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PROCESS OF IMPROVING INORGANIC FILLER RETENTION IN PAPER BY ADDITION OF ETHYLENE OXIDE HOMOPOLYMER

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This invention, in general, relates to the manufacture of paper and, more particularly, to improvements in retention of fillers and fines in said manufacture.

Paper is manufactured for the most part from wood pulp. A small amount of high grade paper is manufactured from rag pulp. There are five different kinds of wood pulp: mechanical pulp (ground wood), semi-chemical pulp, sulfite pulp, sulfate or kraft pulp and soda pulp. The first is prepared by purely mechanical means, the second by a combination of mechanical and chemical, and the other three by chemical means. The mechanical pulp contains substantially all of the wood except the bark and that lost during storage and transportation. Semi-chemical pulps are partialy free of lignin. Chemical pulps, however, are essentially pure cellulose, the unwanted and unstable lignin and other non-cellulosic components of the wood having been dissolved away by the treatment. Because of this, chemical pulps are much superior to mechanical and semi-chemical pulps for fine paper making. However, because of the special processing required, they are too expensive to serve as the main source of fiber for the cheaper grades of papers such as newsprint.

If the pulp fibers were the only constituents of a paper sheet, the usefulness of the paper would be very restricted because the sheet would be soft, have a yellowish color and could not be written or printed upon with ink successfully. If the sheet were thin, it would be transparent to matter printed upon the opposite side. It is necessary, then, to add other substances, such as sizing, coloring agents, and fillers, to the cellulosic fibers to produce paper suited to its many uses.

Many papers, except the absorbent types, filter papers, and most packaging papers, must have a finely ground filler added to them, the purpose of which is to occupy the spaces between the fibers—thus giving a smooth surface, a more brilliant whiteness, improved printability and improved opacity. The fillers are inorganic substances and may be either naturally occurring materials such as talc, agalite, pearl filler, barytes and certain clays such as china clay or artificial fillers such as suitably precipitated calcium carbonate, crown filler (pearl hardening), blanc fixe, and titanium dioxide pigments. Sizing is added to the paper, other than absorbent papers and filter paper, to impart resistance to penetration by liquids. Common sizing agents added to the pulp before it is formed into a sheet are wax emulsions or soaps made by the saponification of rosin with alkali. The sizes are precipitated with alum.

Pulp stock is prepared for formation into paper by two general processes, beating and refining. Mills use either one or the other alone or both together. The most generally used type of beater is that known as the Hollander. Beating the fibers makes the paper stronger, more uniform, more dense, and less porous. It is in the beater that fillers, coloring agents and sizing may be added. The standard practice in making the finer grades of paper, is to follow the beaters with the refiners, the latter being continuous machines.

While the usual practice is to add filler, sizing and color to the beaters, they may be added prior to the Jordan or to a combination of points in the system. The order

in which the materials are added to the beaters may vary with different mills. Generally, however, the filler is first added to the blended pulp, and, after sufficient beating, the sizing and the coloring are added. In some instances, all or part of the sizing is surface applied to the formed, dried sheet, using animal glues, starches, or gelatin as the sizing.

The machines used for the actual formation of the paper sheet are of two general types, the Fourdrinier machine and the cylinder machine. The basic principles of operation are essentially the same for both machines. The sheet is formed on a traveling bronze screen or cylinder, dewatered under rollers, dried by heated rollers and finished by calender rolls. In the Fourdrinier machine the stock of the foregoing operations is sent to the headbox from which it flows onto a moving, endless bronze wire screen. The pulp fibers remain on the screen while a greater portion of the water, containing unretained fiber fines and unretained filler, drains through. As the Fourdrinier wire moving along it has a sidewise shaking motion which serves to orient some of the fibers and give better felting action and more strength to the sheet. While still on the Fourdrinier wire, the paper passes over suction boxes to remove water and under a dandy roll which smooths the top of the sheet. In the cylinder machine there are several parallel vats into which similar or dissimilar dilute paper stocks are charged. A wire-covered rotating cylinder rotates in each vat. The paper stock is deposited on the turning screen as the water inside the cylinder is removed. As the cylinder revolves further, the paper stock reaches a point where the wet layer comes in contact with and adheres to the moving felt. This felt and paper, after removal of some water, come into contact with the top of the next cylinder and pick up another layer of wet paper. Thus, a composite wet sheet or board is built up and passed through press rolls and onto the drying and smoothing rolls.

