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3,144,380

PROCESS FOR MAKING FILLED PAPERS CONTAINING A REACTION PRODUCT OF EPICHLOROHYDRIN WITH A CONDENSATION PRODUCT OF METHYL ACRYLATE AND A POLYETHYLENE POLYAMINE

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4 Claims. (Cl. 162—164)

The present invention is related to a process for producing filled papers prepared with either organic or inorganic fillers of essentially water-insoluble character. The invention embraces the making of so-called "mineral-filled papers" by a procedure which involves the introduction into a suspension of the pulp of a mineral-filler in finely divided condition. The term "filler" herein is intended to include mineral or organic matters of water-insoluble character which are essentially inert, whether or not they serve a pigmentary or coloring function. The usual purpose of the filler or pigment is to impart opacity and brightness to the paper, and it may also serve to tint or color the paper.

In the production of filler papers, appreciable amounts of the fillers pass through the screen during the deposition of the paper or other fibrous sheet or molding formed of the fiber-filler suspension. The so-called "white-water" which thus passes through during the deposition contains substantial amounts of the filler and is either discarded in plants using a so-called "open system" or is re-circulated for re-use in the so-called "closed system." When the white-water is discarded, there is not only an economic loss of the filler but also a possible stream pollution problem. Even with the re-circulation technique, some white-water is eventually discarded with consequent loss of filler.

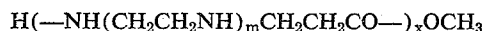
In order to reduce the amount of filler which passes through the screen during the deposition of the fibrous structure, various retention agents have heretofore been used including alum, glue, polyacrylamide, and the condensation products of urea with formaldehyde and polyalkyleneamines. These retention agents have provided some benefit but have various disadvantages. Certain of them, such as alum, cannot be used with calcium carbonate because of the acidity of the alum. Many of the previously used retention agents serve satisfactorily for some mineral or organic fillers but fail or operate poorly with others or with organic fillers. Others, such as glue and the condensation products of urea with formaldehyde and polyalkylene-amines, while improving retention somewhat are not highly efficient retention aids. The use of relatively large amounts of these agents provides only a modest improvement in retention. Certain surface sizes, which are generally applied after sheeting, are unsatisfactory when the sheet has been formed using alum. For example, sizing agents, such as the higher aliphatic ketene dimers, described in U.S. Patent 2,627,477, can only be efficiently used if the filler paper is made in the absence of alum. Another disadvantage of previous processes for making filler papers is the tendency to form one-sided sheets, that is, sheets in which the filler is largely trapped and retained on the top side of the fiber mat.

In accordance with the present invention, the deposition of formed fibrous structures, such as paper from aqueous suspensions containing the fiber and the filler, is greatly improved by the incorporation in the suspension, during the deposition or prior to the deposition, of extremely small amounts, relative to the amount of fiber and/or filler in the aqueous suspension of improved retention agents hereinbelow defined. The improved reten-

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tion appears to be the result of a bridging action between the fiber and the filler effected by the retention agent. Possibly the retention agent acts as a molecular bridge between the fiber and the filler. The retention agents of the present invention are unusually versatile in that they generally operate efficiently with both organic and inorganic fillers. Also, they exhibit a high efficiency over a wide variety of pH conditions from acid through neutral to the alkaline side up to a pH of about 12 and especially from pH's between 3 and 10. Generally, a substantially lesser amount of the retention agents of the present invention may be used as compared to the amounts of retention agents heretofore used to obtain comparable efficiency. Alternatively, greater efficiencies are obtained by using small amounts of the new retention agents than can be obtained with the agents used heretofore regardless of how much of them is used. Because of the adaptability of the new retention agents to be used under a wide variety of pH conditions, filled papers can be obtained which are adapted to receive a wide variety of sizing materials including rosin sizes generally applied under acid conditions, or waxes, and especially higher aliphatic ketene dimers, such as hexa-decyl ketene dimer or any of the others mentioned in the above-cited patent which are especially useful when applied to papers prepared under neutral or alkaline conditions. In some cases, the tendency towards "two-sidedness" in filled sheets may be reduced using these new retention agents.

