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(54) **USE OF POLYVINYLAMINE TO IMPROVE OIL AND WATER SIZING IN CELLULOSIC PRODUCTS**

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(57) **ABSTRACT**

The presence of both a water sizing agent and an oil sizing agent in a paper making furnish is detrimental in that each has an adverse effect on the sizing property of the other. It has now been found that this adverse effect can be counteracted or lessened by the presence in the furnish of a polyvinylamine.

USE OF POLYVINYLAMINE TO IMPROVE OIL AND WATER SIZING IN CELLULOSIC PRODUCTS

FIELD OF THE INVENTION

[0001] This invention relates to an improvement in both oil/grease and water sizing of cellulosic materials, especially paper products, through the use of a polyvinylamine in combination with both oil and water sizing agents.

BACKGROUND OF THE INVENTION

[0002] Sizing agents are used in papermaking processes to repel water or grease; i.e., oils, from adhering or penetrating into the paper, thus weakening and/or staining the paper. Sizing agents can be classified into reactive agents or non-reactive agents. They can also be classified into internal sizing agents or as surface sizing agents. Reactive sizing agents bond with the paper fibers and are usually used for internal sizing.

[0003] Sizing agents can be added to the paper furnish before the furnish enters the wet end of the papermaking machine. Alternatively, same sizing agents can be sprayed or nipped onto the newly formed paper as the paper passes through. If the sizing agent is added to the pulp slurry (i.e., the furnish) it must adhere to the pulp or it will not be retained in the paper. This can be achieved by using an agent that is oppositely charged from the pulp. Sizing agents in paper prevent excess penetration of water or grease into the paper. They are used where water or grease resistance is needed in the paper end use. There are no sizing agents that have adequate resistance properties of both. The most efficient oil-sizing agents for cellulosics, such as paper, contain long, linear fluorocarbons chains. Fluorocarbons in general have low surface energies and are not wetted easily by oil-based materials. Conversely, agents that contain non-fluorinated hydrocarbon chains are good water sizing agents.

[0004] However, when a combination of a fluorocarbon-based agent for oil resistance and a hydrocarbon based product for water resistance are both employed in paper making processes, each has an adverse affect on the other's performance. Accordingly, more material or product must be used to compensate for the adverse loss of resistant properties.

[0005] As described by Bottorff in U.S. Pat. No. 5,252,754, long chained fluorocarbons are efficient oil sizing agents for cellulosic materials such as paper due to their low surface energy. However, these fluorocarbon-based sizing agents are generally inefficient for water resistance, especially if they contain hydrophilic salt groups. On the other hand, hydrocarbon-based size products such as alkyl ketene dimer (AKD), are effective water sizing agents but are inefficient for oil sizing purposes. When combinations of both hydrocarbon and fluorocarbon-based materials are used, they have a negative impact on each other's performance in paper. This adverse relationship generally results in inefficient treatment schemes because elevated product levels are required to achieve both adequate oil and water resistance properties in the same paper.

[0006] It has now been discovered that the presence of a polyvinylamine in a paper or board furnish which furnish contains both oil (or grease), and water-sizing agents, the adverse effect is surprisingly counteracted.

SUMMARY OF THE INVENTION

[0007] In one aspect, the invention is a papermaking or board making process in which a furnish contains both an oil sizing agent and a water sizing agent. The improvement being that the furnish also contains a polyvinylamine.

[0008] Another aspect of the invention is the order of addition of the agents to the furnish. A water sizing agent is added to a paper furnish. The polyvinylamine is then added to the paper furnish either before or after the water sizing agent is added, followed by adding the oil sizing agent.

[0009] In addition the invention provides a paper furnish which contains at least one polyvinylamine, a water sizing agent and an oil sizing agent.

DETAILED DESCRIPTION OF THE INVENTION

[0010] Adding a water-soluble cationic polyvinylamine when both an oil size and a water size are used in the papermaking process is an important aspect of the invention.

[0011] The furnish (i.e., pulp) is passed through a paper machine consisting of a head box, a sheet forming section and a drying section, all in sequence.

