

[54] **METHOD OF MAKING IMPROVED PAPER AND PAPER PRODUCTS**

[75] Inventors: **Danny L. Breen**, Plover, Wis.; **Alvin J. Frisque**, Lagrange, Ill.

[73] Assignee: **Nalco Chemical Company**, Oak Brook, Ill.

[22] Filed: **Jan. 30, 1974**

[21] Appl. No.: **438,050**

[52] **U.S. Cl.** 162/164; 162/168; 162/183
 [51] **Int. Cl.²** **D21D 3/00**
 [58] **Field of Search** 162/168, 164, 183;
 260/29.6 RW, 29.6 R, 29.6 NR

[56] **References Cited**

UNITED STATES PATENTS

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Primary Examiner—S. Leon Bashore

Assistant Examiner—Peter Chin

Attorney, Agent, or Firm—John G. Premo; Robert A. Miller

[57] **ABSTRACT**

Improved paper and paper products are produced by adding to an aqueous suspension of paper pulp fibers from 0.01 – 10% by weight, based on the dry weight of the pulp, of a liquid dispersion of a water-soluble anionic vinyl addition polymer and a water-soluble cationic polymer.

4 Claims, No Drawings

METHOD OF MAKING IMPROVED PAPER AND PAPER PRODUCTS

INTRODUCTION

Many substances are placed into aqueous suspensions of paper pulp fibers in an attempt to produce improved paper and paper products. Chemicals are frequently added to various types of paper pulps to produce finished paper having improved properties, such as wet and dry strength, increased tear resistance, better surface characteristics and the like. Also, chemicals are added to paper pulps to improve the manufacturing characteristics of the pulp as it is processed from an aqueous slurry into a finished sheet. For example, chemicals are added to improve fine and filler retention, to improve the receptivity of the paper for various additives, all of which processes have as their main objective producing better paper with less wastage or better utilization of raw material.

It would be a valuable contribution to the art if a paper-making process and additive or additives could be provided which could produce finished paper products having improved chemical and mechanical characteristics, could be used either alone or in conjunction with other known additives for paper at low economical doses and which would incorporate itself into the paper and be intimately combined therewith to provide a finished paper having improved characteristics.

Also of importance would be a chemical additive for paper pulp which could be used in the various types of papermaking processes such as, for example, mechanical pulping, soda processing, sulfite processing, sulfate processing and semichemical processing. Of further utility would be an additive which would work over a wide variety of pH ranges, would be relatively compatible with other known papermaking additives and would uniformly distribute itself throughout the pulp so that the finished paper contained as an integral part thereof the additives.

THE INVENTION

This invention is based upon the concept that improved paper and paper products are afforded by adding to an aqueous pulp slurry a liquid dispersion of a water-soluble anionic vinyl addition polymer and a water-soluble cationic polymer. The water-soluble anionic vinyl addition polymer may be in the form of a water-in-oil emulsion which contains dispersed therein the finely divided water-soluble anionic vinyl addition polymer. This emulsion or latex contains uniformly distributed therethroughout a water-soluble cationic polymer. Latices of this type are preferred for use in the practice of the invention.

In addition to using anionic latices which contain uniformly distributed therethroughout a water-soluble cationic polymer, the invention also contemplates utilizing metastable dispersions of water-soluble anionic vinyl addition polymers and water-soluble cationic polymers which are dispersed in aqueous brines.

Metastable dispersions of this type are commonly known to the art as Michaels polymers or dispersions. The Michaels polymers are prepared by adding a water-soluble anionic vinyl addition polymer to an aqueous brine and then adding a cationic water-soluble polymer to such brine to form a metastable solution or dispersion of the oppositely charged polymers. The reverse order of addition also may be used. It is now

known that when the salt concentration of such brines is within the range of 5-30% by weight, and the proportions of anionic and cationic polymers are properly adjusted, it is possible to produce dispersions of the two polymers which do not form precipitates or gels. These brine dispersions are stable over periods of time ranging from a few minutes up to several months depending upon the particular polymers selected, the concentrations and ratios of the polymers, the molecular weight of the polymers, the concentration of the brine, and the particular salt in the brine. To improve the stability of such copolymer brine mixtures it is sometimes beneficial to add quantities of polar water-miscible organic solvents such as dioxane.