The retention agent of the present invention is a water-soluble solid thermosetting resin-forming reaction product of (1) epichlorohydrin with (2) a condensation product of methyl acrylate and a polyethylene-polyamine in a mol ratio of about 1:1 comprising a compound of the formula



in which m is an integer having a value of 2 to 4, and x has an average value such as to provide an average molecular weight of about 300 to 1,000, the ratio of the epichlorohydrin to the condensation product being 0.2 mol to m mol of the former to each mol of polyamine used in making the condensation product, and the reaction product having a viscosity of about 3 to about 45 poises at a concentration of 25% in water at 25° C.

The retention agent of the present invention is produced by reaction of an epichlorohydrin on an intermediate which is a linear polymeric reaction product of a polyalkylenepolyamine, or of mixtures thereof with an alkyl-enediamine, obtained by reaction with an ester of acrylic acid or methacrylic acid, especially a (C_1-C_4) -alkyl acrylate, the preferred ester being methyl acrylate from the standpoint of cost and ease of reaction.

In preparing the intermediate, it is preferred that the ester and the polyamine be reacted in approximately a 1:1 mol ratio. However, the mol ratio of ester to polyamine may be in the range from 0.5:1 to 1.8:1. When a high mol ratio of the ester to the polyamine is used, it is merely desirable to limit the extent of condensation so that the condensation product of linear character still retains a substantial proportion of basic nitrogen atoms, either in the form of an amino group $-NH_2$ or an imino group $-NH-$.

A variety of polyalkylenepolyamines including polyethylenepolyamines, polypropylenepolyamines, polybutylenepolyamines, polyamylenepolyamines, poly(hexamethylenepolyamines, and so on may be employed herein of which the polyethylenepolyamines represent an economically preferred class. More specifically, the polyalkylenepolyamines used in this invention are polyamines containing two primary amine groups and at least one secondary amine group in which the nitrogen atoms are linked together by groups of the formula $-C_nH_{2n}-$ where n is a small integer greater than unity and the

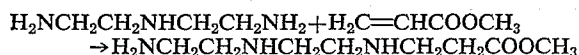
number of such groups in the molecule ranges from two up to about eight and preferably up to about four. The nitrogen atoms may be attached to adjacent carbon atoms in the group $-\text{C}_n\text{H}_{2n}-$ or to carbon atoms farther apart, but not to the same carbon atom. Besides using such polyamines as diethylenetriamine, triethylenetetramine, tetraethylenepentamine, dipropylenetriamine, and the like, in reasonably pure form, there may also be used mixtures and various crude polyamine materials. For example, the mixture of polyethylene polyamines obtained by the reaction of ammonia and ethylene dichloride, refined only to the extent of removal of chlorides, water, excess ammonia, and ethylenediamine, is a very satisfactory starting material. Most preferred are the polyethylenepolyamines containing from two to four ethylene groups, two primary amine groups, and from one to three secondary amine groups.

The term "polyalkylenepolyamine" employed in the claims, therefore, refers to and includes any of the polyalkylenepolyamines referred to above or to a mixture of such polyalkylenepolyamines.

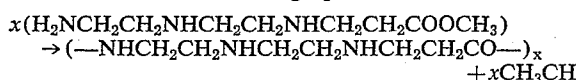
The spacing of secondary amine groups in the molecule of the polyaminoamide intermediate may be increased by substituting an aliphatic diamine such as ethylenediamine, propylenediamine, hexamethylenediamine or a heterocyclic diamine, such as piperazine or the like, for a portion of the polyalkylenepolyamine. For this purpose, up to about 60% of the polyalkylenepolyamine may be replaced by a molecularly equivalent amount of the diamine. Usually, a replacement of about 30% or less is preferred.

While the intermediate condensation product obtained may, in many cases and in fact usually, be composed of mixtures of the various compositions, particularly when the starting materials are not used in a strict 1:1 mol ratio, and when the starting material consists of a mixture of polyamines, the preferred embodiment using methyl acrylate and diethylenetriamine in a 1:1 mol ratio may be considered typical and produces as its primary product a polyaminoamide by virtue of a reaction which may be considered to occur in two stages, although the second stage may occur concurrently or simultaneously with the first stage as such stage or steps are described herein.

