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(54) Method and pulp for improving paper fines and filler retention.

(57) High molecular weight copolymers of 40-60 weight percent acrylamide and 60-40 weight percent diallyldimethylammonium chloride, particularly those copolymers that have an RSV (reduced specific viscosity) exceeding 5 and more particularly exceeding 7.5, give outstanding results as fine and filler retention agents used in the manufacture of paper.

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METHOD AND PULP FOR IMPROVING PAPER FINES AND FILLER RETENTION

This invention, in general, relates to specific polymeric additives useful in the processing of paper. More particularly, to certain polymeric additives having greatly improved activity for the retention of fillers and fiber fines in paper manufacture.

Most paper is manufactured 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 partially 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-mechanical pulps for fine papermaking. 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 colour, 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, colouring 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 capacity. 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. Beating the fibers makes the paper stronger, more uniform, more dense, and less porous. It is in the beater that fillers, colouring 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 colour to the beaters, they may be added to prior to the refiner or to a combination of points in the system or subsequent to the beating operation but prior to the refining steps, as for example, prior to beating. 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 colouring are added. In some instance, all or part of the sizing is surface applied to the formed, dried sheet, using animal glues, starches, or gelatin as the sizing. Again, alum is most generally added to the beater, but in some mills, this practice is varied, and the pulp may be treated with this chemical during the refining step or even later in the paper processing scheme.

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 travelling 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 screen known as a wire. 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 moves 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 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 electro-kinetic 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 colouring 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 the manufacture.

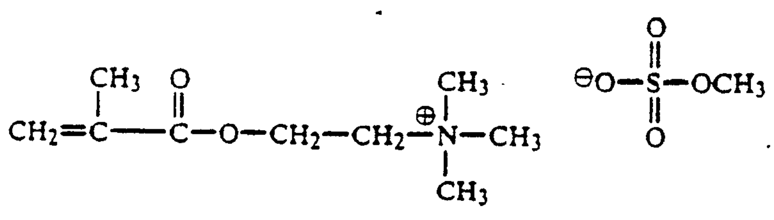
Many prior art filler and fiber fines retention aids fail to achieve the above desired objects. In addition, certain of these known retention additives cannot be employed in effective combinations with various fillers or other paper additives. Oftentimes efficiency is low except when gross uneconomical amounts are added. Adverse effects upon the finished paper product are noted when these retention aids cause poor dispersibility of the system additives with resultant localized non-uniform areas. Lastly, many additives fail by promoting filler trapage on the top side of the fiber material.

Fine and filler retention are further discussed in the well known textbook, Pulp and Paper , Third Edition, Volume 3, edited by James P. Casey, John Wiley & Sons, New York, 1981, at page 1599, et seg.

This work, in discussing fine and filler retentions, has a section dealing with cationic polyelectrolytes. This discussion, at page 1603, is pertinent to the present invention and is reproduced below:

"Cationic Polyelectrolytes."

Cationic charges are generated by introducing sulfonium, phosphonium, or ammonium groups onto the polymer backbone. [1] The ammonium ion is the one most commonly used for producing paper additives. An example of a monomer used as a copolymer agent is METAMS (methacryloyloxyethyl trimethyl ammonium methylsulfate), shown below:



"The molecular weight of these products often exceeds 1,000,000, with a wide variety of charge densities and molecular weights available."

[1]C. P. Klass, A. J. Sharpe, and J. M. Urick, "Polyelectrolyte Retention Aids," in Retention of Fines Solids During Paper Manufacture, (TAPPI C. A. Report No. 57), 1975, p. 55.

[2]H. Tanaka, K. Tachiki, and M. Sumimoto, TAPPI, 62 (1), 41-44 (1979).

