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AQUEOUS CATIONIC EMULSIONS OF PAPER-SIZING ISOCYANATES AND MANUFACTURE OF PAPER THEREWITH

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ABSTRACT OF THE DISCLOSURE

In the manufacture of sized paper wherein a paper-sizing isocyanate and a cationic resin are deposited on cellulose paper-making fibers from aqueous medium, the tendency of the cationic resin to decrease the sizing action of the isocyanate is partially or completely counteracted by depositing on the fibers, prior to the point at which they are dried, a hydrophobic organic acyl compound of acidic character having a melting point below 90° C.

The present invention relates to improved cationic emulsions of hydrophobic organic isocyanates useful as sizing agents in the manufacture of paper, to the manufacture of sized paper by the use of the emulsions (or by use of the components separately), and to the resuling paper.

It is known that sized paper can be manufactured by forming an aqueous emulsion of a hydrophobic organic isocyanate in aqueous medium containing a water-soluble cationic resin, adding the emulsion to a dilute aqueous suspension of cellulose paper-making fibers (a "pulp"), and then processing the pulp into paper in the usual way. The cationic resin acts as depositing agent for the isocyanate, greatly simplifying application of the isocyanate to the fibers.

The isocyanate develops its sizing properties when the water-laid web is dried to form paper; cf. Arlt U.S. Patent No. 3,084,092. The isocyanate reacts with the cellulose, forming a cellulose urethane derivative which is very hydrophobic.

The reaction goes to substantial completion in less than a minute at 200° F. even in the absence of a catalyst, and thus permits "on the machine" sizing.

A recently-observed disadvantage of the process is that the cationic resin causes the natural sizing action of the isocyanate to decrease, often by 50% or more, presumably due to reaction of a part of the isocyanate with the cationic resin during the drying step, so that less of the hydrophobic cellulose urethane derivative is formed per unit weight of isocyanate employed than would otherwise be the case.

The discovery has now been made that this decrease in sizing is partially, and if desired, substantially completely counteracted when there is deposited on the fibers, at any point prior to the drying step, a hydrophobic organic acyl compound of acidic character in highly particulate state. We have further found that aqueous cationic emulsions of hydrophobic organic isocyanates having a content of an emulsified hydrophobic acyl compound of acidic character are of improved effectiveness, due to the latent protective action of the acyl compound therein.

We have still further found that, in the paper-making process, it is unnecessary to employ the aforesaid tri-component emulsion to obtain the benefits of the present discovery, but that the benefits of the present invention are realized when the isocyanate size and the acyl compound are deposited separately or consecutively on the fibers.

Since the hydrophobic acids are of comparatively little effectiveness as sizing agents for paper and are likewise of comparatively little effectiveness on the sizing imparted by paper-sizing isocyanates, it was unexpected and surprising to find that these and other acyl compounds of acidic character, when applied to cellulose fibers in conjunction with paper-sizing isocyanates and water-soluble cationic resins, act powerfully to counteract the inhibitory effect which the cationic resins exert on the development of sizing by the aforementioned isocyanates.

Evidently, when the wet fibers which carry the isocyanate, the cationic size, and an acyl compound of acidic character are heated so as to dry the fibers at a temperature above the reaction point of the isocyanate (150°–200° F.), the acyl compound reacts with at least part of the cationic resin before the isocyanate can do so, thereby diminishing the effect of the cationic resin on the reaction of the isocyanate with cellulose. As a consequence, presumably a larger proportion of the isocyanate reacts with the cellulose than would otherwise be the case. The acyl compound thus inhibits a reaction between the isocyanate and the cationic resin and acts as latent inactivating agent for the cationic resin; the acyl compound thus forces the isocyanate to react preferentially with the cellulose.

The emulsions of the present invention consist essentially of a hydrophobic paper-sizing isocyanate and the hydrophobic organic acyl compound as the dispersed phase, and an aqueous phase containing the water-soluble cationic resin which acts as depositing agent for the isocyanate and the acyl compound.