In the first step, a Michael addition occurs in accordance with the following equation:

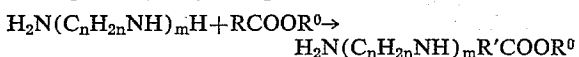


In the second step aminolysis and elimination of methanol result in the production of a linear polymer in accordance with the following equation:



With methyl acrylate, the first step occurs at much lower temperature than the aminolysis but with methyl methacrylate the two steps occur at the same temperature. Hence, the two steps may readily be kept separate with methyl acrylate whereas in the other cases they would occur practically simultaneously. The products are essentially equivalent in either case.

The general equation for the first step reaction applying to polyalkylenepolyamines generally and unsaturated esters generally may be represented as follows:



where

m is 1 or more, such as 1 to 6 and preferably 2 to 4,

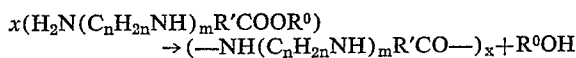
n is 2 to 6 or more, preferably 2 to 3, and most economically 2,

R is $\text{H}_2\text{C}=\text{CH}-$ or $\text{H}_2\text{C}=\text{C}(\text{CH}_3)-$,

R^0 is a hydrocarbon residue of an alcohol, such as (C_1-C_6) -alkyl, preferably methyl, and

R' is $-\text{CH}_2\text{CH}_2-$ or $-\text{CH}_2\text{C}(\text{CH}_3)\text{H}-$

The general reaction applying to the second step is as follows:



The ester and the polyamine may be mixed with or without a solvent and the simple mixture results in an exothermic reaction even when effected at room temperature. Depending upon the quantities and the rapidity of the addition of one reactant to the other, more or less cooling may be desirable to provide a smooth reaction without overheating in portions thereof.

If desired, a basic catalyst, such as an alkali metal hydroxide or an alkali metal alcoholate such as sodium methylate may be used to assist this reaction, but it is generally unnecessary.

After the preliminary reaction, involving the Michael addition, the reaction medium is heated to cause aminolysis of the ester group of some molecules of the adducts with the amino group of others with liberation of methanol or other alcohol. The heating may range from a temperature of about 90° to 130°C ., or even higher. Generally, the reaction mixture is raised to the upper portion of this temperature range to effect aminolysis and, of course, the reaction will liberate methanol or other alcohol which may be allowed to boil off and thereby favor further aminolysis.

The resulting product is a water-soluble linear condensation polymer which may contain more or less alcohol, such as methanol, depending upon the extent to which the latter is removed by distillation. It is generally highly viscous at the elevated temperature where the reaction is completed, generally around 90° to 95°C . and it has a pH value of about 10 to 11.5. Its average molecular weight may range from about 300 to 1,000 or higher, by ebulliometric methods.

The linear condensation product thus obtained is a solid at room temperature and water-soluble. To produce the retention agents of the present invention, it is reacted with an epihalohydrin.

While epibromohydrin or epiodohydrin may be used for producing these condensation products which serve as retention aids, it is preferred from the standpoint of cost and availability to employ epichlorohydrin and discussion herein will specifically refer to this halohydrin.

The retention agents may be produced by the reaction of as low as 0.2 mol of epichlorohydrin per mol of original polyamine used in the making of the polyaminoamide intermediate. However, there may be used as much as m mols of epichlorohydrin per mol of original polyamine used in making the polyamide, the letter m representing the same value as that which it is used to represent in the formula for the initial polyamine used in making the intermediate. Thus, in the case of the intermediate obtained from diethylenetriamine, the mol ratio may be from 0.2 to 2 mols epichlorohydrin per mol of the polyamine. Similarly, in the case of triethylenetetramine, the range may be from 0.2 to 3 mols of epichlorohydrin per mol of the polyamine, since in this case m is 3.

To effect the reaction between the epihalohydrin and the polyamide intermediate, the halohydrin is preferably added gradually to an aqueous solution of the polyamide at a temperature which may be from room temperature to reflux temperature. The concentration of the aqueous solution may vary widely, 10 to 40% being quite practical.

Preferably the temperature is about 50 to 75°C . During the reaction when a high concentration material is used at the start, it may be desirable to gradually dilute the reaction mass to reduce the viscosity so that mixing and uniformity of the reaction mass are facilitated.