"The cationic polymers have the advantage of being readily adsorbed by the normally negative surfaces encountered in the wet-end system, thus eliminating the necessity of using intermediaries such as alum. The high molecular weight allows for the formation of many loops on adsorption, thus providing many bonding points. This results in a strong, tenacious bridge. In one study [2] of a number of different cationic polymers including polyacrylohydrazide, polyvinylpyridine, glycol-chitosan, cationic starch (diethylaminoethyl starch), polyethyleneimine, and polydiethylaminoethylmethacrylate, it was shown that the primary factor causing adsorption is charge interaction and the extent of adsorption on pulp fibers varies with the pH, with the optimum adsorption tending to shift toward a higher pH as the basicity of the amino group is increased."

It, therefore, becomes an object of the invention to provide new water-soluble cationic polymeric materials which are useful as filler and fiber fines retention aids, and a method for improving filler and fines retention in the manufacture of paper by addition of specific copolymers during paper processing.

A further object is to provide polymeric chemical retention aids for improving filler and fines retention which are effective at low economical dosage, which will not interfere with other additives and substances used in the make-up and manufacture of paper, and which have no adverse effects on the chemical and/or physical characteristics of the finished paper sheet. They are easy and safe to handle and will impart to the finished paper sheet certain and desirable characteristics which have not been so far available relative to retention of fines and fillers used in the manufacture of paper.

In the invention, a method of improving fine and filler retention of paper during its manufacture into a sheet from pulp comprises treating the pulp prior to sheet formation with a copolymer which contains between 40-60 weight percent diallyldimethylammonium chloride and between about 60-40 weight percent of acrylamide which polymer has a molecular weight sufficient to provide a reduced specific viscosity (RSV) equal to at least 5.0 deciliters per gram.

$$\text{Reduced specific velocity (RSV)} = \frac{\text{Specific Viscosity}}{\text{Concentration of the polymer in the solution}}$$

Preferably, the copolymer is a 50/50 weight percent copolymer of diallyldimethylammonium chloride and acrylamide. The polymer preferably has a reduced specific viscosity of at least 7.5 deciliters per gram. Most preferably, the copolymer has a sufficient molecular weight to provide for a reduced specific viscosity of at least 8.0 deciliters per gram.

It is preferred that the polymers of our invention are copolymers which have as few as possible NH_2 units hydrolysed to COOH. They should contain less than 2 weight percent hydrolysis-converted acrylamide monomers, in which the conversion by hydrolysis yields a carboxylate mer unit. Preferably, our polymers contain less than one and even more preferably less than 0.1 weight percent of such a hydrolysis product of the acrylamide mer unit originally present in the polymerization.

The starting monomers for our copolymer are acrylamide and diallyldimethylammonium chloride ("DADMAC"). These monomers are well known in the art and may be polymerized by free radical initiation in aqueous solution or in a water-in-oil emulsion. It is preferable to obtain the high molecular weight polymers of our invention to synthesize our polymers using free radical initiation of an appropriate aqueous solution of the admixture of monomers, after this aqueous solution containing the monomers of this invention has been emulsified in oil by the techniques taught in Vanderhoff, U.S. Patent 3,284,393, the disclosure of which is incorporated herein by reference, or in other patents, such as Frisque/Anderson, U.S. 3,624,019, U.S. 3,734,873, and RE-28,474, which are also incorporated herein by reference.

EXAMPLES

To illustrate the preparation of the acrylamide and diallyldimethylammonium chloride polymers of this invention, the following are given by way of examples:

A mixture of 50 weight ratios of acrylamide and DADMAC was dissolved in water to form a solution which contained between 40-60 weight percent total monomer. This aqueous solution was then added to a hydrophobic oil in the presence of a water-in-oil emulsifying agent and was vigorously stirred to form a water-in-oil emulsion, which emulsion contains, in its aqueous phase, the acrylamide and DADMAC monomers. This emulsion is formed by the use of water-in-oil emulsifiers, such as those exemplified in

Vanderhoff, U.S. Patent 3,284,393. This emulsion is deoxygenated by blowing nitrogen, or any other inert gas, through the emulsion, then a free radical initiator is added. Any of the free radical initiators known in the art may be used, including, but not limited to, peroxides, redox initiators, U.V. light, and the like.