The water-soluble anionic vinyl addition polymers that are used to prepare the liquid dispersions may be illustrated by the following list of polymers:

TABLE I

Number	Name
1	Polyacrylic acid-sodium salt
2	Polymethacrylic acid-sodium salt
3	Maleic anhydride-vinyl acetate copolymer
4	Polyvinyl methyl ether-maleic anhydride copolymer
5	Methacrylic acid-acrylamide copolymer
6	Polyacrylic acid
7	Isopropenyl acetate-maleic anhydride sodium salt
8	Itaconic acid-vinyl acetate
9	Methyl styrene-maleic anhydride sodium salt
10	Styrene-maleic anhydride
11	Methylmethacrylate-maleic anhydride sodium salt
12	Acrylic acid-styrene
13	Acrylamide-acrylic acid (5% by weight)
14	Acrylamide-acrylic acid (50% by weight)
15	Polystyrene sulfonic acid
16	Acrylamide-acrylic acid (80% by weight)

The above polymers may vary in molecular weight. They may be as low as 10,000 or as high as 12 million or more. In most instances, significant effects in the finished paper are noticed when the molecular weight is greater than 1 million.

The invention contemplates using as preferred water-soluble anionic vinyl addition polymers the homo- and copolymers of acrylic acid as well as the water-soluble salts thereof.

THE WATER-SOLUBLE CATIONIC POLYMERS

These polymers also may be selected from a wide variety of known polymeric materials. Several of these polymers are listed below in TABLE II.

TABLE II

Number	Name
1	Ethylene dichloride-ammonia condensation polymers
2	Tetraethylene pentamine-epichlorohydrin condensation polymers
3	Epichlorohydrin-ammonia condensation polymers
4	Polyethylene imine
5	Ethylene diamine
6	Polydiallyl amine
7	Dimethylamino ethyl methacrylate
8	The methyl chloride quaternary of Number 1
9	The benzol chloride quaternary of Number 7
10	Guanidine formaldehyde condensation

TABLE II-Continued

Number	Name
11	polymers Acrylamide-diallylamine (30%)

The above polymers are illustrative of typical water-soluble cationic polymeric materials that may be used in the practices of the invention. A preferred class of these polymers may be described as alkylene polyamines which are illustrated by polymers 1, 2, 3, 4, 5 and 8 above.

Many of the above polymers have been described with respect to the reactants from which they are prepared. A detailed discussion of the above polymers and other cationic polymers appears in Canadian Pat. No. 731,212, the disclosure of which is incorporated herein by reference. The polymers may be employed as solutions or in the form of a water-in-oil latex or emulsion. When the polymers are of the vinyl addition type, they may be copolymers of other ethylinically saturated monomers. Such copolymers should contain at least 5% by weight of the cationic monomer.

THE ANIONIC VINYL ADDITION POLYMER POLYMERIC LATEX

The invention in its preferred embodiment contemplates utilizing the water-soluble anionic vinyl addition polymers in the form of water-in-oil emulsion which contains dispersed therein the water-soluble anionic vinyl addition polymer. Emulsions of this type are prepared by dispersing the anionic vinyl addition polymer into a water-in-oil emulsion. These polymers are produced by most manufacturing processes are in the form of powders or lump-like agglomerates of varying particle size. It is desirable that the particles, before being placed into the emulsion, be comminuted by grinding, abrading or the like so that their average particle size is less than 5 millimeters and preferably is within the range of 1-5 microns. After the powders have been comminuted, they may be dispersed into the water-in-oil emulsion by means of agitation provided by such devices as stirrers, shakers and the like. To be commercially practical, the amount of polymer in the emulsion should be at least 2% by weight. The invention contemplates using emulsions containing between 5-75% by weight with preferred emulsions having a polymer concentration within the range of 10-45% by weight. In some cases the starting emulsions are converted to suspensions due to the nature and the amount of the polymer present therein.

