

A LIGHT COLORED MODIFIED ISOCYANATE MIXTURE AND PREPARATION METHOD THEREOF

TECHNICAL FIELD

5 The invention relates to a light colored modified isocyanate mixture and preparation method thereof, the modified isocyanate mixture contains carbodiimide (CDI) and/or uretonimine (UTI) derivatives, which is liquid at normal temperature and with low-color number, and has good stability at normal temperature storage and at high temperature.

TECHNICAL BACKGROUND

10 Isocyanates can form carbodiimide derivatives after releasing CO₂ by polycondensation under certain conditions, the carbodiimide group can be adducted with the isocyanate to form the uretonimine group. By this method, the isocyanate is allowed to contain CDI and UTI substances, which can reduce the melting point of the isocyanate, make it liquid at normal temperature, and form a stable low-viscosity liquid that is easy to transport and has good storage stability. And the
15 products prepared from such modified isocyanate have been improved in the properties such as light resistance, flame resistance, hydrolysis resistance, and increased initial strength and the like to a certain degree.

High-efficiency catalyst of phospholene, especially high-efficiency catalyst of phospholene oxide can be simply used for isocyanate group. Under certain reaction conditions, the isocyanate is
20 heated and partially converted into carbodiimide and/or uretonimine derivatives, and the preparation method can refer to the methods in US-A-6120699, US-A-2853473 and EP-A-515933.

Phospholene catalyst, especially phospholene oxide catalyst, is expected to have high activity, in order to be able to activate the carbodiimidation under mild temperature conditions, but the
25 catalyst still has sufficient activity at room temperature to affect the storage stability of products containing free NCO groups, and during the process, the NCO groups are continuously consumed which makes the viscosity continuously increase, thus the catalyst needs to be deactivated by chemical or physical or other methods.

In order to terminate the reaction of forming NCO to continuously produce CDI groups and UTI
30 groups, a limited amount of terminator can be added to the reaction solution, thereby deactivating the high-efficiency catalyst. Suitable terminators are mentioned in patent specifications EP-A-515933, CN-A-1721395, US-A-4120884, CN-A-1789241, and CN-A-102718683,

including Lewis acids, acyl chlorides, chloroformic acids, aromatic sulfonic acids/esters, silylated acids, alkyl sulfates and halides of main group elements. Terminating the catalysis with acids is not effective enough, in which the acid can also exist in the form of acyl chloride.

With reference to the publication of patent specification EP-A-515933, for the isocyanate mixture containing CDI/UTI groups prepared by phospholene catalyst, the activity of the catalyst is terminated by using at least the equimolar amount of, preferably 1-2 times molar amount of such as trimethylsilyl trifluoromethanesulfonate (TMST) as the catalyst. However, it has been proved in practice that the modified isocyanate prepared by this method has problems such as incomplete termination and poor storage stability, especially in the environment where the outdoor temperature is relatively low in winter, the product needs to be water bathed to melt in the process of using, and during the process of melting, gas will be generated, which will lead to high pressure in the storage vessel, and NCO of the product will decrease significantly and the viscosity will increase significantly.

With reference to the publication of patent specification CN-A-1721395, the silylated acid such as trimethylsilyl trifluoromethanesulfonate is used to terminate the activity of catalyst, the intended purpose can be achieved by the amount of terminator, but the appearance color number of the product rises rapidly. By compounding trimethylsilyl trifluoromethanesulfonate with non-silylated acid, acyl chloride and sulfonate, the patent improves the termination effect of the terminator, improves the stability of the product, and the color number of the product can reach to 50-60APHA, however in the current technical field, the appearance color still cannot meet our needs, and the viscosity of the product increases significantly during the high temperature heating process.

With reference to the publication of the patent specification US-A-4120884, dimethyl sulfate is used to terminate the phospholene oxide catalyst, and the storage stability has a certain improvement compared to using TMST, but the viscosity during the process of melting the material increases significantly.

According to the specification of CN-A-1789241, the alkylation reagents such as trifluoromethanesulfonates are used to terminate the reaction, the stability can be achieved by increasing the molar equivalent ratio of the terminator and the catalyst to achieve complete termination, but the color number of the product is not ideal.

CN-A-102718683 optimizes this, acid anhydride terminator is used to terminate the phospholene or phospholene oxide catalyst, and the preferred terminator is trifluoromethylsulfonic anhydride and/or p-toluenesulfonic anhydride. It has been proved in practice that the storage stability at

room temperature has been improved to a certain extent, but the high temperature stability is not ideal, the NCO has decreased significantly, and the color number of the product has increased rapidly, the trifluoromethylsulfonic anhydride and/or p-toluenesulfonic anhydride terminators are now the most effective terminators in the prior art.

- 5 The existing methods for preparing liquid isocyanates containing CDI and/or UTI groups are difficult to overcome the above drawbacks.