The class of paper-sizing isocyanates (including polyisocyanates) is generally known. Members are disclosed in the Arlt patent and in British Patent No. 804,504. They are typically liquid or low melting point solids which are insoluble in water. The long chain isocyanates, for example, hexadecyl and octadecyl isocyanates and the alkaryl isocyanates, for example, hexylphenyl isocyanate, and dodecylphenyl isocyanate are preferred because of their low cost, the ease with which they can be prepared, and the very satisfactory sizing properties which they impart.

The hydrophobic acyl compounds of acidic character referred to above are those which have melting points below about 90° C. (and preferably below 75° C.) so that they are fluids (and preferably mobile fluids) when the fibers on which they are deposited are dried at about 200° F. or higher. They contain a CO—C—C grouping, and either are acids or are compounds which decompose to acids when used in papermaking, as described herein. Preferably they are the higher fatty acids (i.e., the fatty acids which contain 12 carbon atoms or more), and the anhydrides, the acid chlorides, and the ketene dimers which derive from these acids. The preferred compounds in this group are those which are substantially insoluble, which are substantially straight chain in configuration. Other suitable acyl compounds are the water-soluble soaps of the above; these soaps form water-insoluble reaction products with the cationic resin when dried at normal paper-drying temperatures.

Illustrative suitable preferred hydrophobic acyl compounds are stearic acid, distearic anhydride, octadecanoyl chloride, rosin containing a melting point depressant, and hexadecyl ketene dimer, lauric acid, palmitic acid, arachidic acid, their anhydrides, and acid chlorides, as well as mixtures thereof. These compounds, when in molten state, are compatible with hydrophobic isocyanates in liquid state, and do not detract from the sizing imparted by these isocyanates.

Unsaturated hydrophobic acids (for example, oleic acid and castor oil fatty acids) and the acyl chlorides may be used, but these materials in general are less efficient than the saturated fatty acids.

The cationic polymers which are present in the emulsions as depositing agents are water-soluble, and may be of the thermosetting and non-thermosetting types. Illustrative suitable cationic polymers include polyethylenimine and polyvinyl amine; the hydrophilic melamine-formaldehyde acid colloid of U.S. Patent No. 2,345,543; the melamine- and urea-formaldehyde polyalkylenepolyamine resins of U.S. Patents Nos. 2,657,132 and 2,796,362; and the polyalkylenepolyamine-epichlorohydrin resins of U.S. Patents 2,563,897; 2,595,935; 2,601,597; 2,926,154; 3,248,353 and 3,258,393 and French Patent No. 1,389,389. Cationic starch and chitosan are cationic polymers and are particularly well suited for use as depositing agent in emulsions of the present invention.

The compositions of the present invention may contain supplementary cationic, anionic and non-ionic emulsifying agents for the isocyanate and hydrophobic acyl components, as well as emulsion stabilizers and protective colloids. In addition, the emulsions may contain materials customarily employed in the manufacture of paper which are not incompatible with the components of the emulsions. The emulsions may thus contain starch and mannolactan gums as dry-strength agents; neutral fillers and extenders; pigments and dyes; supplementary sizing agents as for example wax size; scents; hydrophobic, cyclic compounds as for example rosin esters and mold growth inhibitors and germicides.

The amount of cationic resin present in the emulsion should be at least sufficient to deposit an effective amount of the sizing solids (isocyanate plus acyl compound) on the fibers. In general, a preferred amount of cationic resin is present when the emulsified particles are strongly cationic, as determined by a cataphoresis cell.

The optimum ratio of hydrophobic acyl compound of acid character in the emulsion to the cationic agent depositing resin (and any other cationic material which may be present) is not constant. The ratio in manner not yet predicted varies with the cationic strength of the cationic resin, the comparative ease with which the cationic resin reacts with hydrophobic acyl compounds, the carboxylic (anionic) strength of the acyl compound, the rapidity with which the particular acyl compound reacts with cationic centers, the anionic strength of the acyl compound, and perhaps other factors. In any instance, however, a suitable amount of the hydrophobic acyl compound (or the optimum amount) can be found by making a series of laboratory trials. As shown in the examples below, the preferred amount in any instance is that amount of hydrophobic acyl compound which causes the best improvement in sizing without requiring a significant lengthening of the drying time or significant an increase in the temperature at which the paper is dried.