In an attempt to improve filler and fines retention in the paper manufacturing operation several attempts have been made to incorporate chemical additives with the paper stock before it reaches either the cylinder vat or the Fourdrinier wire. These additives, for the most part, have not been entirely satisfactory from several operational points of view. One of the chief drawbacks of most chemicals used to improve a fiber and fine retention in the manufacture of paper is that they must possess certain characteristics and properties which are extremely difficult to achieve in any particular chemical. For instance, the particular chemical used should not be affected by other additives normally used in the paper processing operations such as rosin size, alum, sodium aluminate, starch, clays, and the like. Also important for a particular additive to be effective for improving fiber and fine retention is that it must not be affected by variations in pH. Similarly, the ideal additive chemical should not be affected by a particular electrokinetic charge on the cellulose fibers and fines. The use of a chemical must, of course, be such that it does not have any adverse effects on the finished sheet and it should be relatively safe to handle.

In addition to possessing the above desirable characteristics an additive for improving filler and fines retention must be capable of acting both upon the filler and fines in the system to efficiently cause such materials to be retained in the finished sheet rather than with one being preferentially acted upon by the additive. Another important characteristic that must be possessed by any chemical used as a filler and fines retention additive is that it must be capable of operating on a large variety of stocks.

Also of importance in the selection of fines and filler

retention agent is that it must not affect dyestuffs which are frequently used as coloring agents for various types of paper stocks nor must it interfere with the beneficial effects imparted to paper stocks by coatings which are frequently placed on different types of paper during its manufacture.

It therefore becomes an object of the invention to provide a new and improved method for improving filler and fines retention in the manufacture of paper. A further object is to provide a chemical agent for improving filler and fine retention which is effective at low economical dosages, will not interfere with other additives and substances used in the makeup and manufacture of the paper, and which will have no adverse effects on the chemical and physical characteristics of the finished sheet.

An important object of the invention is to provide a chemical additive for improving filler and fines retention in the manufacture of paper which will operate on a wide variety of paper stocks, is fairly safe to handle and will impart to the finished sheet certain desirable characteristics which have not heretofore been available when attempts have been made to use other chemicals as fines and filler retention aids. Other objects will appear hereinafter.

In accordance with the invention it has been found that filler and fines retention may be greatly improved in the manufacture of paper by treating the stock prior to its formation into a sheet with a small fraction of a pound per ton of paper produced with a water soluble ethylene oxide polymer. The ethylene oxide polymers which are useable in the invention are a relatively new type of commercially available materials.

The polymerization of ethylene oxide using conventional catalysts and techniques forms a polymer which has repeating $-CH_2CH_2O-$ units which when combined into a finished polymeric structure provides water soluble polymers which have molecular weights which rarely exceed 5,000. Due to recent innovations in catalysis as well as in manufacturing techniques, new high molecular weight ethylene oxide polymers are now available which have molecular weights as low as about 50,000 and frequently they may be produced having molecular weights in excess of about 10,000,000. Surprisingly, these high molecular weight materials are soluble in water and form relatively stable solutions at temperatures below 100° C.

Small amounts of these polymers will thicken water so that it becomes a very viscous mass. As evidence of the extreme thickening properties of these new high molecular weight ethylene oxide polymers one commercial grade has an average viscosity of 3,000 centipoises in a 1% aqueous solution. This particular material has a molecular weight of approximately 3,000,000. Another commercially available material has an average viscosity, as a 1% water solution, of approximately 7,000 centipoises with its average molecular weight being approximately 6,000,000.

Although there is not an arithmetical or geometrical correlation between the viscosity and moleclular weights of these polymers, it may be stated, as a general rule, that to achieve a given viscosity at a given solution strength, it will take more of the low molecular weight materials than of the higher molecular weight materials. That is to say, that the centipoise viscosity of a .1% solution of a polyethylene oxide polymer having a molecular weight of 10,000,000 will be in substantial excess of the centipoise viscosity of a .1% solution of an ethylene oxide polymer having a molecular weight in excess of 50,000.

