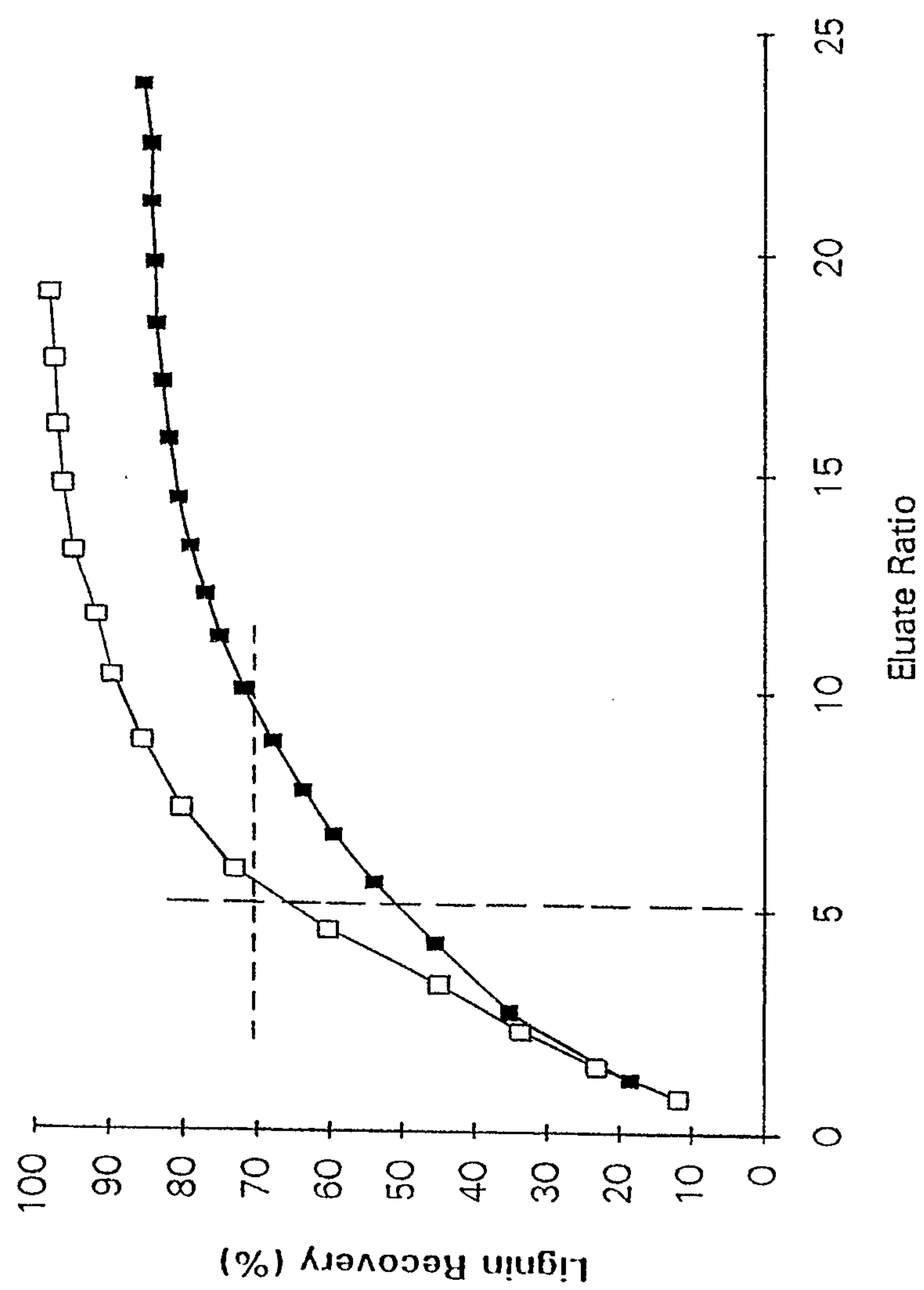


FIG. 1