There appears to be not threshold as we have found that even a very minor amount of the hydrophobic acyl compound causes a detectable improvement.

The emulsions of the present invention can be prepared in any of the ways in which cationic emulsions of hydrophobic organic materials have been prepared in the past. Emulsions possessing heat-sizing properties, however, are prepared by separately emulsifying the isocyanate and the acyl compound, and mixing the two emulsions. This method permits the temperature of the isocyanate to be held to a minimum during emulsification thereby minimizing the amount of hydrolysis which is undergoes during the operation. According to this preferred method, the isocyanate can usually be emulsified in a suitable aqueous medium at or slightly above room temperature; usually hot aqueous medium will be required to emulsify the acyl compond. After the initial emulsification it is advantageous to homogenize the emulsion hot, and then to cool it rapidly below the melting point of the acyl compound.

The aqueous media, in which the emulsifications are performed may be non-ionic, in which event sufficient of a water-soluble cationic resin must be added later to render the dispersed phase cellulose-substantive. Preferably the components are emulsified in the presence of water-soluble cationic resin as such resins act to some extent as emulsifying agents and thereby decrease the amount of emulsifying agent that would otherwise be required. If desired, one component may be emulsified in non-ionic medium and the other component may be emulsified in cationic medium. If further desired, the acyl compound can be emulsified in water containing autogenously formed soap, whereby an anionic emulsion is formed. Such emulsion is readily deposited on the fibers by the action of previously added cationic resin.

The emulsions are prepared at any convenient solids content. In general, they are prepared in the range of 6%–15% solids, and before use they are advantageously diluted to 1%–5% solids by addition of water.

In the present application, the term "emulsion" is used in its usual industrial sense to designate an aqueous substantially non-creaming dispersion of dispersed hydrophobic material. In such dispersions the hydrophobic material may be in liquid or solid state. The water-soluble cationic resins may be classically water-soluble or may be in water-soluble colloid form, described in U.S. Patent 2,345,543.

As non-ionic emulsifying agents there may be used, for example, the higher ethylene oxide adducts of t-butylphenol (Triton X–100), alkyl aryl polyethylene glycol ether (Surfonic N–95), and polyoxyethylene thioether (Adsee 85).

The invention does not depend upon the method by which the emulsified hydrophobic organic acyl compound is deposited on the fibers. Any method may be used which deposits a sufficient amount of a suitable organic acyl compound uniformly on the fibers while the fibers are in ambient aqueous medium, i.e., before the fibers are dried.

If desired, the acyl compound, the isocyanate size and the cationic resin which acts as depositing agent for the first two components can be added as a unitary cationic emulsion, such as is described above. The dispersed material, being strongly cationic, is rapidly deposited on the normally anionic fibers by electrostatic attraction. Such emulsion may be and is advantageously added close to the wire, for example, at the fan pump.

Another method is to add the hydrophobic isocyanate to the fibrous paper-making suspension as a cationic emulsion and then to add the hydrophobic acyl compound as an anionic emulsion. The cationic isocyanate particles or droplets deposit themselves uniformly and automatically on the fibers by reason of the opposite electrostatic charge of the fibers, and the anionic particles of the hydrophobic acyl compound deposit themselves uniformly on the fibers because of the cationic sites introduced by the cationic resin. In this method the cationic emulsion may be introduced into the discharge from the beater (or refiner), and the anionic emulsion may be added at the fan pump.

Another method proceeds as described above, except that the order is reversed in which the dispersions are added to the pulp.

According to another method the two dispersions are added as separate streams to the pulp at the fan pump.

According to still another method a cationic emulsion of a hydrophobic acyl compound and a cationic emulsion of a hydrophobic isocyanate are added separately to the the pulp.

Moreover, the above-described emulsions can be applied by the tub method, i.e., as a spray to or by impregnation of preformed cellulosic web, provided they are added while the fibers are still wet with the aqueous medium. The acyl compound can thus be applied by a convenient method to the wet web at any point between the wire and the point at which the temperature of the wet web rises above about 200° F.