The polymers of ethylene oxide used in the invention are completely soluble in water up to a point where it is impossible to dissolve any more due to the extreme viscosities achieved. The polymers tend to precipitate from water solution at elevated temperatures around the boiling point of water. Surprisingly, all of the ethylene oxide polymers having molecular weights in excess of 50,000 become insensitive to precipitation of solutions thereof

below about 100° C.; this phenomena being experienced over the entire molecular weight range as well as over a wide span of solution concentrations. Various techniques for producing the above type polyethylene oxide polymers are set forth in an article by F. N. Hill et al., entitled "High Molecular Weight Polymers of Ethylene Oxide," appearing at pages 5–7 of volume 50, No. 1, January 1958 issue of Industrial and Engineering Chemistry. Particular reference is made to the paragraph entitled "Polymerization" on page 7 of this article.

An important property of the polymers is that at the use concentrations which will be hereinafter specified, they are relatively insensitive to the presence of electrolytes and other types of dissolved solids commonly found in the many typical furnishes used in the manufacture of paper. This is particularly important since it has sometimes been the experience of the art that dissolved electrolytes will tend to either precipitate or have adverse effects on various types of polyelectrolyte polymers which have been at one time or another suggested as filler and fines retention additives.

Due to their high molecular weight the polymers of the invention are, in all probability, colloidally dispersed when they are in so-called "aqueous solution." For purposes of the present discussion even though the word "solution" or "dissolved" has been used, it will be understood that if the polymers are present as a colloidal suspension, such does not affect or limit in any way their operational activity when used in the practices described.

To utilize the high molecular weight ethylene oxide polymers, it is beneficial that they be made up into dilute aqueous solutions to provide a convenient feeding concentrate for placing the polymers into the papermaking system. Since dilute solutions of the polymers are relatively viscous, it is expedient to make up extremely dilute solutions, e.g., under 1% by weight, for purposes of preparing the feeding concentrate. The polymers are subject to being degraded both as to their viscosity and molecular weight if they are subjected to conditions of extreme agitation or to conditions of high shear. To avoid polymer degradation it is therefore helpful that polymers be prepared under conditions of make-up and use wherein they are not subjected to conditions of high agitation and shear. It is therefore suggested that air sparges, properly designed stirring equipment, and the like be used in preparing solutions to insure that the polymer does not degrade.

One of the most startling features of the invention resides in the extremely low dosages at which the polymers tend to substantially improve fines and filler retention in all types of papermaking stocks. As a general rule, dosage range of the polymer is usually in the range of between 0.04 to 5 pounds per ton with a preferred range being from 0.05 to 1 pound per ton. The particular dosage ranges described refer to the tonnage of the air dried fiber and is not based upon the total weight of the furnish going to the Fourdrinier wire or cylinder vat.

In addition to improving the filler and fines retention, the polymers, when used in the treatment of paper stock, also impart to the stock many other valuable characteristics such as, for instance, a paper having smoother surfaces, a more brilliant whiteness, improved printability and/or improved opacity.

An important benefit also derived from the practices of the invention is that a certain residual amount of the polymer passes through the Fourdrinier or cylinder into the saveall systems which are frequently used as recovery and disposal mechanisms for papermaking white waters. These residual amounts of the polymer which are probably substantially less than .1 of a part per million very frequently improve the operational characteristics of the saveall systems by allowing a purer quality water to be produced as well as allowing substantial increases to be made in the amount of fiber and filler that are re-

covered in the systems which are then in many cases returned to the papermaking system for further use and reprocessing. This added advantage not only increases the overall efficiency of these saveall systems but allows the production of a low suspended solids and a resultant high quality water which then may be discharged to sewage and disposal systems without there being any substantial danger of stream pollution occurring where such waters are finally channeled into such bodies of water.

For purposes of illustration, the invention will be further understood from the following examples:

EXAMPLE I

This particular test was conducted in a paper mill located in the North Central area of the United States. The particular grade of paper being made was a 22 pound sheet which was used for the production of high quality magazine stock. The make-up pulp comprised 50% of groundwood sheet stock with the balance being de-inked, semi-chemical and sulfite stock. The head box solids when sampled, usually averaged about ½% with this concentration producing a relatively uniform 22 pound weight sheet. The ash specification set by the manufacturer was 6 to 8% by weight with typical runs at the mill, prior to the addition of the chemicals of the invention, averaging between 6.5 to 7.5% ash content. The pH of the system fluctuated between 4.0 and 4.7.

