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# CELLULOSIC PAPER SIZED WITH AN ALKYL ACRYLATE OR PROPIOLATE AND A POLYALKYLENEIMINE

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## ABSTRACT OF THE DISCLOSURE

A composition comprising an alkyl acrylate or an alkyl propiolate and a polyalkyleneimine which is useful in the preparation of sized cellulosic paper substrates.

This invention relates to the sizing of cellulose paper substrates. More particularly this invention provides new combinations of materials which are very effective as sizing agents, especally under neutral and alkaline conditions of papermaking.

Much of the cellulosic paper produced at the present time is prepared under acid conditions, that is, with pulp slurries having pH's in the range of from about 4.5 to 5.5. When sizing of this type of paper is done, economical sizing is being accomplished using commercially available rosin size formulations and papermaker's alum which are added into the pulp slurries used to make the paper. Lately, however, in response to demands for long lasting papers, papermakers have been trying to develop methods for manufacturing paper under alkaline pH conditions. Such papers are believed to be more resistant to aging.

It has been found that rosin sizes mixed into aqueous alkaline pulp slurries do not give the desired degree of water resistance to the resulting paper product. There is a need for sizing materials which are effective in the alkaline pH range, and still are compatable with presently used papermaking conditions.

An object of this invention is to provide sizing compositions which will size paper under alkaline conditions to give permanent sizing while being compatible with present papermaking procedures.

Briefly, this invention provides a sizing combination of ingredients which are particularly useful for sizing textiles and paper products. The sizing combinations comprise a mixture of (1) one or more higher alkyl propiolate or higher alkyl acrylate compounds, or mixtures of such propiolates and acrylates and (2) a polyalkyleneimine or a poly(N-methylalkyleneimine), or mixtures thereof having from 2 to 3 carbon atoms in each alkylene moiety. This combination type of sizing operation provided for by this invention is particularly surprising in view of the substantially lowering sizing effectiveness demonstrated by the alkyl propiolates alone and the complete absence of sizing by the polyalkyleneimine and/or poly(N-methylalkyleneimine) component when used alone. The alkyl propiolate or alkyl acrylate to polyalkyleneimine or poly(N-methylalkyleneimine) polymer weight ratios may range from about 1:10 to about 10:1, although we prefer to use them in a weight ratio of about 1:1 to 1:3.

The preferred method of applying the sizing materials to the cellulosic substrate is to add to an aqueous dispersion of the pulp used to make the cellulosic paper sheet or article an emulsion of the alkyl propiolate or alkyl acrylate and the polyalkyleneimine or poly(N-methylalkyleneimine) in a mixing vessel and then to form sheets or webs from the treated aqueous pulp slurry in the



conventional manner. The alkyl propiolate or alkyl acrylate and the polyalkyleneimine or poly(N-methylalkyleneimine) may be mixed into one emulsion prior to adding them to the aqueous pulp slurry or the two components may be added separately. Optimum results are obtained when the pH of the treated pulp slurry is adjusted to the basic pH range, preferably at from about 7 to 10. With the higher alkyl acrylates, substantial sizing is lost as pH is lowered much below about 7. The alkyl propiolates are not as sensitive to pH and form effective sizing agents when used with the polyalkyleneimines or poly(N-methylalkyleneimine) at pH's ranging from about 4.8 and higher. The alkyl acrylates are also more sensitive to the use of alum in the papermaking process. As the alum content increases, the effectiveness of the alkyl acrylates diminishes. However, the alkyl acrylates in combination with the polyalkyleneimines or poly(N-methylalkyleneimines) provide a high degree of sizing in the basic pH range where no or little alum is being used. The alkyl propiolates may be used with the polyalkyleneimines and poly(N-methylalkyleneimine) even in the presence of alum. Use of more than about 3% alum, based on the dry pulp used reduces the sizing effectiveness of these materials somewhat, especially in the acid pH papermaking range.

Effective sizing of cellulosic substrates may also be accomplished by dipping the cellulosic paper into dilute aqueous emulsions or organic solvent solutions of the alkyl propiolate and/or the alkyl acrylate and the polyalkyleneimine or poly(N-methylalkyleneimine). Papers and textiles in general, including those from synthetic polymeric fibers may also be sized with these materials by spraying them on the surface of the substrate being sized.