Once the emulsion has been formed, the emulsion is normally purged with an inert gas, such as nitrogen, and heated to a temperature of about 40-50°C. A free radical initiator is added and a polymerization reaction maintained temperatures ranging between about 40-60°C for reaction times of at least one hour. After reaction has been completed, reaction is stopped, preferably by blowing air into the reaction emulsion and the contents of the reaction vessel are cool to room temperature.

Chromatographic analysis using gas chromatography and liquid chromatography along with various spectrophotometric methods can indicate the synthesis of the polymers of this invention.

The polymerization procedure and its utilization in preparing typical copolymers of this invention is to form the water-in-oil emulsions containing the DADMAC and acrylamide and containing the following four basic components. These components and their weight percentages in the water-in-oil emulsions are listed below:

A. Water soluble vinyl addition polymer containing DADMAC and acrylamide:

1. Generally from 5-60 percent;
2. Preferably from 20-40 percent; and
3. Most preferably from 25-35 weight percent.

B. Water:

1. Generally from 20-90 weight percent;
2. Preferably from 20-70 weight percent; and
3. Most preferably from 30-60 weight percent.

C. Hydrophobic oil:

1. Generally from 5-75 weight percent;
2. Preferably from 10-40 weight percent; and
3. Most preferably from 15-35 weight percent.

D. A water-in-oil emulsifying agent:

1. Generally from 0.1-20 weight percent;
2. Preferably from 1-15 weight percent; and
3. Most preferably from 1.2-10 weight percent.

It is also possible to further characterize the water-in-oil emulsions of water soluble polymers of this invention with respect to the aqueous phase of these emulsions. This aqueous phase is generally defined as the sum of the copolymer present in the emulsion plus the amount of water present in the emulsion. This terminology may also be utilized in describing the water-in-oil emulsions useful in our invention.

Utilizing this terminology, the aqueous phase of the water-in-oil emulsions of this invention generally consists of 25-95 percent by weight of the emulsion and preferably the aqueous phase is between 40-90 weight percent of the emulsion. Most preferably, the emulsions containing the copolymers of this invention have an aqueous phase ranging between about 55-85 weight percent.

These emulsions may also be characterized in relation to the water/oil ratios. This figure is simply a ratio of the amount of water present in the emulsion divided by the amount of hydrophobic liquid present in the emulsion. Generally the water-in-oil emulsions of this invention have a water/oil ratio ranging from about 0.25 to about 18. Preferably, the water-in-oil ratio will range from 0.5-14, and most preferably, this ratio will range between about 1.0-5.

The oily liquid may be chosen from any hydrocarbon oil, which oil is essentially immiscible with water. As an example, a common paraffin oil, such as LOPS, may be used.

THE WATER-IN-OIL-EMULSIFIERS

The water-in-oil emulsifiers are exemplified by sorbitan monooleate or a mixture of sorbitan monooleate with a ethylene oxide adduct of sorbitan monostearate. The combination can provide for rapid invertibility of the emulsion of the polymers of this invention when the emulsion is added directly to an aqueous solution, as taught in the Anderson/Frisque patents U.S. 3,624,019, U.S. 3,734,873 and RE-28,576. The polymer may be added to the pulp in any form, e.g. as a water-in-oil emulsion or as a previously inverted oil-in-water emulsion.

EXAMPLES

Several polymers using the techniques described above have been manufactured, which polymers have measured reduced specific viscosities (RSV's) measuring between 4.0 deciliters per gram up to and including reduced specific viscosities of 8.2 deciliters per gram and above.

These polymers were then tested to compare the retention abilities of this high reduced specific viscosity DADMAC/acrylamide copolymer. The results of this test are presented in the figure.

The figure presents the results of three polymers having reduced specific viscosities of 4.0, 5.6, and 8.2, all polymers being a 50/50 mixture of acrylamide and DADMAC, all polymers having been made as water-in-oil emulsions using techniques similar to those described above. These materials were tested to demonstrate their retention abilities using a Britt jar screening technique known in the art. This Britt jar test measures small particle retention in terms of the present transmittance of simulated white water, plotted on the Y axis in Figure 1 vs. polymer dose in kg/t. An increased percent transmittance indicates improved performance.