In addition to using the make-up stock described above, the furnish also contained alum which was used for pH adjustment, rosin size and starch. To maintain ash specifications it was necessary for the mill operators to add approximately 150 pounds of clay per ton of paper. For purposes of comparing the beneficial effects of the invention, runs were made using a commercial cationic water soluble polymer and also a high grade sodium aluminate material. These chemicals were fed just prior to the head box at a dosage range of 2–4 pounds per ton. After running for five hours the ash content of the paper was determined and it was found that practically no improvement over the nontreated system was obtained.

After the chemicals had dissipated themselves from the system, a five hour run was set up to test the efficacy of the water soluble ethylene oxide polymer having an average molecular weight of 6,000,000. The polymer was made up as a 0.055% by weight feed solution and was fed to the system just before the head box at a dosage rate of 0.15 pound per ton based on the weight of the air dried fibers.

During the run the ash content of the paper was measured and was found to be 8.8%. After the polymer had dissipated itself from the system, the ash content dropped drastically to 5.5% by weight. During the run the clay content added to the stock was reduced from 150 pounds per ton to 50 pounds per ton, but the ash content of the paper still remained at about 8.8% by weight.

During the run a careful note was made of the white water consistency. The white water consistency averaged during normal operations between 30 and 35 pounds of suspended solids per 1,000 gallons of water. This, coupled with the great improvement in the ash content of the paper dramatically illustrates the beneficial results obtained when the chemicals of the invention are used in the paper making process.

Another important benefit observed during the run was that the smoothness of the sheet was improved by 35% with the density of the sheet being improved by 26%. The density figure clearly illustrates the improved formation and integration of the filler with the fines that have been formed in the sheet.

During the run, it was found that the rosin size that was normally used at the saveall could be eliminated.

EXAMPLE II

This example shows the improvements obtained in a midwestern mill using the chemicals and practices of the invention in treating a carbonizing sheet stock which consists of 100% kraft type stock. An ethylene oxide polymer having an average molecular weight of 3,000,000 was fed at varying dosages during the test run of six hours with the dosage ranging between 0.6 and 1.1 pounds per ton. The pH of the system was 5.0 with the fiber content in the stock at the head box being at approximately 0.26% by weight. The make-up stock also contained alum and rosin size. At the end of the run the paper was inspected and it was noted that the Gurley-type porosity increased from the blank run over 50%. The average pinhole count decreased about 50%. This improvement in the pinhole count is particularly important since pinholes in this particular type of stock render it unsuitable for carbon sheet manufacture.

EXAMPLE III

In another north central mill a test was run with the particular stock being white box cover stock which was composed of a blend of bleached kraft and bleached sulfite pulps. Added to the stock were amounts of clay and titanium dioxide with the paper being sized with rosin size and alum. The pH of the system was approximately 5.0 with the concentration of slurry going to the head box being approximately .5% by weight. A test was run using a commercial cationic starch at a dosage of 3 pounds per ton. Chemicals of the invention were fed throughout a five hour test period at dosages ranging from 0.05 pound per ton to 0.1 pound per ton with all chemicals added to the system being fed into the head box. There were three pulpers in the line, each with a capacity of 3,000 pounds. The clay fed into the system was approximately 175 pounds per pulper. The titanium dioxide fed to the unit during normal runs was approximately 80 pounds per 3,000 pound pulper unit.

During the run using the polyethylene oxide polymer of Example II, the clay fed to the pulper was reduced from 175 pounds to 150 pounds with the titanium dioxide being reduced from 80 pounds to 70 pounds.

To show the beneficial results obtained with the practices of the invention, the following is presented. The table not only shows the improved ash results but also indicates the opacity results as well as the improvement in the operation efficiency of the vacuum type saveall unit which was connected with the system.