In application to paper sizing the hard sizing is developed with the preferred alkyl propiolates, such as $C_{16}$–$C_{20}$ alkyl propiolates and with polyethyleneimines in the normal drying operation of papermaking. If desired the paper may be cured at room temperature for a few days or at relatively elevated temperature say 100–110° C. for from 10 to 120 minutes to enhance the speed of the sizing action. The alkyl propiolates, and methods for preparing them are described in U.S. Patent 3,100,794. When the alkyl propiolates having from 8 to about 12 carbon atoms in the alkyl group are used, they should be used in concentrations of at least about 0.3 to 1.0% by weight based on the dry weight of the material being sized. Alkyl propiolates having about 12 carbon atoms and higher may be used in lower concentration down to about 0.05 concentration, based on the substrate, especially if higher quantities of the polyalkyleneimines are used. As stated above, the preferred unsaturated esters are the alkyl propiolates having from 16 to about 20 carbon atoms. The propiolate ingredient may be one compound or may be a mixture of compounds.

The higher alkyl acrylates having from 8 to 30 carbon atoms may be prepared in a similar manner to that described above in preparing the propiolic acid esters in U.S. Patent 3,100,794. The preferred alkyl acrylates are those having from about 16 to about 20 carbon atoms.

The polyalkyleneimines used in this invention are the polymerization products of ethyleneimine or derivatives thereof. Those used in this invention are those having from 2 to 3 carbon atoms in each alkylene group which are water soluble. Such products are described, for example, in U.S. Patent 2,182,306. The poly(N-methylalkyleneimines) are the polymerization products of N-methylethyleneimine, N-methylpropyleneimine, or mixtures thereof.

The following examples will further illustrate the nature of the invention but the invention is not intended to be restricted thereto.

Example 1

This example illustrates the use of the preferred combination of sizing ingredients in what we call the "wet-end" method of application.

A typical alkyl propiolate, or acrylate e.g., 0.75 g. of octadecyl propiolate was dissolved in a suitable organic solvent such as xylene or dimethylbenzyl alcohol. The resulting propiolate solution was emulsified with 20 ml. of 0.1% aqueous hexadecyltrimethyl-ammonium bromide.

Cellulose pulp used to make paper was slurried with water to give 2% pulp solids and then refined to 480–520 Canadian Standard Freeness. The chosen polyalkyleneimine, e.g., polyethyleneimine, was diluted with water to a concentration of 1%. An amount of this 1% polyethyleneimine solution equivalent to the desired weight percent of the polyethyleneimine based on the dry pulp was added to the pulp slurry and stirred.

The pH of the treated aqueous pulp slurry was adjusted to the desired test pH, usually 5, 7, or 9 and then a quantity of the propiolate or acrylate aqueous emulsion was added to the pulp slurry to give 1% (or other test concentration of the chemical or chemicals being evaluated) based on the dry cellulose pulp. Handsheets are prepared from the treated pulp slurries thus obtained on a Noble and Wood machine and the dried paper sheets obtained are tested for the amount of water repellancy ("sizing") possessed by the sheet by floating a sample of the treated paper sheet on a standard ink bath having a pH of 1.5, and observing the time (in seconds) needed for the first traces of a blue coloration to appear on the observed surface of the test sample. A high number of seconds (over 500) is an indication of hard sizing of the paper by the added chemicals. For some applications, for example, where slack-sizing is desired, only a moderate degree of sizing (10 to 500 seconds) is desired; slack sizing is evidenced by a moderately high number of seconds of resistance to ink penetration. Resistance levels of under about 10 seconds are taken as an indication of no or minimal sizing effectiveness of the added chemical or combination of chemicals.

The results are summarized in Table I.