SUMMARY OF THE INVENTION

The invention relates to a light colored modified isocyanate mixture and preparation method thereof, the modified isocyanate mixture contains carbodiimide (CDI) and/or uretonimine (UTI) derivatives, which is liquid at normal temperature and with low-color number and has good
10 normal temperature storage and high temperature stability.

The present invention has found in research that halosilane organics and sulfonic anhydride substances do not contain -OH or active hydrogen atoms, thus have better termination effects, which are better than that of acid substances, alkylating agents and single anhydride terminators,
15 and the modified isocyanate prepared containing CDI and/or UTI groups has good stability, and the viscosity will not increase even during high temperature degradation.

The specific technical solutions are as follows:

A method for preparing a light colored modified isocyanate mixture, the modified isocyanate mixture contains carbodiimide (CDI) and/or uretonimine (UTI) derivatives, and the method
20 includes the following steps:

- a) subjecting the isocyanate group of a raw material isocyanate to carbodiimidization under the action of a phospholene catalyst to obtain a reaction solution of modified isocyanate containing carbodiimide and/or uretonimine derivatives;
- b) adding a compounded terminator to the reaction solution obtained in step a) to terminate the
25 carbodiimidization;

the terminator is a compound of a halosilane organic and a sulfonic anhydride substance.

The reaction of step a) can be carried out at a temperature of 40°C-210°C, preferably 100°C-200°C, more preferably 150°C-200°C, and further preferably 190-200°C.

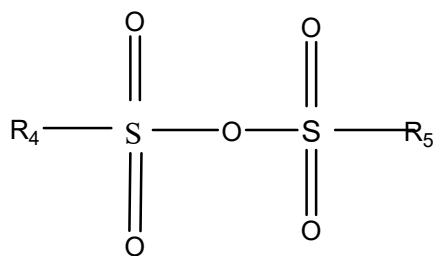
Furthermore, the halosilane organic has a chemical formula of the following formula (I),



(I)

in the molecular formula (I), R_1 , R_2 and R_3 independently represent an aliphatic, aromatic, araliphatic, and cycloaliphatic group optionally containing heteroatoms, wherein "optionally" means that it may contain or not contain heteroatoms. In the molecular formula (I), R_1 , R_2 and R_3 independently represent aliphatic (such as, C1-C10 hydrocarbyl, preferably C1-C6 hydrocarbyl, for example methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, etc.), aromatic (such as C6-C15 aromatic groups, specifically for example, phenyl, tolyl, ethylphenyl, etc.), araliphatic (such as C7-C15 araliphatic groups, specifically for example, phenmethyl, phenethyl, etc.), cycloaliphatic (such as C3-C12 cycloaliphatic groups, specifically for example, cyclopropyl, cyclobutyl, cyclohexyl, cyclopentyl, etc.) and other groups, which may contain heteroatoms and/or other functional groups, wherein R_1 , R_2 and R_3 may be the same or different; two of R_1 , R_2 and R_3 may be connected to each other to form a ring structure, that is, for $R_1R_2X_2Si$, R_1 and R_2 may be connected to each other to form a ring structure or not to form a ring structure; for $R_1R_2R_3X_1Si$, any two groups of R_1 , R_2 and R_3 may be connected to each other to form a ring structure or not to form a ring structure; X represents the halogen element and may be represented as fluorine, chlorine and bromine and other elements. Specifically, the subscript numbers 1, 2, and 3 in X_1 , X_2 , and X_3 all refer to the number of X in the molecular formula; for R_1X_3Si or $R_1R_2X_2Si$, in which two or three of X may be the same or different; and the subscript number of R groups such as R_1 , R_2 and R_3 are only for the convenience of distinguishing each R group, not the meaning of number, and the meanings of other similarities in the invention are the same. The halosilane organic is preferably one or two or more of diphenyldifluorosilane, diphenyldichlorosilane, tritylfluorosilane, and tert-butyltrichlorosilane.

Further, the said sulfonic anhydride substance has the following structural formula (II) :



(II)

in the structural formula (II), R_4 and R_5 independently represent an aliphatic, aromatic, araliphatic, and cycloaliphatic and the other groups optionally containing heteroatoms and/or other functional groups, wherein "optionally" means that it may contain or not contain heteroatoms and/or other functional groups. Furthermore, R_4 and R_5 independently represent aliphatic (such as C1-C10

hydrocarbonyl, preferably C1-C6 hydrocarbonyl, for example methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, etc.), aromatic (such as C6-C15 aromatic groups, specifically for example, phenyl, tolyl, ethylphenyl, etc.), araliphatic (such as C7-C15 araliphatic groups, specifically for example, phenmethyl, phenethyl, etc.), cycloaliphatic (such as C3-C12
5 cycloaliphatic groups, specifically for example, cyclopropyl, cyclobutyl, cyclohexyl, cyclopentyl, etc.) and other groups, which may contain heteroatoms and/or other functional groups, wherein R₄ and R₅ may be the same or different, the two groups R₄ and R₅ may optionally be connected to each other to form a ring structure, wherein "optionally" means that they may be connected to each other to form a ring structure or not to form a ring structure. The said sulfonic anhydride
10 substance is preferably one or two or more of p-toluenesulfonic anhydride, methanesulfonic anhydride, ethylsulfonic anhydride, and trifluoromethanesulfonic anhydride.