[0012] Polyvinylamines useful in this invention include but are not limited to ones produced through free radical solution polymerization of n-vinylformamide. The resulting nonionic polyvinylformamide can then be base-hydrolyzed, creating a primary amine cationic functionality on the polymer and sodium formate as a byproduct. Products effective for the purpose include, but are not limited to, vinylamine polymers that have been reacted to a hydrolysis level of 35-100% velocity 50-100% with molecular weight ranging from 300,000-400,000 via size exclusion chromatography (SEC) Copolymers of polyvinylamine can be used. Comonomers include vinyl acetate or vinyl propionate monomers.

[0013] The polyvinylamine polymers can be incorporated into the aqueous suspension of fibers used to form the web, i.e., the furnish.

[0014] By furnish is meant the mixture of various materials that are blended in the stock suspension from which paper or board is made; the chief constituents are fibrous material (pulp), sizing or strength materials, or other additives such as fillers and dyes.

[0015] By pulp is meant fibrous materials prepared from wood, cotton, grasses, etc, by chemical or mechanical processes for use in making paper, board, or cellulose products.

[0016] By wire is meant a woven material made of plastic or metal for use in forming the web of paper or board from the dilute pulp slurry.

[0017] By headbox is meant a flow control chamber that receives the dilute paper stock or furnish from the stock preparation system and acts to spread the flow uniformly across the full width of the forming wire.

[0018] By sheet forming is meant the process by which the dilute fiber furnish is formed into a wet web through vacuum and gravity drainage effects.

[0019] By drying section is meant the part of the papermaking process that involves the removal of excess water from the wet web of paper or board through direct contact with heated-drying cylinders.

[0020] By web is meant the sheet of paper or board coming from a paper machine in its full width.

[0021] Suitable water sizing agents include alkyl ketene dimers (AKD) or alkenyl ketene dimer (AKD), alkenyl succinic anhydride (ASA), rosin-based sizes such as rosin soap, dispersed rosin, and the like.

[0022] Suitable oil sizing agents include fluorocarbon-containing polymers such as those which have fluorinated alkyl groups.

[0023] In a preferred process aspect of the invention, the oil size and water size can be added to the furnish in amounts of 0.005% to 1.0% (weight percent) active treatment solids based upon total furnish solids, and the polyvinylamine can be present in an amount of between 0.001% and 1% active treatment solids based on upon total furnish solids.

[0024] The following Example A highlights the typical adverse relationship between oil and water sizing agents in cellulose-based systems requiring high levels of water and oil sizing.

EXAMPLE A

[0025] To make handsheets of paper, a Noble and Wood laboratory former was used to prepare 20 cm×20 cm handsheets at a basis weight of 160 grams/square meter.

[0026] A furnish containing bleached softwood Kraft pulp and bleached chemi-thermomechanical pulp were obtained from a commercial specialties manufacturer requiring significant water and oil sizing properties. The pulps were blended at a 1:1 ratio and refined in a laboratory cycle beater to 470 ml Canadian Standard Freeness (CSF). As outlined in Table A, commercial water and oil sizing agents were added sequentially to aliquots of the pulp. Stock agitation was accomplished with an overhead mixer assembly set at 1,400 rpm. The oil size treatment was added to the pulp (furnish), 30 seconds after the addition of the water sizing agent. Handsheet preparation commenced after an additional 30 seconds of mix time following the oil size treatment. Handsheets were formed on a 100 mesh screen, passed through a felted roll press set at 35 psi (single pass), and dried to 3-4% moisture using a drum dryer.

[0027] Performance testing was conducted with both a Hot Water Cobb test and a Hot Oil Cobb test to demonstrate water and oil resistance properties in the finished paper. The procedures for these tests are set forth below. The Hot Water Cobb test involves paper samples cut to 12.5 cm×12.5 cm, weighed to the nearest 0.01 g, and subsequently clamped inside a 100 ml Cobb ring apparatus. A 50 ml sample of water at 180° F. is then poured into the Cobb ring and on top of the paper. After exactly two (2) minutes of contact time with the paper sample, the water is quickly poured from the ring. The wetted paper sample is removed from the apparatus and placed between two pieces of blotting paper (wetted side up). The excess water is removed from the paper specimen by moving a Cobb hand roller once back and forth over the sample without exerting any additional force. The wetted paper sample is immediately reweighed to the nearest 0.01 g. The weight of water absorbed in grams per square meter is calculated by subtracting the conditioned weight of the sample from its final weight and multiplying by 100.

