United States Patent

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[54] **METHOD OF WATERPROOFING PAPER USING AN N'-ALKYL, N1N1'-ALKYLENE-N,N1-BIS-UREA**
3 Claims, No Drawings

[52] **U.S. Cl.** **162/158,** 8/116.2
[51] **Int. Cl.** **D21h 3/02**
[50] **Field of Search** ..... 162/164, 168, 158; 8/116.2; 260/239 E, 239 R

[56] **References Cited**

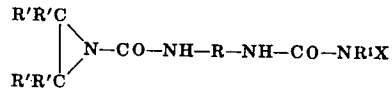
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ABSTRACT: Aqueous paper sizing compositions are prepared by combining an N'-alkyl,N-substituted urea containing an isocyanate group with an alpha, beta-alkylenimine to form an

(N'-alkyl),(N_1N$_1$'-alkylene)-N,N_1-bis-urea of the formula Formula I



which is in situ, or subsequently, with the aid of an emulsifying agent dispersed in water. In the formula each R'is a group such as hydrogen, methyl or ethyl, which are independently selected and which contain from zero to not more than two carbon atoms. R is generally a divalent organic radical, namely an arylene, alkylarylene, arylalkylene, cycloalkylene, or alkylene radical, which may or may not contain ethylenic double bonds. $R_1$is alkyl, alkenyl, aralkyl, alkylaryl, cycloalkyl or cycloalkenyl and X is independently selected from the same groups or is aryl or hydrogen. The carbon atoms of R, R_1 and X combined should total at least eight and preferably not more than 52 carbon atoms.

METHOD OF WATERPROOFING PAPER USING AN N'-ALKYL, N1'N1'-ALKYLENE-N,N1-BIS-UREA

DESCRIPTION OF INVENTION

The present invention relates to production and use of novel waterproofing and sizing compounds, particularly useful in application to paper and paper pulp, derived by the reaction of alkyl-urea substituted isocyanates and alpha, beta-alkylenimines to form (N'-alkyl), (N_1', N_1'-alkylene)-N,N_1-bis-urea complexes which will chemically react with cellulosic fibers of paper or textiles.

It is a primary object of the present invention to provide novel paper sizing compounds which will render the paper resistant to water as such or to aqueous compositions, such as ink, fruit juices, milk, blood, beverages and the like.

Another object is to provide a novel paper size which may be used in internal or beater sizing, where the sizing compositions are added to the paper pulp in the beater of the paper making system, prior to the forming of the paper web, in contrast to the external or surface sizing process, where a sizing composition is applied to the surface of an already formed paper.

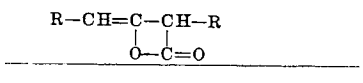
A further object is to provide a novel paper size which is superior to rosin and does not require an acid pH with addition of alum to precipitate the size on the pulp for physical adherences, which acid sizing results in paper, impaired in its aging properties and also unsuitable for many purposes on account of its undesired stiffness and brittleness, and which is for sizing under neutral or alkaline conditions.

A still further object is to prepare a novel paper size which is stable in aqueous environment, by being not substantially or highly reactive toward water with low-shelf life, and the aqueous compositions of which do not require acid resistant materials for drums, bulk storage containers and the equipment for feeding continuously to the head box of paper making machines.

Still further objects and advantages will appear in the more detailed description set forth below, it being understood, however, that this more detailed description is given by way of illustration and explanation only and not by way of limitation, since various changes therein may be made by those skilled in the art without departing from the scope and spirit of the present invention.

Alkylketene dimers used as reactive paper sizes are not satisfactory. These dimers of the formula

FORMULA II



while being reactive to cellulose, are also reactive to water. This is detrimental to their storage life which is limited for aqueous emulsions to 1 month at a storage temperature of 75° F., a temperature requiring refrigerated store rooms during the summer. In an effort to achieve more stability, the alkylketene dimer emulsions are made slightly acidic, to minimize loss of efficiency due to hydrolysis. However, this acidic reaction causes metal corrosion and requires the use of acid resistant materials.

Furthermore, sizing with these dimers requires, for optimal performance, low-temperatures and an acid pH during the wet stages of the paper making process and an alkaline pH and temperatures of about 200° F. for several minutes for curing the size on the dry paper. The low-temperature required during the wet stage of the processing, including the drying of the paper web, results in prolonged drying times, a condition which is not compatible with high-speed processing, as demanded by present day manufacturing requirements.

The isocyanate-alkylenimine derived sizes of the present invention are stable products, the aqueous emulsions of which are shelf-stable products and suitable for use under neutral and alkaline conditions and are substantially free from the above cited disadvantages of the alkylketene dimer sizing agents. Using them provides a simple and effective process of sizing paper by their addition to the paper pulp prior or during the paper forming.