The preferred terminator is a compound of diphenyldifluorosilane and p-toluenesulfonic anhydride.

The amount of compounded terminator is based on the weight of raw material isocyanate, the
15 amount of organosilane terminator (halosilane organic terminator) is 50-2000ppm, preferably 100-600ppm, most preferably 100-200ppm; the amount of sulfonic anhydride terminator is 10-200 ppm, preferably 10-100 ppm, and most preferably 10-50 ppm. The compounding ratio (mass ratio) of the halosilane terminator to the sulfonic anhydride is preferably 2-6:1, further preferably 3-5:1, and more preferably 4:1.

20 The catalyst used for preparing the isocyanate containing carbodiimide and/or uretonimine derivatives is a phospholene catalyst and/or a phospholeneoxide, the phospholene or phospholene oxide catalyst is preferred. The catalysts are known, such as described both in EP-A-515933 and US-A-2663737, and the typical examples of these catalysts are known in the art.

Preferred catalyst is 1-methyl-3-methyl-3-phospholene-1-oxide or
25 1-phenyl-3-methyl-3-phospholene. The polycondensation of isocyanate is performed in the presence of the above-mentioned catalyst, and the amount of the catalyst is 0.1-10 ppm, preferably 0.2-2 ppm, and the preferred amount is 0.5 ppm, relative to the weight of the raw material isocyanate.

Any suitable isocyanate can be used as the raw material isocyanate in the method of the present
30 invention. However, in the method of the present invention, diisocyanate is preferred, such as one or more selected from the group consisting of aromatic, araliphatic, aliphatic, and cycloaliphatic diisocyanates, and it is particularly preferred that the diphenylmethane diisocyanate is subjected to carbodiimidation.

In some embodiments, the raw material isocyanate is diphenylmethane diisocyanate, wherein the diphenylmethane diisocyanate contains 97-100 wt% 4,4-isomer, 0-1 wt% 2,2-isomer, and 0.5-1.8 wt% 2,4-isomer.

The carbodiimidation is carried out in the presence of a high-efficiency catalyst, and the reaction is carried out at a temperature of 40-210 °C, preferably between 190°C -200°C, of course, the reaction can also be carried out at a mild ambient temperature, but this requires a large amount of catalyst, and the large additive amount of terminator will lead to the color number of the product to be unsatisfactory; a small amount of catalyst will cause a slow reaction rate, which is not conducive to industrial production.

Because the carbodiimidation is an NCO polycondensation and the process is accompanied by the generation of CO₂, such reaction process can be monitored by measuring the amount of CO₂ released; or the change in the refractive index of the reaction solution can be continuously determined to reflect the changes in NCO content. When the carbodiimidation time reaches 10min-24h, preferably between 1h-4h, a compounded terminator is added to terminate the reaction.

In some specific embodiments, the temperature condition of adding a compounded terminator to terminate the carbodiimidation of step b) is 40-70°C, further preferably 40-60°C, more preferably 50-60°C, such as 60°C.

According to some embodiments of the present invention, 5-20% of, preferably 10-15% of the NCO group of the raw material isocyanate is converted into CDI group by carbodiimidation, and then the CDI group reacts with the unreacted NCO group to form UTI group, so that the UTI group is easily introduced into the isocyanate system. Since the conversion of CDI group to UTI group is a reversible process, a small amount of CDI groups will remain in the product.

After the reaction of step a) and before adding the terminator, an appropriate amount of the raw material isocyanate can be further added, of course, this step can also be performed without the further adding operation, further adding the isocyanate raw material mainly can accelerate the cooling process; after adding the terminator, an appropriate amount of the raw material isocyanate can be further added again, or not be further added again, further adding isocyanate after adding the terminator is mainly for adjusting the target NCO value; the total amount of the further added isocyanate raw material is determined according to the NCO value to be adjusted as needed.

The positive effects of the present invention are as follows: a) the modified isocyanate product

obtained by the present invention has excellent storage stability at normal temperature, and will not undergo polycondensation during the process of melting at high-temperature, the content of NCO group does not decrease even at high temperatures in the storage of the product, and the viscosity change is very small; b) the modified isocyanate prepared by the present invention has a lower color number, which is generally stable at 20-30 APHA, and the color number is significantly reduced compared with the prior art.

The invention further relates to a liquid modified isocyanate mixture containing CDI and/or UTI groups obtained by the above method, the NCO content is 20-32wt%, preferably 28-30wt%; the viscosity is 10-200cp, preferably 20-60cp, the color number is 20-40 APHA; preferably, the initial value of the product's Hasen color number is 20-30, and the value after 2 months is 25-35. The advantages of the method according to the present invention are obvious, since a compound of halosilane organic and sulfonic anhydride terminator is used, the isocyanate containing CDI and/or UTI groups is basically light-colored and has storage stability at normal temperature and high temperature. These and other advantages and benefits of the invention will be apparent from the following specific embodiment of the invention.