According to an additional method the cationic isocyanate emulsion is added at or upstream from the fan pump, and the fatty acid is deposited on the fibers by spraying the wet web, prior to the drying step, with an aqueous cationic, non-ionic or anionic emulsion of the acyl compound. While the particles of the fatty acid are well retained by the filtering action of the fibers, they exert less of a counteracting effect than when they are added to the pulp.

The pH of the paper-making fibrous suspension during and after addition of the hydrophobic acid should be sufficiently low that saponification of the acid (i.e., conversion of the acid to a soap) does not occur to any significant extent prior to the drying step. Any pH in the range of 4–9 may be used with beneficial results. In general, best sizing and sheet properties are obtained at pH 6–7, and lower and higher pH conditions are employed when wet-strength resins or dry-strength resins or other factors which require such values are present.

The following examples are best embodiments of the invention known to the inventors. They are illustrations, and the claims are not to be construed as limited thereto.

EXAMPLE 1

The following illustrates the effect of several water-insoluble hydrophobic organic acyl compounds applied in an anionic emulsion in overcoming the decrease caused by cationic resins on the sizing imparted by octadecyl isocyanate.

An aqueous cationic organic isocyanate emulsion is prepared by slowly adding with vigorous agitation 16 g. of octadecyl isocyanate to 150 g. of water at 50° C. (to promote most rapid emulsification) containing 3.0 g. of a water-soluble cationic starch (Cato 8) and 0.4 g. of sodium lignosulfonate as dispersants. The mixture is homogenized for 90 seconds to decrease the particle size of the octadecyl isocyanate to about 1–2μ, after which the resulting emulsion is rapidly cooled to 20° C. and diluted to 0.5% solids by addition of water.

A stearic acid emulsion is prepared by rapidly agitating 10 g. of a hydrophobic organic acyl compound with 90 g. of water at 90° C. containing 1.0 g. of gum ghatti and 0.3 g. of sodium lignosulfonate, homogenizing the resulting crude anionic emulsion, and rapidly cooling the product to 20° C.

Aliquots are taken from an aqueous suspension composed of a 50:50 mixture of bleached hardwood kraft and bleached softwood kraft fibers at 0.6% consistency and pH 6.

To each is separately added sufficient of the isocyanate emulsion, sufficient of the water-soluble cationic wet-strength 1:1:0.9 molar ratio adipic acid:diethylenetriamine:epichlorohydrin resin of Keim U.S. Patent No. 2,926,154 and sufficient of the stearic acid emulsion to provide the amounts of each of the materials shown in the table.

The aliquots are gently agitated for a minute after each addition, after which handsheets are prepared at a basis weight of 100 lb. per 25" x 40"/500 ream. The

handsheets are dried for 1.5 minutes on a rotary laboratory drum drier having a drum temperature of 230° F.

The sizing of the handsheets is determined by application thereto of hot (100° F.) 20% aqueous lactic acid solution by penescope under a 12"-head; the amount of sizing is the number of seconds required for the acidic solution to penetrate the sheets.

Results are as follows, and are shown in comparison with control sheet A (prepared by impregnating 100 lb. basis weight waterleaf handsheet of the same fibers with a 0.20% solution of octadecyl isocyanate in benzene, air drying the sheet, and then drum-drying the sheets as described), and control sheet B is prepared in the same manner except that the paper used contains 0.20% by weight of the wet-strength resin. The control sheets show the ultimate sizing imparted by octadecyl isocyanate in the absence and in the presence of the cationic resin.

Run	Percent[1] OI[2]	Percent cationic polymer	Percent stearic acid	Percent total size solids	Sizing Secs.	Percent Change[3]
Control A	0.20	None	None	0.2	10,650	Control
Control B	0.20	0.20	None	0.2	2,500	−75.6
1	0.18	0.20	0.02	0.2	5,600	−47.3
2	0.16	0.20	0.04	0.2	10,120	−4.6
3	0.14	0.20	0.06	0.2	8,750	−17.8

[1] Based on dry weight of fibers.

[2] Octadecyl isocyanate.

[3] Percent of decrease resulting from presence of cationic polymer which is overcome by action of the hydrophobic acyl compound.