[0028] The Hot Oil Cobb test is identical to the Hot Water Cobb Test except that oil (Wesson® Corn Oil) is used at 220° F. in place of the water. The only other difference in the oil testing is that the Cobb hand roller is not used to remove the excess oil but rather the wetted paper sample is pressed by hand between blotter paper before the sample is gently wiped with a clean Kimwipes® towel. The Hot Oil Cobb test quantifies the weight of the hot oil absorbed in grams/square meter using the same calculation described under the Hot Water Cobb test.

[0029] In both the Hot Water and the Hot Oil Cobb tests, a higher test result indicates a greater degree of absorption by the paper sample. Conversely, a lower Cobb test value is indicative of low surface welting and penetration and better sizing properties. The data in Table A shows the typical negative impact of a water sizing agent on the performance of an oil sizing product. For example, as the treatment level of the water size is increased, the water sizing improved while the oil size property is reduced. The water sizing agent is comprised of alkyl ketene dimer while the oil size is a perfluoroalkyl-containing product.

TABLE A

Water and Oil Sizing Results

Commercial Water Size (wt. %)	Commercial Oil Size (wt. %)	Hot Water Cobb (g/m^2)	Hot Oil Cobb (g/m^2)
0.132	0.225	162	89
0.155	0.225	71	118

[0030] The following definitions apply for Table A:

[0031] Commercial AKD Water Size: Hercon® 79—Hercules Incorporated

[0032] Commercial Oil Size: imPress® FP-100—Hercules Incorporated

[0033] Weight %: % Addition of Active Treatment Solids Based Upon Total Furnish Solids

[0034] The following Examples are illustrative of the surprising beneficial effect of polyvinylamine on both water and oil resistance in cellulose-based systems requiring high levels of water and oil sizing.

EXAMPLE 1

[0035] The data from Example 1 is summarized in Table 1. In this study, handsheets were prepared using the same papermaking procedure described in Example A with the exception that the furnish was comprised of 60% southern bleached softwood Kraft and 40% northern bleached hardwood Kraft commercial market pulps refined to 480 ml Canadian Standard Freeness (CSF). The target basis weight was 248 grams/square meter. The chemical addition sequence was as described in Example A except that when polyvinylamine was included in the testing, it was added to the mixing furnish 30 seconds prior to the addition of the water sizing agent. Handsheet performance testing was conducted using the same procedures as described in Example A except that a 2% Ambient Saline Cobb test was conducted in place of the Hot Water Cobb test. The saline used in the test is at ambient temperature and is derived from

deionized water treated with NaCl at 2% by weight. Aside from these differences, the test procedure is identical to the Hot Water Cobb test method described in Example A.

[0036] The data summarized in Table 1 shows the simultaneous positive effect of polyvinylamine on both water and oil sizing test results. The low Saline and Hot Water Cobb test values demonstrate that an effective balance in water and oil resistance is achieved through the addition of the polyvinylamine. The water sizing agent is comprised of alkyl ketene dimer while the oil size is a perfluoroalkyl-containing product. The polyvinylamine is a solution polymer that has been reacted to a hydrolysis level of 50%.