EMBODIMENTS

The present invention is further illustrated by the following examples, but the scope of the present invention is not limited to the following examples.

The raw material: diphenylmethane diisocyanate, wherein the diphenylmethane diisocyanate contains 97-100 wt% 4,4-isomer, 0-1 wt% 2,2-isomer, and 0.5- 1.8 wt% 2,4-isomer, the content of NCO is 33.6wt%.

The catalyst is: a solution of 1-methyl-3-methyl-3-phospholene-1-oxide or 1-phenyl-3-methyl-3-phospholene-1-oxide, using dichloromethane as the solvent, and the concentration of catalyst was 1% relative to the mass of the solvent dichloromethane; both the catalyst and the solvent were purchased and available from Sinopharm.

Diphenyldifluorosilane, purity 96%, color number 10 #, from Suzhou Yake Technology Co., Ltd.

Tritylfluorosilane, purity 96%, available from Sinopharm.

P-toluenesulfonic anhydride, purity 95%, available from Sinopharm.

Trifluoromethanesulfonic anhydride, purity 98%, available from Sinopharm.

Trimethylsilyltrifluoromethanesulfonate, purity 95%, available from Sinopharm.

Dibutyl phosphate, purity 98%, available from Sinopharm.

Comparative Example 1

500 g diphenylmethane diisocyanate was heated to about 50°C under the protection of N₂ while stirring, and a high-efficiency catalyst solution of phospholene (i.e., a solution of 1-phenyl-3-methyl-3-phospholene-1-oxide) with a catalyst amount of 0.5 ppm (0.025g) was added, after mixing, the mixture was quickly heated to 200°C, and after reacting for 90 minutes, 200 g diphenylmethane diisocyanate was further added, and 200 ppm (0.1 g) of terminator diphenyldifluorosilane was added, the temperature was rapidly reduced to 60°C, after stirring the mixture for 30 minutes, 200g diphenylmethane diisocyanate was further added again, then the temperature was raised to 70-80°C, and stirred for 120 min to obtain the final product. The test results of the final product are shown in tables 1-2.

This comparative example can also be carried out according to the following steps: 500 g diphenylmethane diisocyanate was heated to about 50°C while stirring under the protection of N₂, and a high-efficiency catalyst solution of 1-phenyl-3-methyl-3-phospholene with a catalyst amount of 0.025g was added, after mixing the mixture was quickly heated to 200°C, and 400g diphenylmethane diisocyanate was further added after reacting for 90 minutes, and after the temperature was rapidly cooled to 60°C, 0.1g terminator diphenyldifluorosilane was added, and the mixture was stirred for 30 minutes and then heated to 70-80°C, and stirred for 120 minutes to obtain the final product. There is no significant change in the properties of this product relative to the properties of the product prepared according to the aforementioned steps.

Example 1

500 g diphenylmethane diisocyanate was heated to about 50°C under the protection of N₂ while stirring, and a high-efficiency catalyst solution of 1-phenyl-3-methyl-3-phospholene (i.e., a solution of 1-phenyl-3-methyl-3-phospholene-1-oxide) with a catalyst amount of 0.5 ppm (0.025g) was added, after mixing the mixture was quickly heated to 200°C, and after reacting for 90 minutes, 200 g diphenylmethane diisocyanate was further added, then 200 ppm (0.1 g) of terminator diphenyldifluorosilane and 50ppm (0.025g) of terminator p-toluenesulfonic anhydride were added, the temperature was rapidly cooled to 60°C, after stirring the mixture for 30 minutes, 200g diphenylmethane diisocyanate was further added again, and the temperature was raised to 70-80 °C, and stirred for 120min to obtain the final product. The test results of the final product are shown in tables 1-2.

This example can also be performed according to the following steps:

500 g of diphenylmethane diisocyanate was heated to about 50°C while stirring under the

protection of N₂, and a high-efficiency catalyst solution of 1-phenyl-3-methyl-3-phospholene with a catalyst amount of 0.025g was added, after mixing the mixture was quickly heated to 200°C, and after reacting for 90 minutes, 400g diphenylmethane diisocyanate was further added, the temperature was rapidly cooled to 60°C, 0.1g terminator diphenyldifluorosilane and 0.025g terminator p-toluenesulfonic anhydride were added, and the mixture was stirred for 30 minutes and then heated to 70-80°C, and stirred for 120 minutes to obtain the final product. There is no significant change in the properties of this product relative to the properties of the product prepared according to the aforementioned steps.