If desired, a hydrogen chloride acceptor such as caustic soda may be added, but this is generally unnecessary. When it is used, however, it should be added slowly along with the epichlorohydrin.

The reaction is carried on until the viscosity of the reaction mass reaches a value in the range of about 3 to 45 poises or about M to Z on the Gardner-Holdt scale when measured at 25% concentration at 25° C. During the reaction, the pH drops to about 7 or 8 when no caustic is used.

It is clear that the condensates thereby obtained embrace a wide range of compositions depending upon the starting materials and the particular mol ratios employed as well as the extent of reaction. All of these condensation products are useful as retention agents.

The utilization of the retention agents of the present invention in the preparation of filled papers may be accomplished in several ways. In the preferred manner, the retention agent is added to the suspension containing the fiber and filler suspended or dispersed therein. In the preparation of the fiber/filler suspension, either of these two insoluble substances may be dispersed in the aqueous medium before the other and, if desired, a wetting or dispersing agent may be employed to assist the dispersion or suspension. On the other hand, mechanical action alone may be resorted to in order to effect the dispersion or suspension thereof in the aqueous medium.

The conventional consistencies of the pigment dispersion or suspension and/or of the fiber suspension may be employed. For example, the fibrous suspension may have a consistency of anywhere from about 0.1% to 6% fiber on the weight of the suspension. When beaten pulps are used, the filler and retention agent may be added to the pulp suspension while it is of the consistency, generally about 3% to 5% or 6%, of the pulp during the beating operation. Thereafter, the aqueous system may be diluted with water to provide the desired consistency that is conventionally used during deposition, which may amount to from 0.01% to 0.5% fiber on total suspension weight. If desired, the pulp may be diluted approximately to the consistency at which the deposition is to be made and the pigment and retention agent thereafter added.

The amount of the filler may be from 1% to 50% by weight on the weight of fiber (based on dry weights) and the amount of retention agent may be from about 0.01% to 1% by weight thereof on the weight of the dry fiber. When large proportions of fillers are used, based on the weight of the paper fiber, it is preferable to employ an amount of retention agent between 0.1% and 1.0%, based on the weight of filler.

The conventional inert fillers or pigments may be used, such as clays, titanium dioxide, barytes, blanc fixe, talc, calcium carbonate, and also colored inorganic pigments (having the designated numbers which refer to the Color Index of the American Association of Textile Chemists and Colorists) such as Chrome Orange No. 21 (CI 77601) a basic lead chromate, Cadmium Yellow (CI 77199), basic zinc chromate (CI 77955), and precipitated iron oxide (CI 77492). In addition, organic fillers may be used such as Monastral Blue No. 15 (CI 74160) a copper phthalocyanine pigment, Pigment Blue No. 17 (CI 74200) a trisulfonated copper phthalocyanine, Pigment Green (CI 74255) octachlorocopper phthalocyanine, and Monoazo Pigment Red No. 18 (CI 12350).

The filler is in finely divided form and may be dispersed directly into the fiber suspension with the aid of a dispersing agent or by mere mechanical action, but it is preferably pasted in a small amount of water with from 0.01% to 1% on the weight of the filler of a dispersing agent. Typical dispersants are sodium hexametaphosphate, sodium tetrapolyphosphate, formaldehyde condensates of naphthalene sulfonates and the sodium salts of 50:50 mol ratio copolymers of maleic anhydride with styrene, diisobutylene and the like.

Any suitable pulps may be used for making the fibrous products including bleached and unbleached pulps. They may be sulfite, kraft, soda, semi-chemical, groundwood, rag pulp, rope pulp, jute pulp, and so on.

Where deposition on the acid side is desired, the fiber suspension may include alum or alum and rosin. When rosin is present, it is desirable that the alum be added before the retention agent. In this way, when rosin is used, a rosin-sized filled paper sheet may be obtained. Alternatively, the paper sheet may be surface-sized after it has been formed by the application of aqueous dispersions or emulsions of waxes, higher aliphatic ketene dimers, or the like.

In the examples which are illustrative of the invention, the parts and percentages given are by weight unless otherwise noted. The "brightness" values were determined by the measurement of light reflectance on a photovolt meter using a standard blue filter and a MgO plate as a basis of comparison, i.e., the MgO plate represents 100% reflectance.

