United States Patent Office 3,006,806 Patented Oct. 31, 1961

3,006,806

SIZED PAPER AND PROCESS THEREFOR

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No Drawing. Filed Feb. 15, 1957, Ser. No. 640,335
10 Claims. (Cl. 162—158)

This invention relates to an improved sized paper, made from stock of such filler content as to be opaque, and so treated as to possess enhanced water-repellency and other desired properties.

Prior proposals have been inadequate to provide sized paper of the desired characteristics by an economical manufacturing process.

The requirements, which have been satisfactorily met by the product and process of this invention, are illustrated in the properties recognized as desirable in white paper for use as the jacket over the mouthpiece of cigarettes, particularly those provided with a filter tip.

A thin layer of cork has been used for such jackets and has the desirable attributes of water-repellency and freedom from any marked tendency to stick to the smoker's lips, or to disintegrate in use, as when moistened with saliva. However, past attempts to provide an attractive white paper to serve as mouthpiece jacket have been attended by disadvantages and inadequacies.

Attractive white paper generally has a sufficiently high content of filler, such as calcium carbonate, to display considerable porosity and absorbency for water, tending to stick to the lips and undergo an unslightly loss of opacity when moistened. Conventional sizing of such papers with rosin, stearate or wax sizes precipitated with alum offered no satisfactory solution to the problem.

While satisfactory appearance and water-repellency may be obtainable by the use of various lacquer coatings, these may create other difficulties such as blocking, i.e., sticking together of packaged cigarettes, the presence of residual off-odors and off-tastes, and marring of the tips by marking during the assembly of the cigarettes. Also, such lacquer coating adds considerably to the manufacturing cost.

Resins such as melamine-formaldehyde and urea-formaldehyde, which have been used for imparting wet strength to paper, did not provide the solution to this problem, as the fibers of the resulting paper are too readily wet by moisture with loss of opacity and the paper sticks excessively to the lips. Likewise, similar unsatisfactory results were obtained in the paper mill with paper impregnated with alkylketene dimers or other previously known sizing agents. By way of example, when sufficient paraffin wax was used to size the paper to the necessary extent, the opacity of the tipping was altogether too low.

Accordingly, the main object of this invention has been the provision of sized opaque paper sheet displaying improved properties, particularly enhanced water-repellency and resistance to penetration by aqueous solutions, together with a process for readily and economically manufacturing such sheet. Other objects include the provision of attractive white tipping paper containing sufficient filler to be opaque and so sized as to withstand moistening without loss of opacity and resist adhesion to smokers' lips.

In accordance with this invention, the foregoing objects are attained with the provision of paper having improved properties by the use, with paper fibers in the presence of opacifying filler, of a sizing agent comprising a unique combination of an alkylketene, preferably in the form of dimer, which is reactive with cellulose to become permanently attached thereto, and a cationic organic polymer. The resulting paper sheet is found to possess unusual desirable characteristics, and, in particular, enhanced water-repellency and resistance to penetration by aqueous solutions, not obtainable under practicable conditions with the use of the individual sizing components. It is evident that the ketene and the cationic polymer interact or affect each other in a unique and beneficial manner.

Illustrative embodiments of the invention are described in the following specific examples.

Example 1

A furnish of beaten bleached kraft wood pulp in water was prepared at 3% consistency. A colloidal dispersion of a cationic melamine-formaldehyde polymer, for example, "Parez 607" sold by American Cyanamid Company, acidified with hydrochloric acid, was added to the furnish during efficient stirring. Alkylketene dimer, for example, "Aquapel" sold by Hercules Powder Company, was then added with good mixing to the furnish as an emulsion in water containing sufficient sodium bicarbonate to raise the pH of the furnish to about 7.5. Precipitated chalk, finely-divided calcium carbonate, was then added and after thorough mixing, the furnish was ready for the formation of paper. A paper web, weighing 40 grams per square meter on a dry basis and containing about 30% by weight calcium carbonate was formed from the furnish and the web was pressed, dried and aged. Two additional papers were prepared as described above with omission of the cationic polymer in one and of the ketene in the other. The solid constituents of the three furnishes were in the proportions listed in the following table.

	1	2	3
Wood Pulp	55	55	55
Cationic Polymer	2		2
Alkylketene Dimer	0.5	0.5	
Precipitated Chalk	42.5	42.5	42.5

Despite the high filler content, sheet 1 was found to be highly water-repellent throughout and to be highly resistant to penetration by water. In contrast, sheets 2 and 3 were readily wetted and absorptive to water, with considerable loss of opacity.