TABLE 1

Water and Oil Sizing Results

Commercial Polyvinylamine (wt. %)	Commercial Water Size (wt. %)	Commercial Oil Size (wt. %)	2% Ambient Saline Cobb (g/m^2)	Hot Oil Cobb (g/m^2)
0	0.075	0.15	51	134
0.013	0.075	0.15	35	116
0	0.075	0.20	111	111
0.013	0.075	0.20	31	33

[0037] The following definitions apply for Table 1:

[0038] Commercial Polyvinylamine: Hercules® PPD M-1189—Hercules Incorporated

[0039] Commercial AKD Water Size: Hercon® 80—Hercules Incorporated

[0040] Commercial Oil Size: imPresse FP-100—Hercules Incorporated

[0041] Weight %: % Addition of Active Treatment Solids Based Upon Total Furnish Solids

EXAMPLE 2

[0042] The data from Example 2 is summarized in Table 2. In this work, handsheets were prepared to 160 grams/square meter using the same papermaking procedure and furnish blend described in Example A. The target Canadian Standard Freeness for pulp refining was 470 mls. The chemical addition sequence was consistent with the description provided in Example A except that when an anionic polymer was included in the testing, it was added to the mixing furnish 30 seconds after to the addition of the water sizing agent and 30 seconds prior to the addition of the oil size material. When polyvinylamine was included in the testing, it was added to the mixing furnish 30 seconds prior to the addition of the water sizing agent. Handsheet performance testing was conducted using the same procedures as described in Example A.

[0043] The data in Table 2 further demonstrates the beneficial effect of polyvinylamine on both water and oil sizing properties as low Cobb values are achieved with the addition of polyvinylamine to the test furnish. The water sizing agent is comprised of alkyl ketene dimer. The oil size is a perfluoroalkyl-containing product, and the polyvinylamine is a solution polymer that has been reacted to a hydrolysis level of 50%. The anionic polymer is a solution copolymer of acrylamide and acrylic acid (Hercobond 2000). Anionic polymer is used as a retention aid to enhance the retention of fine solids in the web during the sheet forming process.

TABLE 2

Water and Oil Sizing Results

Commercial Poly-vinylamine (wt. %)	Commercial Water Size (wt. %)	Commercial Anionic Polymer (wt. %)	Commer-cial Oil Size (wt. %)	Hot Water Cobb (g/m^2)	Hot Oil Cobb (g/m^2)
0	0.35(1)	0	0.24	74	40
0	0.35(1)	0.2	0.24	99	51
0.1	0.35(1)	0.2	0.24	49	39
0.05	0.125(2)	0	0.24	255	53
0.1	0.125(2)	0	0.24	82	39
0.2	0.125(2)	0.1	0.24	43	35

[0044] The following definitions apply for Table 2:

[0045] Commercial Polyvinylamine: Hercules® PPD M-1189—Hercules Incorporated

[0046] Commercial Water Size (1): 60:40 Blend ReTen® 204LS/Hercon® 70—Hercules Incorporated

[0047] Commercial Water Size (2): Hercon® 70—Hercules Incorporated

[0048] Commercial Anionic Polymer: Hercobond® 2000—Hercules Incorporated

[0049] Commercial Oil Size: imPress® FP-100—Hercules Incorporated

[0050] Weight %: % Addition of Active Treatment Solids Based Upon Total Furnish Solids.

EXAMPLE 3

[0051] The data from Example 3 is summarized in Table 3. In this study, handsheets were prepared using the same papermaking procedure described in Example A with the exception that the furnish was comprised of 70% southern bleached softwood Kraft and 30% northern bleached hardwood Kraft commercial market pulps refined to 405 ml Canadian Standard Freeness. The target basis weight was 149 grams/square meter. The chemical addition sequence was consistent with the description provided in Example A except that when either the polyvinylamine or branched polyamine were included in the testing, it was added to the mixing furnish 30 seconds prior to the addition of the water sizing agent. In addition, the anionic polymer and colloidal silica were added in sequential order 30 seconds after the addition of the water size and 30 seconds prior to the addition of the oil sizing agent with 30 seconds of mix time between each product addition. Handsheet performance testing was conducted using the same procedures as described in Example A

[0052] The data in Table 3 summarizes the positive effect of polyvinylamine on water and oil sizing results. The trends associated with the polyvinylamine further demonstrate that it is possible to reduce the addition level of the water and oil sizing agents while maintaining an effective low balance of Cobb test values indicative of high water and oil resistance properties. The test data associated with the branched polyamine indicate that it is difficult to achieve the same effective balance in water and oil sizing properties as compared to the test conditions involving polyvinylamine.