From a commercial standpoint it is beneficial that the polymer emulsions thus described be stable, yet at the same time contain relatively large amounts of polymers. One method of insuring that the polymers do not precipitate when dispersed in the emulsion is that the particle size of the polymer be as small as possible. Thus, polymers dispersed in the emulsions are quite stable when the particle size is within the range of 5 millimicrons up to about 5 microns. To produce particle sizes within these limitations, spray dryers with appropriate size nozzles may be used. It also is possible to prepare the polymer-containing emulsion of the water-soluble vinyl addition polymers directly from the vinyl monomers from which these polymers are synthesized. Such polymer-containing emulsions may be synthe-

sized by using the water-in-oil emulsion polymerization technique set forth in U.S. Pat. No. 3,284,393. The teachings of this patent comprise forming a water-in-oil emulsion of water-soluble ethylenic unsaturated monomers. The emulsion is formed by utilizing a water-in-oil emulsifying agent. To this monomer is added a free radical-type polymerization catalyst and then heat is applied under free radical-forming conditions to form water-soluble polymer latices. The polymeric latices produced by this patent are relatively unstable and frequently must be treated with additional emulsifiers to render the products stable.

The water-in-oil emulsions used to prepare the above polymers may be formulated by any number of known techniques.

The oils used in preparing these emulsions may be selected from a large group of organic liquids which include liquid hydrocarbons and substituted liquid hydrocarbons. Aliphatic liquid hydrocarbons are preferred. The oil should be inert to the polymer or the monomer from which the polymer is prepared.

A preferred group of organic liquids are the hydrocarbon liquids which include both aromatic and aliphatic compounds, with the latter being most preferred. Thus, such organic hydrocarbon liquids as benzene, xylene, toluene, mineral oils, kerosenes, naphthas, and, in certain instances, petrolatums may be used. A particularly useful oil from the standpoint of its physical and chemical properties is the branch-chain isoparaffinic solvent sold by Humble Oil & Refining Company under the Tradename ISOPAR M. Typical specifications of this narrow-cut isoparaffinic solvent are set forth below in TABLE III.

TABLE III

Specification Properties	Minimum	Maximum	Test Method
Gravity, API at 60/60°F.	48.0	51.0	ASTM D 287
Color, Saybolt	30	—	ASTM D 156
Aniline point, °F.	185	—	ASTM D 611
Sulfur, ppm	—	10	ASTM D 1266 (NEPHELOMETRIC MOD.)
Distillation, °F.			ASTM D 86
IBP	400	410	
Dry point	—	495	
Flash point, °F. (Pensky-Martens closed cup)	160	—	ASTM D 93

The amount of oil used in relation to the water to prepare the emulsion may be varied over wide ranges. As a general rule, the amount of oil-to-water may vary between 5:1 - 1:10 with preferable emulsions being prepared in the ratio of 1:2 - 1:10. These ratios are illustrative of emulsions that can be prepared, although it should be understood that the invention is not limited thereby.

The emulsions may be prepared by any number of techniques. For example, the emulsions may be prepared by using high speed agitation or ultrasonic techniques. In most instances, however, it is desirable that the emulsion be a stable emulsion and to achieve this end it is often necessary to employ an oil-soluble emulsifying agent. The amount of emulsifying agent to provide an emulsion will have to be determined by routine experimentation. As a general rule it may be said that the amount of oil-soluble emulsifier may range from 0.1 - 30% by weight based on the weight of the oil. To produce stable emulsions the amount of emulsifier will

normally be within the range of 12 – 20% by weight of the oil.

Rather than provide a listing of suitable emulsifiers, recommended as being satisfactory are the so-called low HLB materials which are well documented in the literature and are summarized in the Atlas HLB Surfactant Selector. Although these emulsifiers are useful in producing good water-in-oil emulsions, other surfac-

shipped to a use point and then diluted with an organic liquid just prior to use.

PREPARATION OF THE LIQUID DISPERSIONS

To illustrate the preparation of liquid dispersions a variety of emulsions were prepared containing different water-soluble anionic vinyl addition polymers. These emulsions are set forth below in TABLE IV.