A drop of water weighing about 40 milligrams was allowed to fall on each sheet from a height of 18 inches. On sheet 1, the drop was subdivided into numerous droplets which remained unabsorbed. On sheet 2, the drop flattened and was gradually absorbed, with attendant loss of opacity. On sheet 3 the drop of water was absorbed immediately.

Example 2

The procedure of Example 1 was repeated, using the furnish proportions in the following table and an aqueous dispersion of a cationic urea-formaldehyde resin, for example "Uformite 711" sold by Rohm and Haas.

	1	2	3
Wood Pulp	55	55	55
Cationic Polymer	2		
Alkylketene Dimer	1	1	
Precipitated Chalk	42	42	42

Test results of the three resulting papers paralleled those of the preceding example.

Example 3

The procedure of Example 1 was repeated, using the furnish proportions in the following table, employing as ketene an emulsion of hexadecylketene dimer, and as cationic polymer, an aqueous dispersion of a cationic starch, comprising a starch rendered cationic by incorpo-

ration of amino or substituted amino groups, for example, modified corn starch named "Cato Starch," sold by National Starch Products, Inc.

	1	2	3
Wood Pulp	52	52	52
Cationic Polymer	3	------	3
Alkylketene Dimer	3	3	------
Precipitated Chalk	42	42	42

Test results of the three resulting papers paralleled those of Example 1.

Example 4

This example describes commercial scale manufacture of white paper suitable for the jacket of cigarette tips, having a basis weight of 44 grams per square meter.

Bleached kraft wood pulp is well beaten in the conventional Hollander, and then passed through a Jordan beater at a consistency of about 3%. The pulp suspension is subsequently thoroughly mixed with a suspension of about 2 pounds of precipitated chalk per gallon of water and with white water from the Fourdrinier machine to reduce the pulp consistency to about ½%. An aqueous dispersion of cationic melamine-formaldehyde polymer, acidified with hydrochloric acid, and containing about 18.5 grams per liter of the polymer is thoroughly mixed with the furnish. Then, an alkylketene dimer aqueous emulsion, containing about 37 grams per liter of the ketene and about 46 grams per liter of sodium bicarbonate, is added to the furnish with thorough mixing. The resulting furnish as supplied to the headbox of the paper machine contains solid ingredients in the following proportions, by weight:

Wood pulp	100
Cationic polymer	1
Alkylketene dimer	3
Calcium carbonate filler	40

The paper sheet formed in the Fourdrinier machine is pressed and dried, and has a filler content of about 30%, an alkylketene content of about 2½% and cationic resin content of about 0.5%.

The paper product in accordance with this invention is well suited in appearance and properties for the jacket on cigarette mouthpieces, as it has an attractive white appearance, does not lose opacity on being moistened, and does not stick excessively to the smoker's lips. While there may be some tendency toward slight deposition of filler particles on moist contacting surfaces from the "felt" side of the sheet, there is no such tendency on the "wire" side. For such use, it is therefore preferred that the "wire" side constitute the external surface. As in the previous examples, the paper having a combination of alkylketene dimer and cationic polymer is far more water-repellent and resistant to penetration by water than paper made in the identical manner excepting for the omission of either the ketene or polymer.

The novel compositely sized paper displays a remarkable retention of opacity even after it has been soaked in water for 15 minutes or longer. In contrast papers which have been heavily sized with conventional materials such as rosin, paraffin, or stearic acid undergo substantial loss of opacity after only several minutes' contact with water, especially when pressure is applied at the wetted area, as when the sheet is held between moist lips. Also, the novel paper product of this invention displays a remarkably high wet scuff resistance in comparison with conventionally sized paper containing a similar proportion of pigment.

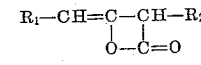
The filler which is an essential component of the paper product of this invention may advantageously constitute 5 to 35% of the finished paper, although generally a range of 10 to 20% is preferred. An alkaline filler such as finely-divided calcium carbonate will generally be the most useful, but may be replaced for particular

applications partially or completely by other finely-divided filler materials, for example, magnesium carbonate, titanium dioxide, barium sulfate, and co-precipitated zinc sulfide and barium sulfate.