As Figure 1 demonstrates, the polymers of this invention having reduced specific viscosities above 5.0 gives preferred and improved performance, even against polymer D, which is another type of cationic polymer commercially used as a retention aid, which polymer does not contain DADMAC and which polymer has a higher molecular weight than the highest molecular weight described herein. It is however highly viscous and difficult to handle.

The effective paper fine and filler retaining amount of our polymer, as shown in Figure 1, is at least 0.1 kg of polymer (as active polymer) per metric ton of paper pulp solids (or active) being treated (i.e. about 0.25 lb/ton). Although as much as about 2.5 kg/t (approx. 5 lbs/ton) active polymer may be used, preferably the fines and filler effective retaining amount of polymer is between about 0.25 to 1.25 kg/t (about 0.5 to about 2.5 lbs/ton) of paper pulp.

By comparing the results presented in Figure 1, one concludes that the copolymers of the instant invention are an improvement over the art, even when other cationic polymers derived from different cationic monomers and having higher molecular weight are tested, which higher molecular weight polymers do not contain the DADMAC monomer.

Products of our invention having reduced specific viscosities above 5 show significantly improved retention aid performance when the polymers contain between 40-60 weight percent DADMAC and between 60-40 weight percent acrylamide and the acrylamide contained within the polymer is hydrolyzed below 2 weight percent, based on starting acrylamide monomer, and preferably below 0.1 weight percent based on starting acrylamide monomer.

Claims

1. A method for improving paper fines and filler retention which comprises treating paper pulp prior to sheet formation with a copolymer which contains between 40-60 weight percent diallyldimethylammonium chloride and between 60-40 weight percent acrylamide, and has a molecular weight sufficient to provide a reduced specific viscosity equal to at least 5.0 deciliters per gram.
2. A method according to claim 1 wherein the copolymer is a 50/50 weight percent copolymer of diallyldimethylammonium chloride and acrylamide.
3. A method according to claim 1 or claim 2 wherein the copolymer is at a concentration ranging between about 0.5 lbs/ton of pulp actives to about 2.5 lbs/ton pulp actives.
4. A method according to claim 1, claim 2 or claim 3 wherein the polymer has a molecular weight sufficient to provide for a reduced specific viscosity of at least 7.5 deciliters per gram.
5. A method according to any one of the preceding claims wherein the copolymer is in the form of a water-in-oil emulsion prior to be adding to the paper pulp.