TABLE IV

Com- po- sition Num- ber	Water (% by Weight)	Oil (% by Weight)	Polymer	% In Emul- sion	Polymer Particle Size Range
I	72	28 (I)	93% acrylamide 7% methacrylic acid	35%	0.05–7.0 microns
II	72	28 (I)	93% acrylamide 7% methacrylic acid	35%	0.05–7.0 microns
III	72	28 (T)	70% acrylamide 30% acrylic acid	35%	0.05–7.0 microns
IV	67	33 (I)	93% acrylamide 7% methacrylic acid	32%	<30 microns
V	70	30 (I)	70% acrylamide 30% acrylic acid	34%	.01–10 microns
VI	71	29 (I)	Sodium Polyacrylate	37%	<1 mm.

tants may be used as long as they are capable of producing these emulsions. For instance, we have found that certain high HLB surfactants are capable of producing stable water-in-oil emulsions. A typical low HLB emulsifier is sorbitan monooleate.

PREPARATION OF THE STABLE LIQUID DISPERSIONS

Once latices containing the water-soluble anionic vinyl addition polymers are prepared the water-soluble cationic polymers are combined therewith by the utilization of conventional mixing techniques. Preferably the water-soluble cationic polymers are in the form of aqueous solutions which contain 5 – 40% by weight of the polymer and are added to the polymeric latex. Alternatively, they may be nearly water-free. After uniformly mixing the two components there results a stable liquid dispersion of a water-soluble anionic vinyl addition polymer and a water-soluble cationic polymer.

The proportions of the two polymers may be varied to a considerable degree. For instance, the ratio of the water-soluble anionic vinyl addition polymer to water-soluble cationic polymer may vary between 1:10 – 10:1 on a weight basis. A preferred ratio is 1:5 to 5:1. The most preferred ratio is 1:2 – 2:1.

The amount of the water-soluble vinyl addition polymers plus the water-soluble cationic polymers present in the finished liquid dispersion may be varied over a wide range of concentrations, e.g. dispersions containing from 0.001 – 75% by weight are useful. In many instances the total weight of the two polymers contained in the dispersion will be within the range of 5 – 40% by weight, with a very beneficial dispersion being one which contains between 10 – 30% by weight of the two polymers.

The finished dispersions are stable at room temperature for periods of time ranging between several days to as long as 6 months since they may be prepared over a wide variety of concentrations. Concentrates containing large amounts of polymers may be prepared and

DISPERSION A

To emulsion in TABLE IV, COMPOSITION NUMBER VI, there was added 30% by weight of an aqueous dispersion containing 23% by weight of an alkylene polyamine prepared from the condensation of ethylene dichloride and ammonia. The polymer was prepared using the techniques set forth in Canadian Pat. No. 785,829.

DISPERSION B

To COMPOSITION NUMBER VI in TABLE IV there was added an aqueous dispersion which contained 25% by weight of an ammonia ethylene dichloride polymer of the type used in DISPERSION A above with the exception it had been quaternized with methyl chloride.

To illustrate other novel dispersions of the invention, TABLE V is presented below:

TABLE V

ANIONIC LATEX TABLE IV	% by Weight	CATIONIC POLYMER	% by Weight
I	60	20% solution of a tetra-ethylene pentamine epichlorohydrin reaction product (Canadian Pat. 731,212)	40
VI	50	Ethylene diamine	10
V	70	75% acrylamide, 25% dimethylamino ethyl methacrylate copolymer in the form of a latex (water-in-oil - see TABLE II, U.S. 3,624,019)	30

All of the above dispersions were stable and were capable of being stored under a variety of conditions without interreaction of the two polymers.

As previously indicated, it is possible to utilize metastable dispersions of water-soluble anionic vinyl addition polymers and cationic water-soluble addition polymers which are dispersed in an aqueous brine. In the

practice of the invention, such dispersions are preferably prepared at the paper mill at a point at or near the addition point in the pulp processing portion of the papermaking operation. Also, as indicated, since these dispersions are stable for periods of time ranging from several hours up to several months it is possible to make small batches which would be continuously fed to the pulp system. It has been found that a convenient way to prepare such metastable dispersions is to take a small portion of the pulp and use it as the brine into which the anionic and cationic polymer are added. This approach for making up the metastable dispersions works very well in those cases where the pulp contains relatively large amounts of dissolved solids of polyvalent metal salts such as aluminum salts (e.g., alum or sodium aluminate) in addition to other metal salts such as calcium or magnesium salts which are often times normally associated with the make up water used to prepare the pulp. The ratio of anionic to cationic polymer may be varied in the same proportions used in preparing the stable latices previously described. A preferred ratio is 1:5 to 5:1.