TABLE I

| Compound | Percent | Compound | Percent | Cure | Ink sizing (seconds) |
|---|---|---|---|---|---|
| Octadecyl propiolate | 1 | Polyethyleneimine | 1 | No | 79,000+ |
| Do | 1 | Polypropyleneimine | 1 | No | ,000+ |
| Do | 1 | do | 1 | Yes | 7,000+ |
| | | Polyethyleneimine | 1 | No | 0 |
| | | | | Yes | 0 |
| Do | 1 | Poly(2-hydroxy-1,3-propyleneimine). | 1 | No | 4 |
| | | | | Yes | 263 |
| Octadecyl acrylate | 1 | Polyethyleneimine | 1 | No | 11,000+ |
| | | | | Yes | 11,000+ |
| Octadecyl propiolate | 0.7 | | | No | 0 |
| | | | | Yes | 0 |
| 1-hexadecyl propiolate | 0.3 | Polyethyleneimine | 0.3 | No | 2,900 |
| | | | | 1 day R.T | 2,300 |
| Do | 0.7 | do | 0.7 | No | 12,000 |
| | | | | 1 day R.T | 9,500 |
| Octadecyl propiolate | 0.3 | do | 0.3 | No | 3,000 |
| | | | | 1 day R.T | 2,450 |
| n-Decyl propiolate | 0.7 | do | 0.7 | No | 2,250 |
| | | | | 1 day R.T | 180 |
| Octadecyl propiolate | 3.0 | do | 6.0 | No | 10,000+ |
| | | | | 3 days R.T | 30,000+ |

Example 2

This example illustrates the effect of pH in the pulp slurry-additive mixture on sizing efficiency of higher alkyl propiolate-polyalkyleneimine combination.

For this example 0.5% of polyethyleneimine and 0.5% of octadecyl propiolate as aqueous emulsions were incorporated into aqueous slurries of bleached sulfite pulp adjusted to pH's of 5, 7, and 9. Bleached pulps are, in general, more difficult to size than unbleached pulps. Alum was added to some aqueous pulp slurries at 1% concentrations, based on the weight of the dry pulp used.



In other samples no alum was added. The treated aqueous pulps were formed into paper sheets on a Noble and Wood handsheet machine. The resulting "off machine" test papers were tested for sizing effectiveness. The results are summarized in the following table.

TABLE II

| pH of pulp slurry | Alum content, percent | Sizing ink resistance, seconds |
|---|---|---|
| 9 | 0 | 10,000 |
| 9 | 1 | 10,000 |
| 7 | 0 | 5,000 |
| 7 | 1 | 7,000 |
| 5 | 0 | 1,500 |
| 5 | 1 | 6,000 |

When the test papers were cured at 105° C. for 1 hour and then tested, the sizing results were as follows:

TABLE III

| pH of pulp slurry | Alum content, percent | Sizing ink resistance, seconds |
|---|---|---|
| 9 | 0 | 10,000 |
| 9 | 1 | 10,000 |
| 7 | 0 | 7,000 |
| 7 | 1 | 15,000 |
| 5 | 0 | 7,000 |
| 5 | 1 | 7,000 |

Example 3

This example illustrates the use of mixtures of alkyl propiolates and polyalkyleneimines as effective sizing agents. For this example, a standard bleached Gatineau sulfite pulp refined to a Canadian Standard Freeness of 500±20 ml. as a 2% pulp solids aqueous slurry of pH 9 was treated with a 1% aqueous emulsion of a 50:50 molar mixture of the indicated alkyl propiolates in an amount sufficient to provide varying weight percents of the mixture based on the dry pulp. The treated pulp was mixed 15 minutes and then polyethyleneimine was added in quantity sufficient to provide varying weight percents thereof based on the dry weight of the pulp used. The treated pulp was mixed another 15 minutes to insure complete dispersion and then handsheets were prepared. The results are summarized in the following table.