The isocyanate-alkylenimine derived sizes of the present invention are characterized in that they carry as one effective principle a long chain alkyl group attached to the isocyanate reactant. A further characteristic is that this long chain alkyl group is attached to the isocyanate in the form of an alkylurea group, so that an alkylurea substituted isocyanate of the form

FORMULA III $XR_1N—CO—NH—R—NCO$

is the general isocyanate to be reacted with an alpha,beta-alkylenimine to form the size composition of this invention, where R, R_1 and X are the same as in formula I.

The term alkylurea is intended to include the various compounds referred to in the definition of R_1 and X and Formula III which are obtainable by a reaction between a primary or secondary amine with a diisocyanate, as described below, or, less desirably a triisocyanate, by partial reaction with primary or secondary amines.

Representative of such isocyanates, having an isocyanate functionality of at least and preferably two are phenylenediisocyanates, substituted phenylenediisocyanates, including the preferred tolylenediisocyanates, naphathalenediisocyanates, methylene-bis (4-phenylisocyanate) and its substituted derivatives, benzidinediisocyanates and derivatives, triphenylmethanetriisocyanates and derivatives; diisocyanates and triisocyanates, in which two benzene rings are joined through an ether, thioether, sulfone or carbamide group can also be used. Other useful isocyanates are the aliphatic or cycloaliphatic hexamethylenediisocyanate, cyclohexylenediisocyanate, 2,2,4-trimethylhexanediisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate, the so-called DDI-diisocyanates, as produced by General Mills, Inc., as derivatives of the "Dimer Acids" obtained by Diels-Alder condensation of linseed oil fatty acids and unsaturated fatty acids.

While all the polyisocyanates cited and also others, as e.g. the polymethyl polyphenyl isocyanates of functionality two to three are useful for the production of alkylurea substituted isocyanates, the preferred polyisocyanates are those having isocyanato functionality of two, and of these the most desirable the tolylenediisocyanates, of which the 2,4 and the 2,6-isomers, as well as their mixtures with each other, are commercially available. Besides being in most abundant supply, they are the most economical diisocyanates with the further attraction that each of their isocyanate groups has a specific reactivity. It is this characteristic which recommends the tolylenediisocyanates for preferred use in the present invention.

Generally, on partial and selective reaction of a diisocyanate with an amine to form the corresponding urea substituted monoisocyanate, its yield will be diminished by the unavoidable formation of more or less bis-urea. When using equimolecular quantities of diisocyanate and amine, the formation of bis-urea will have as its consequence, that an amount of diisocyanate, equal to the amount of bis-urea formed, remains unreacted. Optimal yields of monourea substituted isocyanate, on reaction of a diisocyanate with a given amount of amine will be obtained

1. the larger the excess of diisocyanate over amine employed, and
2. the wider the spread in reactivity of the isocyanate groups towards amine.

The first expediency, if an essentially pure urea substituted isocyanate is desired, requires its isolation, preferably by recovery of the excess unreacted diisocyanate. The second condition, however, if sufficiently met, leads to optimal yield without further ado, when using equimolecular quantities of diisocyanate and amine.

When using tolylenediisocyanate, the condition of difference of reactivity between the two isocyanate groups towards amine is decidedly met by the faster reaction rate of the 4-isocyanate group in the 2,4-isomer, and sufficiently in the 2,6-isomer, where both of them have, initially, the same reactivity, but after reaction of one of them, the remaining one is deactivated to a diminished reactivity. Hence, both commercial tolylenediisocyanates, the 2,4-isomer and the 2,6-isomer as well as their mixtures are well suited for the efficient production of alkylurea substituted isocyanates without substantial formation of unwanted byproducts.

The alpha,beta-alkylenimines to be reacted with the alkylurea substituted tolyulisocyanates to produce the sizing compositions of this invention are, according to definition, ethylenimine and its C-substituted homologues. For the purpose of this invention, the number of carbon atoms contained in the alkylenimines may be limited to four, so that besides the ethylenimine only its monomethyl, monoethyl and dimethyl substituted derivatives, as well as propylenimine, 1,2 and 2,3-butylenimines and 1,2-dimethylethylenimine, all of which still contain a hydrogen atom, bound to nitrogen, are to be included. Of these, the preferred imines are ethylenimine and propylenimine.

The purpose of the presence of the imine group in the sizing compositions is to provide a group which is capable of reaction with the cellulose of paper or textile fibers, for permanent attachment of the hydrophobic principle, in the form of the long chain alkyl group, incorporated in the sizing composition by way of urea substitution.