In preparing the metastable dispersions a certain amount of experimental trial-and-error techniques are required to determine the ratio of anionic to cationic polymer, their concentration, and the like in order to produce a dispersion that does not cause the two polymers to interact and form a precipitate or gel. Such experimentation is well within the skill of an ordinary papermaking chemist or mill operator.

To illustrate typical dispersions which may be used, reference should be made to Example 1 in U.S. Pat. No. 3,271,496 which shows the preparation of such a dispersion.

TREATMENT OF THE PULP WITH THE LIQUID DISPERSIONS

As previously indicated, the liquid dispersions of the type described above are used to treat aqueous suspensions of paper pulp at dosages ranging from as little as 0.1 - 10% by weight, based on the dry weight of the pulp. In most applications the dosage ranges between 0.5 - 5% by weight. The dosage used in the practice of the invention is dependent upon many factors. Illustrative of some of these factors is the effect sought to be achieved, the nature of the pulp, the type of pulping process used and the particular chemical makeup of the stable liquid dispersion. Also factors are the pH of the pulp, the pulp concentration, the temperature of the pulp and the dissolved solids and other additives present in the aqueous phase of the pulp suspension. Therefore, it is evident that while a dosage range has been given, it is dependent upon the particular pulp system sought to be treated and the particular effect sought to be achieved in the finished paper produced from such pulp.

The above-described liquid dispersions are added to either concentrated brine solutions, which solutions include concentrated alum and sodium aluminate solutions. These brine dispersed suspensions remain relatively stable. When the brine is removed from the diluted stable liquid dispersion, it tends to release into the aqueous phase the anionic vinyl addition polymer and the cationic polymer. These two polymers, upon release into water, tend to react with each other, forming a cross-linked, gel-like structure which is water and oil

insoluble and is flexible and somewhat porous in nature.

In using the liquid latex dispersions in the papermaking process, it is desirable that when the concentrated dispersions are initially supplied such as, for example, by a manufacturer shipping concentrates containing as much as 10-30% by weight of the polymer, that the stable liquid dispersion be either added to a brine or it may be first diluted with an appropriate hydrocarbon oil or other hydrophobic liquid to dilute the polymer concentration to between 5-10% by weight. These diluted materials may be then added to the paper pulp which in many instances contains a sufficient amount of dissolved solids, such as alum, sodium aluminate and the like, where the polymers tend to uniformly distribute themselves throughout the pulp slurry allowing them to combine with and upon the individual fiber surfaces in a surprisingly uniform manner. After the pulp has thus been treated, it is then processed in accordance with known papermaking methods to form a water laid sheet on a device such as a fourdrinier machine.

When the metastable liquid dispersions are used, they are added to the pulp system in the same manner as that used for adding the stable latices. When added to the pulp system, the oppositely charged polymers do not react with each other to form a cross-linked gel-like structure but rather tend to disperse themselves into the and about the cellulosic fibers in a uniform manner, thereby producing a homogeneity of treatment heretofore unobtainable by prior art processes.

When the pulp is diluted by washing at a point at or about the fourdrinier wire or papermaking felt, the anionic and cationic polymers react with each other to form a flexible three-dimensional cross-linked structure which imparts outstanding properties to the finished paper formed from the pulp containing such polymers.

Using the practices described above, far superior paper and paper products are produced as opposed to similar paper pulp which has been treated by separate additions of anionic and cationic polymers of the type described. The success of the invention is believed to be predicated on the fact that by adding the polymers jointly and simultaneously with each other, a more homogeneous coating of the individual fibers by these polymers is achieved and that cross-linking, when it does occur, tends to produce more intimate and rigidly bonded structures about the fiber surfaces, thus assuring a paper having improved properties.

The polymeric mixtures of anionic and cationic polymers tend to react with each other upon dilution of the pulp just prior to or during the sheet-formation stage of the papermaking process. When the thus-formed sheet is subjected to the usual drying steps, the cross-linking reaction of the polymers is further increased which tends to additionally improve the characteristics of the finished paper.