Example 2

500 g diphenylmethane diisocyanate was heated to about 50°C under the protection of N₂ while stirring, and a high-efficiency catalyst solution of 1-phenyl-3-methyl-3-phospholene (as a solution of 1-phenyl-3-methyl-3-phospholene-1-oxide) with a catalyst amount of 0.5ppm (0.025g) was added, after mixing the mixture was quickly heated to 200°C, and after reacting for 90 minutes, 200 g diphenylmethane diisocyanate was further added, then 200 ppm (0.1 g) of terminator diphenyldichlorosilane and 50 ppm (0.025g) of terminator trifluoromethylsulfonic anhydride were added, the temperature was rapidly cooled to 60°C, after stirring the mixture for 30 minutes, then 200g diphenylmethane diisocyanate was further added again, and the temperature was raised to 70-80°C, and stirred for 120min to obtain the final product. The test results of the final product are shown in tables 1-2.

This example can also be performed according to the following steps:

500 g diphenylmethane diisocyanate was heated to about 50°C while stirring under the protection of N₂, and a high-efficiency catalyst solution of 1-phenyl-3-methyl-3-phospholene with a catalyst amount of 0.025g was added, after mixing the mixture was quickly heated to 200°C, and after reacting for 90 minutes, 400g diphenylmethane diisocyanate was further added, the temperature was rapidly cooled to 60°C, 0.1g terminator diphenyldichlorosilane and 0.025g terminator trifluoromethylsulfonic anhydride were added, and the mixture was stirred for 30 minutes and then heated to 70-80°C, and stirred for 120 minutes to obtain the final product. There is no significant change in the properties of this product relative to the properties of the product prepared according to the aforementioned steps.

Example 3

500 g diphenylmethane diisocyanate was heated to about 50°C under the protection of N₂ while

stirring, and a high-efficiency catalyst solution of 1-methyl -3-methyl-3-phospholene-1-oxide (i.e., a solution of 1-methyl -3-methyl-3-phospholene-1-oxide) with a catalyst amount of 1ppm (0.05g) was added, after mixing the mixture was quickly heated to 120°C, and after reacting for 200 minutes, 200 g diphenylmethane diisocyanate was further added, then 200 ppm (0.1 g) of terminator tritylfluorosilane and 50ppm (0.025g) of terminator p-toluenesulfonic anhydride were added, the temperature was rapidly cooled to 60°C, after stirring the mixture for 30 minutes, then 200g diphenylmethane diisocyanate was further added again, and the temperature was raised to 70-80°C, and stirred for 120 min to obtain the final product. The test results of the final product are shown in tables 1-2.

This example can also be performed according to the following steps: 500 g diphenylmethane diisocyanate was heated to about 50°C under the protection of N₂ while stirring, and a high-efficiency catalyst solution of 1-phenyl-3-methyl-3-phospholene-1-oxide (i.e., a solution of 1-phenyl-3-methyl-3-phospholene-1-oxide) with a catalyst amount of 0.05 g was added, after mixing the mixture was quickly heated to 120°C, and after reacting for 200 minutes, 400g diphenylmethane diisocyanate was further added, the temperature was rapidly cooled to 60°C, 0.1 g terminator tritylfluorosilane and 0.025g terminator p-toluenesulfonic anhydride were added, after stirring the mixture for 30 minutes, the temperature was raised to 70-80°C, and stirred for 120 min to obtain the final product. There is no significant change in the properties of this product relative to the properties of the product prepared according to the aforementioned steps.

Example 4

500 g diphenylmethane diisocyanate was heated to about 50°C under the protection of N₂ while stirring, and a high-efficiency catalyst solution of 1-methyl -3-methyl-3-phospholene-1-oxide (as a solution of 1-methyl -3-methyl-3-phospholene-1-oxide) with a catalyst amount of 0.5ppm (0.025g) was added, after mixing the mixture was quickly heated to 200°C, and after reacting for 90 minutes, 200 g diphenylmethane diisocyanate was further added, then 100 ppm (0.05g) of terminator diphenyldifluorosilane and 20 ppm (0.01g) of terminator trifluoromethylsulfonic anhydride were added, the temperature was rapidly cooled to 60°C, after stirring the mixture for 30 minutes, then 200g diphenylmethane diisocyanate was further added again, then the temperature was raised to 70-80°C, and stirred for 120min to obtain the final product. The test results of the final product are shown in tables 1-2.

This example can also be performed according to the following steps: 500 g diphenylmethane diisocyanate was heated to about 50°C under the protection of N₂ while stirring, and a high-efficiency catalyst solution of 1-phenyl-3-methyl-3-phospholene-1-oxide (a solution of

1-phenyl-3-methyl-3-phospholene-1-oxide) with a catalyst amount of 0.025g was added, after mixing the mixture was quickly heated to 200°C, and after reacting for 90 minutes, 400g diphenylmethane diisocyanate was further added, the temperature was rapidly cooled to 60°C, 0.05g terminator diphenyldifluorosilane and 0.01g terminator trifluoromethylsulfonic anhydride were added, after stirring the mixture for 30 minutes, the temperature was raised to 70-80°C, and stirred for 120min to obtain the final product. There is no significant change in the properties of this product relative to the properties of the product prepared according to the aforementioned steps.