The reaction of the tolylenediisocyanates leading to the urea substituted isocyanates and, finally, to the production of the sizing agents proper, may be carried out as follows:

For the first reaction, a tolylenediisocyanate is reacted with a primary or secondary amine, containing a long chain group, in the presence of an organic solvent, preferably of a low-boiling point, and inert to isocyanate.

The subsequent reaction of the resulting isocyanate with ethylenimine will take place in the solution of the first reaction, by adding it to the ethylenimine or vice versa, and the sizing agent formed may be isolated by either crystallization and filtration or boiling off the solvent, if necessary in vacuo.

Inasmuch as the most advantageous application of the sizing agents will be from aqueous emulsion, it has been found advantageous also in the preparation of emulsions to effect the latter reaction of the isocyanate with the imine also in an aqueous medium, containing an emulsifying system. A suitable emulsifying system may contain nonionic surface-active agents of the ethylenoxide condensate type. Of these the sorbitan-monofatty ester polyethylenoxide condensates, known under the trade names "Tween" and "Span" and sold by Atlas Chemical Industries, are suitable.

Suitable emulsions of the paper sizing compounds may also be obtained by incorporating emulsifying agents, substantially free from hydroxyl group and inert to isocynate, with the substituted toluylisocyanate, after isolating it from the solvent, used in its preparation and prior to its reaction with the ethylenimine in the aqueous phase. Suitable emulsifying agents of the ethylenoxide condensate type, free from hydroxyl groups, are described by Cyrus A. Weissgerber in U.S. Pat. No. 2,856,310.

In paper sizing with the compounds of this invention, their performance is much enhanced when used in combination with a retention aid. Retention aids effect deposition of additives on the fibers of paper pulp with more or less complete exhaustion of the effluent. Preferred retention aids are polyethylenimines and other polyalkylenimines.

Other retention aids are the polyamide-epichlorohydrin resins, known under the trade name "Kymene 557" and sold by Hercules, Inc., and the so-called cationic starches, such as "Cato-8" of the National Starch & Chemical Corporation and "Epic-N" of A. M. Meincke & Son, Inc.

The amount of retention aid used in relation to sizing agent is dependent on cost. In general, the amount used may vary from 10 to 85 percent by weight of the sizing agent and the cost of it will in most cases not exceed the cost of the amount of sizing agent used. The retention aid may be added to the head box of the paper making equipment separately from the sizing agent emulsion or it may be incorporated in it, especially there, where its presence adds to the stability of such emulsions. In general, and when applicable, it is preferred to add the size first and then the retention aid.

The preparation of the alkylurea substituted toluylisocyanate-intermediates and of the sizing agents themselves as well as of their emulsions and of their use in the sizing of paper is set forth in the examples.

EXAMPLE I

To a solution of 174 g. of tolylene-2,4-diisocynate in 500 g. of benzene, there are added, while stirring and cooling, 524 g. of melted commercial dioctadecylamine at such a rate as to maintain a reaction temperature of 35° C. Ten minutes after the completion of the amine addition, solid amine, accumulated in the reaction mass, has completely dissolved. Stirring is discontinued, after the evolution of heat has substantially subsided and the reaction mass is allowed to remain in the flask overnight, surrounded by a waterbath at ambient temperature.

On the following morning the benzene solvent is removed from the obtained clear solution by distillation in vacuo, first at a pressure of 125 Torr., and then at 15 Torr. at a temperature not exceeding 100° C.

The residual liquid is substantially 4-N- (2-isocyanatotoluyl)-N', N'-dioctadecylurea.

To the liquid, amounting to 701 g., 56 g. of the acetylated emulsifying agent, described in example I of U.S. Pat. No. 2,856,310, are added. The homogeneous liquid is then gradually added to a well stirred solution of 43 g. ethylenimine and 53 g. "Tween 80" in 1,620 g. of water at 40° C. The resulting crude emulsion is then passed twice through a homogenizer. The obtained thin, white emulsion is adjusted to a pH of 8 to 8.5 by the addition of ammonia. The emulsion is stable on storage and, after standing for 6 months at a temperature ranging from 55° to 90° F., was found without cream and as effective for paper sizing as a freshly prepared emulsion. Its active ingredient is chemically 2-N_1-4-tolylene-bis-(N_1', N_1'-ethylene)-N',N'-dioctadecyl) urea.

EXAMPLE II

Example I is repeated, except that 300 g. of commercial oleylamine is used instead of the dioctadecylamine. Four hundred seventy-seven g. of 4-N-(2-isocyanato-toluyl)-(N'-oleyl) urea are obtained, after removal of the solvent.