In certain instances the pH of the papermaking system will invert the liquid dispersion of polymers that has been added thereto and thereby cause the gel-like structures to form about the paper fibers. The dispersions give excellent results when the pH of the pulp is or is adjusted to between 4.5-9.5 and preferably 4.5-8.5.

Each of the numerous liquid dispersions that can be prepared and their method of reaction in the presence

of the pulp may be suitably selected for the particular conditions and effects sought to be achieved while at the same time allowing ease of feed and application of the dispersions to the paper pulp.

The various liquid dispersions used in the practice of the invention allow special effects to be achieved in paper products using relatively low dosages. By controlling the amount and nature of the polymeric components of the liquid dispersions, it is possible to produce paper and paper products having improved wet and dry strength. Sizing effects are readily achieved heretofore unobtainable by wet end addition of sizing agents such as rosin. Specialty papers, such as waterproof and greasproof papers can be easily produced. Paper products can be manufactured where high amounts of the liquid dispersion polymers are used, which products resemble plastic laminates which can be used in the manufacture of high grade industrial paper products, such as felts, building materials, and the like.

Since papers can be modified to produce a variety of different effects, it is possible to produce such papers having superior qualities which qualities are achieved by chemicals which are uniformly distributed throughout the sheet and which are closely associated with each of the individual fibers. This phenomenon allows papers to be uniform in their properties throughout the entire sheet and does not rely upon surface effects which are frequently the mechanism by which many additives work. Since the polymers form flexible, three-dimensional, cross-linked substances, they provide a remarkable degree of adhesiveness and cohesiveness for the individual fibers, thus allowing papers to be produced having unusual properties of physical and mechanical strength.

To illustrate the practices of the invention, the following is given by way of example:

EXAMPLE I

Dispersion A would be used by diluting it with kerosene to provide a polymer concentration of 5% by weight. This concentration would then be added to a kraft or sulfate pulp to give a dosage of 2% by weight based on dry pulp. If the pulp contains sufficient alum or sodium aluminate to produce a dissolved salt content of about 2% by weight, then the diluted dispersion added thereto would uniformly distribute itself throughout the pulp without reacting to cause the anionic vinyl addition polymer to react with the cationic polymer. After being added to the pulp and thoroughly admixed therewith, a small amount of nonionic disper-

sant, e.g., 0.1% by weight of the pulp, is added to invert the liquid dispersion of the polymer so that it uniformly reacts so that the polymeric components react with each other to form an insoluble mass about the individual fiber surfaces. After the reaction has taken place, the pulp is processed by forming into finished kraft paper. The paper, thus treated, would have improved wet and dry strength, would be slightly waxy to the feel, and would be capable of acting as heavy duty wrapping paper. The same paper untreated would have far less wet or dry strength and is only of use in light duty service.

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

1. A process for manufacturing paper having improved properties which comprises the steps of:
 - A. Adding to a concentrated aqueous suspension of paper pulp fibers containing at least 2% by weight of a polyvalent metal salt from 0.1 to 10% by weight based on the dry weight of the pulp of a stable liquid dispersion of a water-soluble anionic vinyl addition polymer and a water-soluble cationic polymer comprising:
 - a. a polymeric latex composed of a water-in-oil emulsion which contains dispersed therein a finely divided water-soluble anionic vinyl addition polymer; said polymeric latex having uniformly distributed throughout,
 - b. a water-soluble cationic polymer: With the ratio of (a) to (b) being within the range of 1:10 to 10:1 and the total amount of a and b present within said dispersion being within the range of from 0.001 to 75% wherein a stable dispersion of pulp containing uniformly dispersed polymers without gellation is formed,
 - B. Diluting the stable dispersion of pulp containing uniformly dispersed polymers with water to effect gellation of the said polymers; and then
 - C. Processing the pulp into a paper having improved properties.
2. The process of claim 1 where the weight ratio of (a) to (b) is within the range of from 1:5 to 5:1 and the amount of (a) plus (b) present within said dispersion is within the range of from 5-40% by weight.
3. The process of claim 1 where the weight ratio of (a) to (b) is within the range of from 1:2 to 2:1 and the amount of (a) plus (b) present within said dispersion is within the range of from 10-30% by weight.
4. The process of claim 1 where the pulp is a sulfate pulp.

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