10 **Comparative Example 2**

500 g diphenylmethane diisocyanate was heated to about 50°C under the protection of N₂ while stirring, and a high-efficiency catalyst solution of 1-phenyl-3-methyl-3-phospholene (i.e., a solution of 1-phenyl-3-methyl-3-phospholene-1-oxide) with a catalyst amount of 0.5ppm (0.025g) was added, after mixing the mixture was quickly heated to 200°C, and after reacting for 90 minutes, 200 g diphenylmethane diisocyanate was further added, then 10 ppm (0.025g) of terminator trimethylsilyl trifluoromethanesulfonate was added, the temperature was rapidly cooled to 60°C, after stirring the mixture for 30 minutes, then 200g was further added again, then the temperature was raised to 70-80°C, and stirred for 120 min to obtain the final product. The test results of the final product are shown in tables 1-2.

20 This comparative example can also be performed according to the following steps: 500 g diphenylmethane diisocyanate was heated to about 50°C while stirring under the protection of N₂, and a high-efficiency catalyst solution of 1-phenyl-3-methyl-3-phospholene with a catalyst amount of 0.025 g was added, after mixing the mixture was quickly heated to 200°C, and after reacting for 90 minutes, 400g diphenylmethane diisocyanate was further added, the temperature was rapidly cooled to 60°C, 0.025g of terminator trimethylsilyl trifluoromethanesulfonate was added, and the mixture was stirred for 30 minutes and then heated to 70-80°C, and stirred for 120 minutes to obtain the final product. There is no significant change in the properties of this product relative to the properties of the product prepared according to the aforementioned steps.

30 **Comparative Example 3**

500 g diphenylmethane diisocyanate was heated to about 50°C under the protection of N₂ while stirring, and a high-efficiency catalyst solution of 1-phenyl-3-methyl-3-phospholene (i.e., a solution of 1-phenyl-3-methyl-3-phospholene-1-oxide) with a catalyst amount of 0.5 ppm

(0.025g) was added, after mixing the mixture was quickly heated to 200°C, and after reacting for 90 minutes, 200 g diphenylmethane diisocyanate was further added, then 10 ppm (0.005g) of terminator trimethylsilyl trifluoromethanesulfonate compounding with 200 ppm (0.1g) of dibutyl phosphate was added, the temperature was rapidly cooled to 60°C, after stirring the mixture for 30 minutes, then 200g was further added again, then the temperature was raised to 70-80°C, and stirred for 120min to obtain the final product. The test results of the final product are shown in tables 1-2.

This comparative example can also be performed according to the following steps: 500 g diphenylmethane diisocyanate was heated to about 50°C while stirring under the protection of N₂, and a high-efficiency catalyst solution of 1-phenyl-3-methyl-3-phospholene with a catalyst amount of 0.025g was added, after mixing the mixture was quickly heated to 200°C, and after reacting for 90 minutes, 400g diphenylmethane diisocyanate was further added, the temperature was rapidly cooled to 60°C, 0.005 g terminator trimethylsilyl trifluoromethanesulfonate compounding with 0.1g dibutyl phosphate was added, and the mixture was stirred for 30 minutes and then heated to 70-80°C, and stirred for 120 minutes to obtain the final product. There is no significant change in the properties of this product relative to the properties of the product prepared according to the aforementioned steps.

Comparative Example 4

500 g diphenylmethane diisocyanate was heated to about 50°C under the protection of N₂ while stirring, and a high-efficiency catalyst solution of 1-phenyl-3-methyl-3-phospholene (i.e., a solution of 1-phenyl-3-methyl-3-phospholene-1-oxide) with a catalyst amount of 0.5ppm (0.025g) was added, after mixing the mixture was quickly heated to 200°C, and after reacting for 90 minutes, 200 g diphenylmethane diisocyanate was further added, then 50 ppm (0.025g) of terminator p-toluenesulfonic anhydride was added, the temperature was rapidly cooled to 60 °C, after stirring the mixture for 30 minutes, 200g was further added again, then the temperature was raised to 70-80°C, and stirred for 120 min to obtain the final product. The test results of the final product are shown in tables 1-2.

This comparative example can also be performed according to the following steps: 500 g diphenylmethane diisocyanate was heated to about 50°C while stirring under the protection of N₂, and a high-efficiency catalyst solution of 1-phenyl-3-methyl-3-phospholene with a catalyst amount of 0.025g was added, after mixing the mixture was quickly heated to 200 °C, and after reacting for 90 minutes, 400g diphenylmethane diisocyanate was further added, the temperature was rapidly cooled to 60 °C, 0.025g terminator p-toluenesulfonic anhydride was added, and the

mixture was stirred for 30 minutes and then heated to 70-80°C, and stirred for 120 minutes to obtain the final product. There is no significant change in the properties of this product relative to the properties of the product prepared according to the aforementioned steps.