For the production of an aqueous sizing agent dispersion, it may be treated as in example I, by adding to it 45 g. of the special emulsifying agent and then adding the liquid to a solution of 57 g. propylenimine and 44 g. "between 80" in 1,150 g. of water. The final emulsion contains 30 percent active ingredient, which is 2-N_1-4-N-tolylene -bis-(N_1;N_1'-propylene)-(N'-oleyl) urea.

For the production of the latter compound, free from solvent, the isocyanate solution of the first reaction, before the removal of the benzene solvent, is added to a solution of 57 g. propylenimine in 160 g. of benzene at 35°–55° C., while cooling. To the resulting solution dry ammonia is added to a noticeable odor of ammonia. This solution is then freed from its benzene solvent by distillation in vacuo, first at a pressure of 125 Torr., and then at 15 Torr. at a temperature not exceeding 80° C. The resulting material is a liquid which congeals at 10–15° C.

EXAMPLE III

Similarly as the oleylamine of example II, 316 g. of commercial, rosin derived Amine D (Hercules, Inc.), which is technical dehydroabietylamine, is reacted with 174 g. of the 80:20 percent blend of tolylene-2,4 and 2,6-diiocyanate isomers, to form the benzene solution of the mixture of the 4-N and 6-N-(2-isocyanatotoluyl)-(N'-de-hydroabietyl) urea.

To the benzene solution, there are added, at 45° C. while stirring and cooling, 43 g. of ethylenimine in 150 g. of benzene. After the completion of the reaction, ammonia gas is added, as in example II and the benzene solvent removed in vacuo. The remaining liquid congeals, on cooling, to a tough waxlike mass.

EXAMPLE IV

To a solution of 600 g. of "DDI-diisocynate-1410" (General Mills, Inc.), and described as "liquid aliphatic (C 36) diisocyanate," there are added 139 g. of 2-ethylhexyl-amine, while stirring and maintaining the temperature of 30° C. by cooling. Stirring is discontinued after the evolution of heat has substantially subsided, and the reaction mass is allowed to remain in the flask, surrounded by a waterbath at ambient temperature.

Thereafter the benzene solvent is removed from the solution by distilling in vacuo, first at a pressure of 125 Torr., and then at 15 Torr. at a temperature not exceeding 100° C.

To the resulting viscous liquid, amounting to 777 g. of the N'-2-ethylhexyl substituted DDI-1410-isocyanate, there are added 75 g. of the special acetylated emulsifying agent, cited in example I, and the resulting homogeneous liquid is then added to a solution of 43 g. ethylenimine and 70 g. of "Tween 80" in 1,760 g. of water. The final emulsion contains as the active ingredient N,N_1-DDI-1410-bis-(N_1',N_1'-ethylene)-(N'-2-ethylhexyl) urea.

The cited examples demonstrate the preparation of representative alkylurea substituted isocyanates to be reacted with ethylenimines, to form compounds and compositions which are objects of the invention.

Suitable amines which may be used for the preparation of the alkylurea substituted isocyanates are the mono and dialkyl or alkenylamines, in general derived from the fatty alkyl or alkenyls, such as

behenyl	$-C_{22}H_{45}$
aracchyl	$-C_{20}H_{41}$
stearyl or isostearyl	$-C_{18}H_{37}$
cetyl or palmityl	$-C_{16}H_{33}$
myristyl	$-C_{14}H_{29}$
lauryl	$-C_{12}H_{25}$
oleyl	$-C_{18}H_{35}$
linoleyl	$-C_{18}H_{33}$

When using secondary amines, it is not necessary that both of the groups attached to the nitrogen atom be the same or be alkyl or alkenyl. The amines may be mixed dialkylamines, e.g. N-stearyl, N-oleyl,stearyl-cetyl, cetyl-oleyl, methyl-cetyl, isopropyl-oleyl or phenyl-cetyl, amines.

A further class of alkylamines, useful for the purpose of this invention, are the so-called "Beta-amines," sold by Armour & Co., where the nitrogen is not attached to the terminal or alpha-carbon atom, but to the beta-carbon next to it.

There are, of course, many other amines and the present invention is not limited to the amines cited. All amines of the form HNR_1X, where R_1 is alkyl, alkenyl, aralkyl, alkylaryl, cycloalkyl or cycloalkenyl and X is independently selected from the same groups or is aryl or hydrogen, are suitable.

The following example demonstrates the utilization of the new compositions, namely the reaction products of ethylenimines (substituted or not) with alkylurea substituted isocyanatotoluenes (generally alkylurea substituted isocyanates), and the various modes of their utilization as paper sizes in the manufacture of paper products.