TABLE IV

| Propiolates | Percent | Percent polyethyleneimine | Sizing ink resistance, seconds |
|---|---|---|---|
| Octadecyl 2-ethylhexyl | 0.3 | 0.3 | 1,412 |
| Octadecyl tridecyl | 0.4 | 0.4 | 1,975 |
| Tridecyl 2-ethylhexyl | 0.4 | 0.4 | 140 |
| Do | 0.4 | 0.8 | 4,500 |
| Do | 0.5 | 0.5 | 350 |

Example 4

Poly(N-methylethyleneimine) was dissolved in water and added to a bleached sulfite pulp slurry in an amount to give 1 part of poly(N-methylethyleneimine) to 100 parts of pulp. After 15 minutes stirring an emulsion prepared by dissolving octadecyl propiolate in dimethylbenzyl alcohol, then emulsifying this resulting solution with the aid of "Arquad 2HT" (a dialkyldimethyl quaternary ammonium chloride) was added to the above treated pulp slurry in an amount to give 1 part of octadecyl propiolate to 100 parts of pulp. Sheets of paper were formed from the treated pulp thus obtained, and dried on a Noble and Wood handsheet machine drier. Ink penetration resistance time of these sheets was found to be more than 18,000 seconds.

What is claimed is:

1. Cellulosic paper sized with a combination of (1) at least one member of the group consisting of an alkyl acrylate having from 16 to 20 carbon atoms in the alkyl group and an alkyl propiolate having from 8 to about 20 carbon atoms in the alkyl group and (2) at least one member of the group consisting of a poly-N-methylalkyleneimine and polyalkyleneimine having from 2 to 3 carbon atoms in each alkylene group thereof.

2. Sized cellulosic paper as described in claim 1 wherein the alkyl propiolate (1) is used and is a mixture of two or more alkyl propiolates having from 8 to 20 carbon atoms in each alkyl group, and component (2) is a polyalkyleneimine which is a polyethyleneimine.

3. Sized cellulosic paper as described in claim 2 wherein the mixture of alkyl propiolates (1) is a mixture of 2-ethylhexyl propiolate and tridecyl propiolate.

4. Sized cellulosic paper as described in claim 1 wherein component (1) is an alkyl propiolate and is octadecyl propiolate and component (2) is a polyalkyleneimine which is a polyethyleneimine.

5. A method for preparing sized cellulosic paper which comprises mixing with an aqueous cellulosic pulp slurry being used to prepare paper therefrom an aqueous dispersion of (1) at least one member of the group consisting of an alkyl acrylate having from 16 to 20 carbon atoms in the alkyl group and an alkyl propiolate having from 8 to 20 carbon atoms in the alkyl groups thereof, also mixing with said aqueous pulp slurry with (2) at least one member of the group consisting of polyalkyleneimines and poly(N-methylalkyleneimines) having from 2 to 3 carbon atoms in the alkylene groups in concentrations sufficient to provide at least about 0.05% by weight of component (1) and at least about 0.15% by weight of component (2) based on the weight of the dry pulp, and then forming the treated aqueous pulp slurry thus obtained into paper.



6. A method as described in claim 5 wherein component (1) is an alkyl propiolate and is used as a mixture of alkyl propiolates having from 8 to about 20 carbon atoms in the alkyl groups thereof and component (2) is a polyalkyleneimine having from 2 to 3 carbon atoms in each alkylene group.

7. A method as described in claim 5 wherein component (1) is an alkyl propiolate and is octadecyl propiolate and component (2) is a polyalkyleneimine and is polypropyleneimine.

8. A composition comprising (1) at least one member of the group consisting of alkyl acrylate having from 16 to 20 carbon atoms in the alkyl group and alkyl propiolates having from 8 to about 20 carbon atoms in the alkyl group and (2) at least one member of the group consisting of polyalkylenepolyimines and poly(N-methylalkyleneimines) having from 2 to 3 carbon atoms in the alkylene groups thereof.

9. A composition as described in claim 8 wherein component (1) is an alkyl propiolate and component (2) is a polyalkyleneimine and said components (1) and (2) are present in weight ratios of from about 1:10 to about 10:1 of alkyl propiolate to polyalkyleneimine.

10. A composition as described in claim 9 wherein component (1) is an alkyl propiolate and is a mixture of alkyl propiolates having from 8 to 20 carbon atoms in the alkyl groups of each molecule and component (2) is a polyalkyleneimine and is a polyethyleneimine.

11. A composition as described in claim 9 wherein the alkyl propiolate is octadecyl propiolate and the polyalkyleneimine is a polyethyleneimine.

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