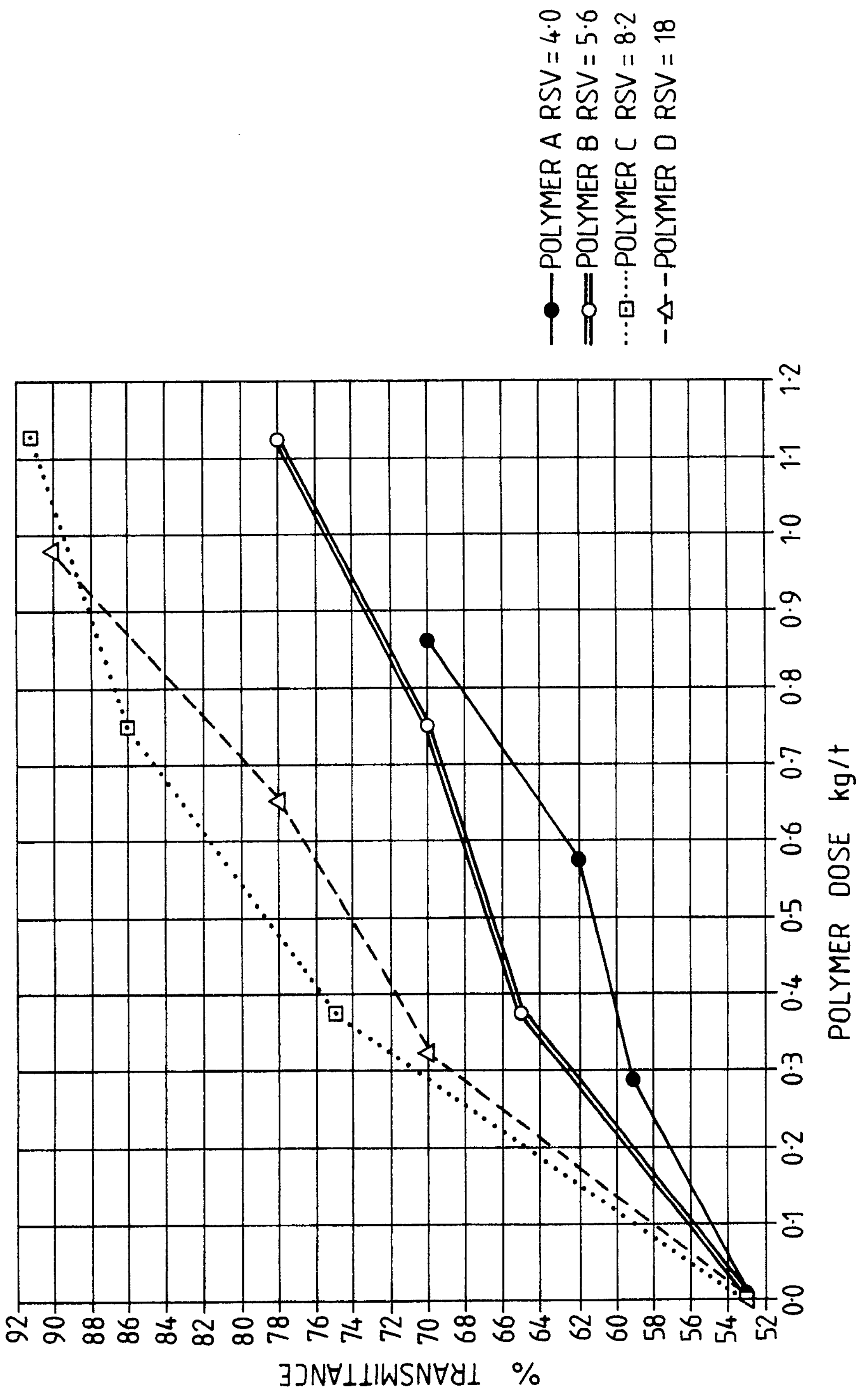
6. A pulp for paper manufacture, containing a copolymer which contains between 40-60 weight percent diallyldimethylammonium chloride and between 60-40 weight percent acrylamide, and has a molecular weight sufficient to provide a reduced specific viscosity equal to at least 5.0 deciliters per gram.

7. A pulp according to claim 6 wherein the copolymer is a 50/50 weight percent copolymer of diallyldimethylammonium chloride and acrylamide.

8. A pulp according to claim 6 or claim 7 wherein the copolymer is at a concentration ranging between about 0.5 lbs/ton of pulp actives to about 2.5 lbs/ton pulp actives.

9. A pulp according to claim 6, claim 7 or claim 8 wherein the polymer has a molecular weight sufficient to provide for a reduced specific viscosity of at least 7.5 deciliters per gram.

10. Paper formed from a pulp according to any one of claims 6 to 9.


POLYMER A RSV = 4·0
POLYMER B RSV = 5·6
POLYMER C RSV = 8·2
POLYMER D RSV = 18
% TRANSMITTANCE
POLYMER DOSE kg/t

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 30 9154

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	FR-A-2 245 671 (CALGON) * page 6, line 29 - page 15, line 3; claims 1-5 * – – –	1-10	D 21 H 17/45
X	EP-A-0 320 512 (SUMITOMO) * page 5, paragraph 3; claim 1 * – – –	1-10	
P,X	EP-A-0 362 770 (HERCULES) * claims 1-5 * – – – – –	1-10	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
D 21 H

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	07 December 90	FOUQUIER J.P.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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