Comparison of runs A and B with run 2 shows that the adverse effect of the cationic resin (run B) was virtually completely overcome by the acyl compound, and that use of the acyl compound permitted the amount of octadecyl isocyanate to be decreased by 25% without significant detriment to the amount of sizing obtained.

EXAMPLE 2

The following illustrates the preparation and utilization of a single emulsion containing an isocyanate size, a cationic resin as depositing agent for the size, and a crude higher fatty acid mixture as agent inhibiting degradation of the sizing effective of the isocyanate by the cationic resin.

An aqueous emulsion of octadecyl isocyanate is prepared by pouring 100 g. of octadecyl isocyanate with vigorous agitation into 1000 cc. of water at 50° C. containing 30 g. of a water-soluble cationic starch (Cato 8) and 4 g. of sodium lignosulfonate. The resulting crude emulsion is given one pass through a laboratory homogenizer at 3000 lbs. per square inch and is immediately cooled to 20° C. The product is a cationic emulsion wherein the octadecyl isocyanate particles are approximately 1–2μ in diameter.

An emulsion of mixed fatty acids is prepared by running 50 g. of molten tall oil fatty acids (a mixture of stearic and palmitic acids as recovered from the tall oil manufacturing process) into 1000 cc. of water at 80° C. containing 30 g. of a water-soluble cationic starch (Cato 8) and 4 g. of sodium lignosulfonate. The resulting emulsion is cationic, and is homogenized and chilled in the same manner as the first emulsion.

A unitary sizing emulsion is prepared by mixing two parts by weight of the first emulsion with one part by weight of the second emulsion and two parts by weight of a 10% solution of the wet-strength resin of Example 1.

The above emulsion is employed in the manufacture of sized paper by forming an aqueous suspension of cellulose paper-making fibers at a consistency of 0.6% and a pH of 6.0, adding sufficient of the emulsion to the suspension to provide 0.2% of octadecyl isocyanate based on the dry weight of the fibers, gently stirring the suspension, sheeting the suspension to form 100 lb. basis weight (25″ x 40″/500 ream) handsheets and drying the handsheets for 1 minute on a laboratory drum drier having a drum temperature of 230° F. The components of the emulsion are deposited on the fibers substantially simultaneously. Hard sizing is obtained.

Improved sizing is also obtained when water-leaf handsheets are impregnated with the above emulsion diluted with water to an octadecyl isocyanate content of 0.2% by weight, followed by drying of the handsheets as is described above.

EXAMPLE 3

An emulsion of octadecyl isocyanate in the melamine-formaldehyde acid colloid solution of U.S. Patent No. 2,345,543 is prepared by emulsifying 10 g. of octadecyl isocyanate in 100 cc. of water at 50° containing 0.2 g. of the ethylene oxide adduct of tertiary butylphenol (Triton X–100) as non-ionic emulsifying agent and mixing the product with 100 cc. of the melamine-formaldehyde acid colloid solution prepared by dissolving 12 g. of a spray-dried trimethylol-melamine powder in 88 cc. of water containing 0.8 mol of HCl per mol of melamine and aging the resulting solution for 16 hours at room temperature.

The resulting emulsion is divided in two. To one portion is added 20 g. of a 5% by weight cationic emulsion of stearic acid made as described in Example 2. The second portion is left untreated.

The two emulsions are employed as beater additives in the manufacture of paper as shown in Example 1 in such proportions as to supply 0.2% of sizing solids (octadecyl isocyanate alone or with stearic acid when present) to the furnish based on the dry weight of the fibers.

The emulsion containing octadecyl isocyanate plus stearic acid as the sizing solids provides 6,500 seconds of lactic acid resistance whereas the emulsion containing octadecyl isocyanate as the sole sizing solid gives only 4,250 seconds of lactic acid resistance.

EXAMPLE 4

The foregoing procedure is repeated except that the melamine-formaldehyde acid colloid solution is replaced by an equal weight of the urea-formaldehyde tetraethylenepentamine cationic wet-strength resin of Daniel et al. U.S. Patent No. 2,657,132. The stearic acid likewise causes an improvement in the amount of sizing which is developed.