Example A

(a) To 1650 grams of commercial diethylenetriamine was added gradually 1290 grams of methyl acrylate containing 40 grams of 25% sodium methoxide. The contents were stirred, and the temperature was allowed to get as high as 127° C. After six hours of refluxing, the temperature dropped down to 90° C. due to the liberated methanol. The methanol was then allowed to distill off at atmospheric pressure until the temperature of the condensate reached 110° C. This temperature was not exceeded. Removal of the remainder of the methanol was done under water-pump vacuum. There was obtained 538 grams of distillate from the above reactants.

The condensate was then treated with water to make up a 70% solids solution with a viscosity of Z4+ on the Gardner-Holdt scale or a 40% condensate solids solution having a viscosity of C. The pH of the 70% condensate solution was found to be 10.8.

(b) One hundred and seventy-two grams of the 70% condensate solution obtained in part (a) hereinabove was diluted further with 172 grams of water. To this solution at about 75° C. was added epichlorohydrin in small increments until the Gardner-Holdt viscosity was greater than Z. At this point, the solution was cooled with an ice bath and 50 grams of 25% H₂SO₄ was added to prevent gelation. The amount of epichlorohydrin used was 30.8 grams. The viscosity of this 26% resin solution was Z on the Gardner-Holdt scale. The resin was further diluted by the addition of 100 grams of water. The solution at 25% solids and 25° C. had a viscosity of 42 poises.

To 127.5 grams of the above solution was added 32 grams of 25% sulfuric acid to bring the pH down to 4.3 and the resin solids to 21%. The Gardner-Holdt viscosity was S+.

Example 1

A pulp was prepared by mixing into 2000 parts of a bleached sulfite pulp at 1% consistency and having a pH of 5.0 a Canadian freeness of 480 ml., 0.4 part of Chrome Orange (CI 77601) and diluting the pulp to 0.02% consistency. A control sheet was formed from a portion of this pulp. The sheet had a basis weight of 38 pounds (per 500 sheets of 24-inch by 36-inch). Drying was effected for two minutes at 200° F.

Other sheets of the same basis weight were formed from the same pulp except that 0.05% and 0.1% based on dry fiber weight of the product of part (b) of Example A was mixed into the pulp before sheeting. Whereas the control sheet was only lightly tinted, the other two sheets were strongly colored.

Example 2

The procedure of Example 1 was repeated except that 0.4 part of Monastral Blue (a copper phthalocyanine pigment) was used instead of the Chrome Orange. The control sheet had a light blue tint whereas the others were strongly colored.

Another sheet was similarly formed from a portion of the pulp containing no condensation product after adding 2% of papermakers' alum, based on weight of fiber. Still another sheet was formed from the pulp containing 2% alum and 0.05% of the condensation product of Example 1. The latter sheet had a much stronger coloration than that formed from alum above.

Example 3

The procedure of Example 1 was repeated using 2% Chrome Orange Pigment No. 21 (CI 77601) based on the weight of pulp solids. Sheets were prepared with and without the additive described in part (b) of Example A. The sheets had brightness values of:

Resin treatment:	Brightness, percent
Untreated	68
0.05% additive	50
0.10% additive	43

With this pigment, the lower the percentage of brightness, the better the retention of pigment.

Example 4

The procedure of Example 2 was repeated except the pulp was treated with 2% and 5% Monastral Blue. The depth of color of the sheets is shown by the following brightness values:

Resin Treatment	Percent Pigment	Percent Brightness
None	2	64
0.05%	2	55
0.10%	2	41
None	5	55
0.1%	5	49
0.3%	5	28
0.4%	5	16

Example 5

A bleached sulfite pulp (2.5% consistency) was beaten to a 480 ml. Canadian freeness and then treated with 5% Titanox RA-50 (rutile TiO_2) based on fiber.

Sheets were made at a pH 5.0 (H_2SO_4) without an additive and also containing 0.05% to 0.1% of the product of part (b) of Example A. The treated sheets had a higher wet and dry opacity as well as higher ash content as shown in the following table:

Resin Treatment	Opacity		Percent Ash
	Dry	Wet	
None	77	55	1.3
0.05%	82	64	
0.10% polymer	85	70	3.7

Higher values of opacity in this case indicate better pigment retention.