[0053] In this example, the branched polyamine is a solution polymer with quaternary amine functionality. The polyvinylamine is a solution polymer that has been reacted to a hydrolysis level of 50% with a predominantly linear structure and primary amine functionality. The water sizing agent is comprised of alkyl ketene dimer, while the oil size is a perfluoroalkyl-containing product. The anionic polymer is an emulsion copolymer of acrylamide and acrylic acid. The silica component is an aqueous dispersion of colloidal silica particles. The anionic polymer and colloidal silica are added to the furnish with the purpose of increasing the retention of fine solids in the paper web in the forming process.

TABLE 3

Water and Oil Sizing Results

Commercial Branched Polyamine (wt. %)	Commercial Poly-vinylamine (wt. %)	Commercial Water Size (wt. %)	Commercial Anionic Polymer (wt. %)	Commercial Colloidal Silica (wt. %)	Commercial Oil Size (wt. %)	Hot Water Cobb (g/m^2)	Hot Oil Cobb (g/m^2)
0.35	0	0.14	0.29	0.09	0.15	49	95
0.35	0	0.14	0.29	0.09	0.17	51	55
0.35	0	0.14	0.29	0.09	0.19	47	39
0.35	0	0.14	0.29	0.09	0.21	51	41
0.35	0	0.14	0.29	0.09	0.23	76	39
0.30	0	0.14	0.29	0.09	0.19	49	36
0.40	0	0.14	0.29	0.09	0.19	57	39
0	0.15	0.14	0.29	0.09	0.19	39	47
0	0.20	0.14	0.29	0.09	0.19	39	36
0	0.20	0.12	0.29	0.09	0.17	39	34
0	0.20	0.10	0.29	0.09	0.15	40	33

The following definitions apply for Table 3:

[0054] Commercial Branched Polyamine: Nalco 7607—Nalco

[0055] Commercial Polyvinylamine: Hercules® PPD M-1189—Hercules Incorporated

[0056] Commercial Water Size: Hercon® 79—Hercules Incorporated

[0057] Commercial Anionic Polymer: PerForm® PA8137—Hercules Incorporated

[0058] Commercial Colloidal Silica: Positek 8691—Nalco

[0059] Commercial Oil Size: imPress® FP-100—Hercules Incorporated

[0060] Weight %: % Addition of Active Treatment Solids Based Upon Total Furnish Solids

1. In a paper making process in which a furnish is used, which furnish contains both an oil sizing agent and a water sizing agent as a part of the materials in the furnish, the improvement in which the furnish also contains a polyvinylamine.

2. The process of claim 1 in which the oil sizing agent is present in the furnish in an amount of between 0.005% and 1% active treatment solids based upon total furnish solids; the water sizing agent is present in an amount of between 0.005% and 1% active treatment solids based upon total furnish solids; and the polyvinlamine is present in an amount of between 0.001% and 1% active treatment solids based upon total furnish solids.

3. The process of claim 1 in which the oil sizing agent is a fluorocarbon containing polymer, and the water sizing agent is an alkyl ketene dimer.

4. The process of claim 2 in which the oil sizing agent is a fluorocarbon containing polymer, and the water sizing agent is an alkyl ketene dimer.

5. The process of claim 2 wherein the polyvinylamine has a hydrolysis level of at least 35%.

6. The process of claim 1 in which the order of addition to the furnish of oil sizing agent, water sizing agent and polyvinylamine, is adding the water sizing agent, then adding the polyvinylamine either before or after the water sizing agent followed by adding the oil sizing agent.

7. The process of claim 3 in which the order of addition of fluorocarbon containing polymer, the alkyl ketene dimer and the polyvinylamine, is adding the alkyl ketene dimer, adding the polyvinylamine either before or after adding the alkyl ketene dimer, followed by adding the fluorocarbon containing polymer.

8. A paper furnish that contains an oil sizing agent, a water sizing agent, and a polyvinylamine.

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