EXAMPLE 5

The following illustrates the process of the present invention, wherein the isocyanate is added as a cationic emulsion, and the acyl compound is added as an anionic emulsion.

An aqueous cationic emulsion of octadecyl isocyanate is prepared by the method of Example 1. To the emulsion is added 2 g. of a 50% by weight solution of polyethylenimine to increase its cationic density. An aqueous anionic emulsion of hexadecyl ketene dimer is prepared by emulsifying 10 g. of the ketene dimer in 90 g. of water at 90° C. containing 0.5 g. of sodium lignosulfonate and 0.5 g. of sodium stearate. The resulting emulsion is homogenized hot and then rapidly chilled.

To an aqueous suspension of cellulose paper-making fibers at pH 6–7 are added first sufficient of the isocyanate emulsion to provide 0.2% of the isocyanate based on the dry weight of the fibers. The suspension is stirred for a few moments to permit deposition of the isocyanate on the fibers to go to substantial completion, after which sufficient of the ketene dimer emulsion is added to provide to provide 0.5% of ketene dimer based on the dry weight of the fibers, after which the pulp is formed into handsheets which are dried for 5 minutes in an oven at 100° C. Hard sized paper is obtained.

EXAMPLE 6

The following illustrates the effect of a hydrophobic ketene dimer in substantially overcoming the detrimental effect of a cationic resin on the sizing action of octadecyl isocyanate.

The procedure of Example 1 is repeated except that stearic acid is replaced by hexadecyl ketene dimer, and the amounts employed are as shown below.

Results are as follows:

Run	Percent OI	Percent cation, polymer	Percent ketene dimer	Percent total size solids	Sizing secs.
Control A	0. 2	None	None	0. 2	>7, 200
Control B	0. 2	0. 3	None	0. 2	5, 100
1	0. 16	0. 3	0. 04	0. 2	>7, 200

EXAMPLE 7

A wet handsheet corresponding to control handsheet B of Example 6 (before drying) is sprayed by atomizer with a 1% aqueous anionic emulsion of stearic anhydride in an amount estimated to provide 0.04% of stearic anhydride on the weight of the fibers. The handsheet is dried and tested as described in Example 1 and has a sizing value of >7,200 seconds.

We claim:

1. An aqueous cationic emulsion consisting essentially of a hydrophobic paper-sizing isocyanate containing a water-soluble cationic resin in the aqueous phase and an effective amount in emulsified state of a hydrophobic organic acyl compound of acidic character having a melting point below 90° C. as latent inactivating agent for said cationic resin.

2. An emulsion according to claim **1** wherein the isocyanate is octadecyl isocyanate and the cationic resin is a polyamine-epichlorohydrin resin.

3. An emulsion according to claim **1** wherein the hydrophobic acyl compound is stearic acid.

4. An emulsion according to claim **1** wherein the hydrophobic organic acyl compound is hexadecyl ketene dimer.

5. An emulsion according to claim **1** wherein the emulsified hydrophobic organic acyl compound has an average particle size of less than 5μ.

6. In the manufacture of sized paper wherein a hydrophobic organic paper-sizing isocyanate and a water-soluble cationic resin as depositing agent for said isocyanate are deposited from aqueous medium on wet cellulose fibers and said fibers are dried at a temperature above 200° F., the improvement which comprises depositing in emulsified state at pH 4–9 on said wet fibers a hydrophobic organic acyl compound of acidic character having a melting point below 90° C. as latent inactivating agent for said cationic resin.

7. A process according to claim **6** wherein the isocyanate, the cationic resin, and the hydrophobic organic acyl compound are deposited on said fibers substantially simultaneously.

8. A process according to claim **6** wherein the isocyanate, the cationic resin, and the hydrophobic organic acyl compound are deposited on the fibers while said fibers are in aqueous suspension by addition of an emulsion of the isocyanate containing the cationic resin to an aqueous suspension of cellulose paper-making fibers, followed by addition of said hydrophobic acyl compound of acidic character in anionic emulsified state to said suspension of fibers.

9. A process according to claim **6** wherein the pH of the aqueous medium is between about 6 and 7.

10. Paper manufactured by a process according to claim **6**.

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