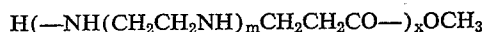
Example 6

The procedure of Example 1 was repeated except that the pulp slurry was adjusted to pH 9.0 with sodium hydroxide. Sheets were prepared with both the Chrome Orange inorganic pigment and the Monastral Blue organic pigment.

The control sheets had a very light tint whereas the sheets containing 0.1% of the product (b) of Example A had a deep color strength.

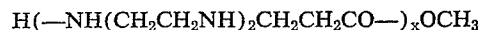
I claim:

1. A process for making filled papers and the like which comprises depositing on a foraminous forming surface an aqueous suspension of cellulose fibers and a water-insoluble inorganic filler, said suspension having a pH between about 3 and 12 and containing 0.01 to 0.5% fibers based on the total suspension weight and containing dissolved therein about 0.01 to 1% by weight, based on the weight of fiber, of a water-soluble reaction product of (1) epichlorohydrin with (2) a condensation product of methyl acrylate and a polyethylene-polyamine in a mol ratio of about 1:1 comprising a compound of the formula



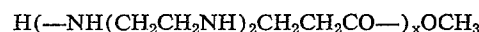
in which m is an integer having a value of 2 to 4, and x has an average value such as to provide an average molecular weight of about 300 to 1,000, the ratio of the epichlorohydrin to the condensation product being 0.2 mol to m mol of the former to each mol of polyamine used in making the condensation product, and the reaction product having a viscosity of about 3 to about 45 poises at a concentration of 25% in water at 25° C.

2. A process for making filled papers and the like which comprises depositing on a foraminous forming surface an aqueous suspension of cellulose fibers and a water-insoluble organic filler, said suspension having a pH between about 3 and 12 and containing 0.01 to 0.5% fibers on the total suspension weight and containing dissolved therein about 0.01 to 1% by weight, based on the weight of fiber, of a water-soluble reaction product of (1) epichlorohydrin with (2) a condensation product of methyl acrylate and diethylenetriamine in a mol ratio of about 1:1 and having the formula



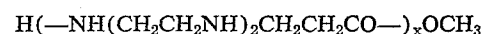
in which x has an average value to provide an average molecular weight of about 300 to 1,000, the ratio of the epichlorohydrin to the condensation product being 0.2 mol to 2 mol of the former to each mol of the original polyamine, the reaction product having a viscosity of about 3 to about 45 poises at a concentration of 25% in water at 25° C.

3. A process for making filled papers and the like which comprises depositing on a foraminous forming surface an aqueous suspension of cellulose fibers and a water-insoluble organic filler, said suspension having a pH between about 3 and 12 and containing 0.01 to 0.5% fibers on the total suspension weight and containing dissolved therein about 0.01 to 1% by weight, based on the weight of fiber, of a water-soluble reaction product of (1) epichlorohydrin with (2) a condensation product of methyl acrylate and diethylenetriamine in a mol ratio of about 1:1 and having the formula



in which x has an average value to provide an average molecular weight of about 300 to 1,000, the ratio of epichlorohydrin to the condensation product being 0.9 mol to 1.5 mol of the former to each mol of original polyamine, and the reaction product having a viscosity of about 3 to about 45 poises at a concentration of 25% in water at 25° C.

4. A process for making filled papers and the like which comprises depositing on a foraminous forming surface an aqueous suspension of cellulose fibers and a water-insoluble organic filler, said suspension having a pH between about 3 and 12 and containing 0.01 to 0.5% fibers based on the total suspension weight and containing dissolved therein about 0.01 to 1% by weight, based on the weight of fiber, of a water-soluble reaction product of (1) epichlorohydrin with (2) a condensation product of methyl acrylate and diethylenetriamine in a mol ratio of about 1:1 and having the formula



in which x has an average value to provide an average molecular weight of about 300 to 1,000, the ratio of the epichlorohydrin to the condensation product being 0.2 mol to 0.7 mol of the former to each mole of the original polyamine, and the reaction product having a viscosity of about 5 to about 6 poises at a concentration of 25% in water at 25° C. 5

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