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Comparative Example 5

500 g diphenylmethane diisocyanate was heated to about 50°C under the protection of N₂ while stirring, and a high-efficiency catalyst solution of 1-phenyl-3-methyl-3-phospholene (i.e., a solution of 1-phenyl-3-methyl-3-phospholene-1-oxide) with a catalyst amount of 0.5ppm (0.025g) was added, after mixing the mixture was quickly heated to 200°C, and after reacting for 90 minutes, 200 g diphenylmethane diisocyanate was further added, then 50 ppm (0.025g) of terminator methyl trifluoromethanesulfonate was added, the temperature was rapidly cooled to 60°C, after stirring the mixture for 30 minutes, 200g was further added again, then the temperature was raised to 70-80°C, and stirred for 120 min to obtain the final product. The test results of the final product are shown in tables 1-2.

This comparative example can also be performed according to the following steps: 500 g diphenylmethane diisocyanate was heated to about 50°C while stirring under the protection of N₂, and a high-efficiency catalyst solution of 1-phenyl-3-methyl-3-phospholene with a catalyst amount of 0.025g was added, after mixing the mixture was quickly heated to 200°C, and after reacting for 90 minutes, 400g diphenylmethane diisocyanate was further added, the temperature was rapidly cooled to 60 °C, 0.025g terminator methyl trifluoromethanesulfonate was added, and the mixture was stirred for 30 minutes and then heated to 70-80°C, and stirred for 120 minutes to obtain the final product. There is no significant change in the properties of this product relative to the properties of the product prepared according to the aforementioned steps.

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The comparison of each product in storage stability and color number is shown in tables 1-2.

Wherein, the viscosity refers to the national standard GB/T 12009.3-2009 of the People's Republic of China, polymethylene polyphenyl isocyanate, determination in the viscosity of the third part.

The determination of NCO refers to the national standard GB/T 12009.4-2016 of the People's Republic of China, aromatic isocyanates for the production of polyurethane, determination of the isocyanate content in the fourth part.

The color number is determined by a color number instrument, and the color number instrument model is BYK- LCSIII.

Table 1: Comparison table of each product in storage stability and color number

	terminator	amount of the terminator	initial viscosity of the product	viscosity stored at 30°C (cp)			viscosity after 8h degradation at high temperature (80°C) (cp)
		PPM	CP	1 month	2 months	6 months	
Comparative Example 1	diphenyldifluorosilane	200	42	43	46	53	90
Example 1	diphenyldifluorosilane/p-toluenesulfonic anhydride	200/50	40	41	42	44	45
Example 2	diphenyldichlorosilane/trifluoromethanesulfonic anhydride	200/50	41	43	44	47	46
Example 3	tritylfluorosilane/p-toluenesulfonic anhydride	200/50	41	43	45	48	48
Example 4	diphenyldifluorosilane/trifluoromethanesulfonic anhydride	100/20	42	43	47	49	48
Comparative Example 2	trimethylsilyl trifluoromethanesulfonate	50	43	48	50	63	120
Comparative Example 3	trimethylsilyl trifluoromethanesulfonate /dibutyl phosphate	10/200	41	42	45	51	105
Comparative Example 4	p-toluenesulfonic anhydride	50	43	52	73	112	180
Comparative Example 5	methyl trifluoromethanesulfonate	50	41	57	83	140	230

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Table 2: Comparison table of each product in storage stability and color number

	terminator	initial NCO of the product	NCO% stored at 30°C			NCO% after 8h degradation at high temperature (80°C)	Hasson color number of the product (color number)	
		%	1 month	2 months	6 months		initial	2 months
Comparative Example 1	diphenyldifluorosilane	28.88	28.82	28.71	28.53	28.12	20	30
Example 1	diphenyldifluorosilane/p-toluenesulfonic anhydride	28.93	28.91	28.88	28.72	28.72	20	25
Example 2	diphenyldichlorosilane/trifluoromethanesulfonic	28.87	28.85	28.78	28.68	28.65	30	35

	anhydride							
Example 3	tritylfluorosilane/p-toluenesulfonic anhydride	28.89	28.87	28.83	28.78	28.79	30	35
Example 4	diphenyldifluorosilane/trifluoromethanesulfonic anhydride	28.87	28.81	28.79	28.74	28.75	30	35
Comparative Example 2	trimethylsilyl trifluoromethanesulfonate	28.85	28.72	28.53	28.31	27.53	150	180
Comparative Example 3	trimethylsilyl trifluoromethanesulfonate/dibutyl phosphate	28.82	28.77	28.62	28.46	27.88	50	60
Comparative Example 4	p-toluenesulfonic anhydride	28.91	28.21	28.03	27.24	26.56	40	70
Comparative Example 5	methyl trifluoromethanesulfonate	28.91	28.61	28.28	27.14	26.35	140	150

Referring to Comparative Example 2, the modified isocyanate product has a high appearance color number and its high temperature stability is not ideal; the modified isocyanate products of Comparative Examples 3-5 have ideal storage stability at room temperature, but the stability is not ideal at high temperature, and NCO decreases significantly and viscosity increases greatly; it can be seen from Comparative Example 1 that by using of diphenyldifluorosilane alone, the stability at high temperature is poor; Examples 1-4 show that after compounding halosilane organic with p-toluenesulfonic anhydride, the stability is ideal at both room temperature and high temperature, and the color number is also lower than that in other examples.