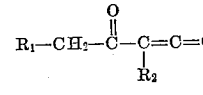
Thus excellent tipping of basis weight of 37 grams per square meter was manufactured as in the preceding example except that the amounts of calcium carbonate and titanium dioxide pigments in the furnish were adjusted until the paper contained 10% and 5%, respectively, of these substances. In another example, the calcium carbonate pigment was omitted and the proportion of titanium dioxide pigment was increased until the paper contained 10% of the latter. Excellent results were also obtained when the melamine resin was replaced with 2 to 3% of "Cato Starch," based on the total weight of the ingredients comprising the furnish.

The wood pulp of the above examples may likewise be replaced in whole or in part by other suitably prepared fibrous cellulosic pulps such as sulfite wood pulp, cotton linters, flax and other vegetable celluloses. Suitable dyes may be added to the furnish if a colored paper is desired.

The preferred ketenes for use in accordance with this invention may be represented by the chemical formula R—CH=C=O, where R is an alkyl group containing 6 to 20 carbon atoms. The ketene is preferably used in the form of a dimer in solution or emulsion, the formula of which may be represented either as:



or



wherein R_1 and R_2 are the same or different alkyl groups containing 6 to 20 carbon atoms.

Excellent results have been obtained with a commercially available hexadecylketene dimer having an apparent molecular weight of about 530 and which is readily reactive with cellulose fibers when dried at above ordinary atmospheric temperatures. Advantageously, the ketene is used in the form of an aqueous emulsion as described in U.S. Patent 2,627,477 to Downey. Other ketenes and their dimers may likewise be employed in accordance with this invention, in which the hydrocarbon substituent may consist of a cycloalkyl or aryl group containing 6 to 20 carbon atoms for example, phenyl ketene, decyl phenyl ketene and cyclohexyl ketene, as described in U.S. Patent 2,762,270 to Keim and Thompson.

The effectiveness of the ketene for the purposes of this invention depends on the conjoint use of cationic polymer, characterized by having positively charged particles when colloidally dispersed in aqueous solution. It seems likely that the ketene and polymer particles unite to form particles having residual cationic areas, which later become attached to available sites on the cellulose fibers which are negatively charged in the presence of water. Thus, conditions are excellent for the attainment of substantially uniform coating of the fibrous cellulose when beater-sized in accordance with this invention, involving the addition of the ketene and cationic polymer ingredients in aqueous dispersion to the furnish, as in the foregoing illustrative examples, prior to the formation of the paper sheets. On subsequent drying of the paper, the ketene reacts with hydroxyl groups of the cellulose to become a permanent part of the molecular structure thereof.

Useful polymers are thus defined as those which are colloidally dispersible in aqueous solutions to yield particles carrying positive charges and are herein termed cationic polymers. All polymers of this nature which have been tested have proved effective, when used in conjunction with the above-described ketenes, to impart

water-repellency and other desirable properties to cellulose fibers containing appreciable amounts of finely-divided filler.

In addition to the cationic polymers specifically referred to in the above specific examples, melamine-formaldehyde resins (as described in U.S. 2,345,543 to Wohnsiedler and Thomas and U.S. 2,559,220 to Maxwell and Lanes), urea-formaldehyde resins (as described in U.S. 2,657,132 to Daniel, Landes and Suen) and cationic corn starch, other useful cationic polymers are included among the following illustrative examples: guanidine-formaldehyde resins, (U.S. 2,745,744 to Weidner and Dunlap), alkylenepolyamine-halohydrin resins (as described in U.S. 2,601,597 to Daniel, Wilson and Landes), and cationic urea-formaldehyde resins (as described in British Patents 675,477 and 677,184).

The conjoint use of a ketene, as described above, and a cationic starch, which may be defined as a modified starch product resulting from chemical treatment of starch so that cationic groups, for example amino or substituted amino groups, are properly incorporated in the molecular structure thereof to result in positively charged particles when colloidally dispersed in aqueous solutions, is of particular advantage for the production of cigarette tipping paper of high quality. This combination provides a paper product in which a tendency toward dusting, and thus fouling of the cigarette-making machinery, is minimized. This beneficial effect probably results from the activity of the modified starch as an effective bonding agent for cellulose fibers and fibrils, which counteracts the softening effect of the ketene dimer on paper in which it is incorporated.

It is noteworthy that substances, which are not cationic polymers, such as glue, starch, carboxymethylcellulose, and triethanolamine, are ineffective for the purposes of this invention when substituted for the cationic polymers as described above.