Table

Ash, blank	8.4–8.6%.
Ash with cationic starch	8.6–8.8%.
Ash with polymer of Example II	10.4–11.0%.
Ash after reduction of clay and titanium with polymer of Example II	8.4%.
Opacity, blank	58.5.
Opacity with cationic starch	59.
Opacity with polymer of Example II	61+.
Opacity after reduction of clay and titanium with polymer of Example II	61+.
Saveall influent, blank	15–30 lbs./1,000 gal.
Saveall influent with cationic starch	15–30 lbs./1,000 gal.
Saveall influent with polymer of Example II	8–17 lbs./1,000 gal.
Saveall effluent, blank	5–10 lbs./1,000 gal.
Saveall effluent with cationic starch	5–10 lbs./1,000 gal.
Saveall effluent with polymer of Example II	0–4 lb./1,000 gal.

This latter test clearly shows not only improved filler and fines retention but also points out several other advantages gained from the invention. Not only was the opacity of the stock increased but the saveall operation

was dramatically improved. The improved characteristic of the paper is clearly evidenced by its opacity. Physical observation of the sheet showed it to be of much higher quality. It is important to note that the cationic starch additive did not improve to any particular degree, the filler and fines retention. It had no effect in the saveall nor did it improve the opacity of the stock produced.

An added advantage of the invention is that not only may rosin size requirements for several types of paper stocks be diminished by the practice of the invention, but also it is possible due to the residual effect in saveall systems to either substantially reduce or omit the use of glue which is frequently used to improve saveall operations.

The compositions of the invention are capable of operating over a wide variety of pH ranges and, in addition, are effective on a large variety of papermaking stocks. Since they are substantially nonionic they are not dependent upon the charge or pH of the system for maximum efficiency of operation. Similarly, it should be noted that the high molecular weight ethylene oxide polymers do not interfere with any of the additive used in processing paper such as dyes or sizings. They are also capable of use in a wide variety of paper mill systems regardless of the nature and quantity of dissolved and/or suspended solids present.

The compositions of the invention are particularly useful in improving the retention in the finished sheet of inorganic fillers, particularly those exemplified by such materials as titanium dioxide, calcium carbonate and the various well known clays.

By the term "polymer," as used in the above discussion to characterize polyethylene oxide, is meant the homopolymer of ethylene oxide.

Having thus described my invention, it is claimed as follows:

1. A process for improving inorganic filler and fiber fines retention in the manufacture of paper which comprises adding to an inorganic filled paper stock at least 0.04 pound per ton of air dried fiber of a water soluble ethylene oxide homopolymer which has an average molecular weight of at least 50,000.

2. The method of claim 1 where the average molecular weight of the water soluble ethylene oxide homopolymer is within the range of about 50,000 to in excess of 10,000,000 and the dosage is within the range of between 0.04 to 5 pounds per ton.

3. The method of claim 1 where the average molecular weight of the water soluble ethylene oxide homopolymer is within the range of about 3,000,000 to 6,000,000 and the dosage is within the range of 0.05 to 1.0 pound per ton.

4. A process for improving inert inorganic filler and cellulose fiber fines retention in the manufacture of cellulosic paper which comprises adding to an inorganic filled paper stock from 0.05 to 1.0 pound per ton of air dried fiber of a water soluble ethylene oxide homopolymer which has an average molecular weight of at least 3,000,000 and thereafter forming a paper sheet from said stock.

5. The process of claim 4 where the chemically inert inorganic fillers are from the group consisting of clays, titanium dioxide and calcium carbonate and the molecular weight of the water soluble ethylene oxide homopolymer is within the range of between 3,000,000 to 6,000,000.

References Cited in the file of this patent

UNITED STATES PATENTS

2,870,101	Stewart	Jan. 20, 1959
2,913,356	Schroeder	Nov. 17, 1959
2,987,489	Bailey et al.	June 6, 1961

FOREIGN PATENTS

815,410	Great Britain	June 24, 1959

OTHER REFERENCES

Bailey et al.: "High Molecular Weight Polymers of Ethylene Oxide," "Industrial and Engineering Chemistry," vol. 50, No. 1, January 1958, pp. 8–11.

"Development News," "Can You Profit by the Unique Properties of Pluronics?," vol. 30, No. 22, June 2, 1952, pp. 2283–2285.