EXAMPLE V

An aqueous pulp of unbleached Kraft paper stock is prepared at 0.28 percent consistency and 450 Canadian Standard Freeness, in the proportioner of a Noble & Wood experimental paper making assembly, and adjusted to a pH of 8 to 8.5.

With slight agitation of the pulp, a definite amount of size, based on the amount of dry paper stock contained in the proportioner, is added within 30 seconds in the form of an aqueous 1 percent emulsion of 1 percent solution in dioxane, followed by the addition of a definite amount of a 1 percent aqueous solution or dispersion of a retention aid, such as "Epic N."

Two minutes after the addition of the retention aid, one-half of the contents of the proportioner are transferred to the Deckle Box, where a paper sheet of the basis weight of 52 lb. (24×36; 500) is formed.

The balance of the contents of the proportioner are likewise made into a duplicate sheet.

The sheets were, immediately after forming, pressed, then dried for 3 minutes on a heated rotating drum at 200° F. and conditioned for at least 48 hours at 25° C. and 50 percent relative humidity.

They were then tested for sizing by the water drop absorption method, according to TAPPI Standard Method T-492, by determining the time, after which a drop of dilute lactic acid solution disappears by being soaked up by the paper.

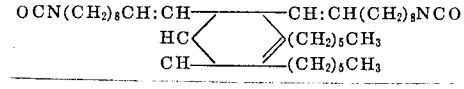
TABLE.—SIZE PERFORMANCE

[Water drop absorption times (seconds)-TAPPI-T-492]

	CONCENTRATION						
Size (retention aid)	.010	.020	.030	0.40	.050	.080	.10
None	18 (18)	18 (18)	18 (18)	18 (18)	18 (18)	18 (18)	18 (18)
Example I	30 (46)	42 (195)	200 (2, 186)	1, 090 (5, 400)	4, 310 (5, 400)	5, 400 (5, 400)	5, 400 (5, 400)
Example II	18 (18)	18 (18)	25 (50)	180 (1, 108)	1, 063 (4, 010)	3, 016 (5, 400)	5, 400 (5, 400)
Example III	18 (25)	29 (65)	150 (933)	2, 010 (4, 560)	5, 400 (5, 400)	5, 400 (5, 400)	5, 400 (5, 400)
Example IV	28 (52)	35 (210)	180 (1, 563)	867 (5, 400)	3, 730 (5, 400)	5, 400 (5, 400)	5, 400 (5, 400)
Example I aged for 6 months	25 (61)	43 (200)	187 (1, 829)	995 (4, 860)	5, 400 (5, 400)	5, 400 (5, 400)	5, 400 (5, 400)

In the table, the concentrations indicated are given in percentage of weight of the size, based on the weight of dry paper stock. The figures without brackets are the absorption times obtained without retention aids, while the bracketed figures were obtained in the presence of an equal amount of retention aid, namely "Epic N." The various sizes are effective in varying degree, but all size at concentrations of less than 0.1 percent. The retention aid proves itself necessary to bring out the full value of the size.

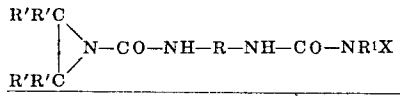
The formulas for derivatives of dimer fatty acids including the terms "DDI-1410" or "DDI-diisocyanate-1410" as set forth above are used to designate derivatives of dimer acid compounds such as



What is claimed is:

1. A process for waterproofing paper which comprises adjusting the pH of an aqueous pulp of paper stock to 8–8.5; adding to said aqueous pulp of paper stock 0.01 to 0.1 percent, based on the weight of the dry paper stock, of an aqueous dispersion of an N'-alkyl, N_1'N_1'-alkylene-N,N_1-bis-urea hav-

ing the formula



wherein R′ is hydrogen or a methyl or ethyl group; R is an arylene, alkylarylene, arylalkylene, cycloalkylene, or alkylene radical which may contain ethylenic double bonds; R_1 is an alkyl, alkenyl, aralkyl, alkylaryl, cycloalkyl, or cycloalkenyl radical; and X is the same as R_1, aryl, or hydrogen, and the total number of carbon atoms of R, R_1, and X is eight to 52; and forming sheet material from the thus-treated dispersion.

2. The process of claim 1 wherein the waterproofing compound is the product of the reaction of an alkylurea-substituted isocyanate and an alpha, beta-alkylenimine.

3. The process of claim 1 wherein the waterproofing dispersion also contains 0.01 to 0.1 percent, based on the weight of the dry paper stock, of a retention aid.

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