Paper made in accordance with this invention also presents an excellent receptive surface for writing and printing. Good resistance against the feathering of ink is secured with the use of as little as ½% of ketene and ¼% of cationic polymer based on the solids' content of the furnish. When the paper product is to be used as tip jacket or similar purposes, preferably ¾% to about 5% of ketene and ½% to about 5% of cationic polymer is used. Higher proportions may be used, but the slight improvement obtained above about 8% of these ingredients, on the above basis, is insufficient generally to justify the additional cost.

Accordingly, the novel beater-sized paper of this invention is advantageously prepared by application of the combination of sizing ingredients to the cellulose fibers in aqueous dispersion before formation of the paper sheet, as described in the foregoing specific examples. The resulting paper sheets display enhanced water-repellency, resistance to penetration by water and marked retention of opacity even after soaking in water, as above described.

What is claimed is:

1. A sized paper of felted cellulose fibers comprising a major content of cellulose and about 5 to 35% by weight of finely-divided filler, said cellulose fibers having been beater-sized with about ¼% to 8% on the dry weight of the paper of an organic cationic polymer and about ½% to 8% of an alkylketene dimer in which the alkyl has 6 to 20 carbon atoms.

2. A sized paper of felted cellulose fibers comprising a major content of cellulose and about 5 to 35% by weight of finely-divided filler, said cellulose fibers having been beater-sized with about ½% to 5% on the dry weight of the paper of an organic cationic polymer and about ¾% to 5% of an alkylketene dimer in which the alkyl has 6 to 20 carbon atoms.

3. A sized paper of felted cellulose fibers comprising a major content of cellulose and about 5 to 35% by weight of finely-divided filler, said cellulose fibers having been beater-sized with about ½% to 5% on the dry weight of the paper of an organic cationic polymer and about ¾% to 5% of hexadecylketene dimer.

4. Paper sizing process comprising providing an aqueous suspension of cellulosic fibers, mixing about 5 to 35% of a finely-divided filler therewith, adding to said suspension ¼% to 8% of an organic cationic polymer in dispersion and ½% to 8% of a ketene dimer in dispersion, said ketene containing a monovalent hydrocarbon group having 6 to 20 carbon atoms, to beater-size said cellulosic fibers and converting said suspension to a paper web.

5. Paper sizing process comprising providing an aqueous suspension of cellulosic fibers, mixing about 5% to 35% of a finely-divided filler therewith, adding to said suspension ¼% to 8% of a cationic melamine-formaldehyde resin in dispersion and ½% to 8% of a ketene dimer, containing a monovalent hydrocarbon group having 6 to 20 carbon atoms, in dispersion, to beater-size said cellulosic fibers and converting said suspension to a paper web.

6. Paper sizing process comprising providing an aqueous suspension of cellulosic fibers, mixing about 5% to 35% of a finely-divided filler therewith, adding to said suspension ¼% to 8% of a cationic starch in dispersion and ½% to 8% of a ketene dimer in dispersion said ketene containing a monovalent hydrocarbon group having 6 to 20 carbon atoms, to beater-size said cellulosic fibers and converting said suspension to a paper web.

7. Paper sizing process comprising providing an aqueous suspension of cellulosic fibers, mixing about 5% to 35% a finely-divided filler therewith, adding to said suspension ¼% to 8% of a cationic urea-formaldehyde resin in dispersion and ½% to 8% of a ketene dimer in dispersion, said ketene dimer containing a monovalent hydrocarbon group having 6 to 20 carbon atoms, to beater-size said cellulosic fibers and converting said suspension to a paper web.

8. A sized paper comprising a major content of felted cellulose fibers and 5 to 35% of finely-divided filler, said cellulose fibers having been beater-sized with about ¼% to 8% on the dry weight of the paper of an organic cationic polymer and about ½% to 8% of hexadecylketene dimer.

9. A sized paper comprising a major content of felted cellulose fibers and 5 to 35% of finely-divided calcium carbonate, said cellulose fibers having been beater-sized with about ¼% to 8% on the dry weight of the paper of an organic cationic polymer and about ½% to 8% of hexadecylketene dimer.

10. A sized paper comprising a major content of felted cellulose fibers and about 30% of finely-divided calcium carbonate, said cellulose fibers having been beater-sized with about ¼% to 8% on the dry weight of the paper of an organic cationic polymer and about ½% to 8% of hexadecylketene dimer.

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