Claims

1. A preparation method of a light colored modified isocyanate mixture, the method includes the following steps:

- 5 a) subjecting the isocyanate group of a raw material isocyanate to carbodiimidization under the action of a phosphorus heterocyclic catalyst to obtain a reaction solution of modified isocyanate containing carbodiimide and/or uretonimine derivatives;
- b) adding a compounded terminator to the reaction solution obtained in step a) to terminate the carbodiimidization;
- 10 the terminator is a compound of a halosilane organic and a sulfonic anhydride substance.

2. The preparation method according to claim 1, wherein, the reaction of step a) is carried out at a temperature of 40°C-210°C, preferably at 190-200°C.

- 15 3. The preparation method according to claim 1 or 2, wherein, the halosilane organic has a chemical formula of the following formula (I):



(I)

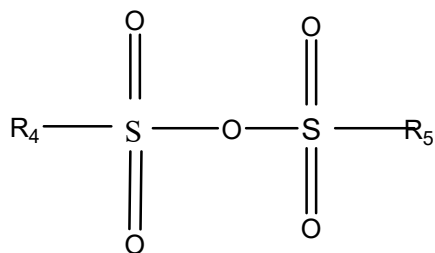
- 20 in the molecular formula (I), R_1 , R_2 and R_3 independently represent aliphatic (such as, C1-C10 hydrocarbyl), aromatic (such as C6-C15 aromatic groups, further for example, phenyl, tolyl, ethylphenyl), araliphatic (such as C7-C15 araliphatic groups, further for example, phenmethyl, phenethyl, etc.), cycloaliphatic (such as C3-C12 cycloaliphatic groups) groups optionally containing heteroatoms, wherein R_1 , R_2 and R_3 can be the same or different; and two groups of R_1 ,
- 25 R_2 and R_3 can be connected to each other to form a ring structure;

X represents the halogen element selected from the group consisting of fluorine, chlorine, bromine and iodine;

preferably, the halosilane organic is one or more selected from the group consisting of diphenyldifluorosilane, diphenyldichlorosilane, tritylfluorosilane, and tert-butyltrichlorosilane.

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4. The preparation method according to any one of claims 1-3, wherein, the said sulfonic anhydride material has the following structural formula (II) :



(II)

in the structural formula (II), R₄ and R₅ independently represent aliphatic (for example, C1-C10 hydrocarbyl), aromatic (such as C6-C15 aromatic groups, further for example phenyl, tolyl, ethylphenyl), araliphatic (such as C7-C15 araliphatic groups, further for example phenmethyl, phenethyl, etc.), or cycloaliphatic (such as C3-C12 cycloaliphatic groups, further for example cyclopropyl, cyclobutyl, cyclohexyl, cyclopentyl, etc.) groups optionally contain heteroatoms and/or other functional groups, wherein R₄ and R₅ can be the same or different, the two groups R₄ and R₅ are optionally connected to each other to form a ring structure; preferably, the said sulfonic anhydride substance is one or more selected from the group consisting of p-toluenesulfonic anhydride, methanesulfonic anhydride, ethylsulfonic anhydride, and trifluoromethanesulfonic anhydride.

5. The preparation method according to any one of claims 1-4, wherein, preferably the terminator is a compound of diphenyldifluorosilane and p-toluenesulfonic anhydride.

6. The preparation method according to any one of claims 1-5, wherein, the temperature condition of adding the compounded terminator to terminate the carbodiimidation of step b) is 40-70°C, further preferably 40-60°C, more preferably 50-60°C.

7. The preparation method according to any one of claims 1-6, wherein, the amount of compounded terminator is based on the weight of the raw material isocyanate, the amount of halosilane organic terminator is 50-2000ppm, preferably 100-600ppm, more preferably 100-200ppm; the amount of sulfonic anhydride terminator is 10- 200ppm, preferably 10-100ppm, more preferably 10-50ppm;

preferably, the compounding mass ratio of the halosilane organic and the sulfonic anhydride is 2-6:1, further preferably 3-5:1, and more preferably 4:1.

8. The preparation method according to any one of claims 1-7, wherein, the catalyst used for preparing the isocyanate containing carbodiimide and/or uretonimine derivatives is a phospholene catalyst and/or a phospholene oxide, the amount of the catalyst is 0.1-10 ppm, preferably 0.2-2

ppm, and most preferably, the amount is 0.5 ppm, relative to the weight of the raw material isocyanate.

9. The preparation method according to any one of claims 1-8, wherein, the raw material isocyanate is one or more selected from the group consisting of aromatic, araliphatic, aliphatic, and cycloaliphatic diisocyanates, and the diphenylmethane diisocyanate is preferred.

10. The preparation method according to any one of claims 1-9, wherein, when the reaction time of the carbodiimidation reaches 10 min-24h, preferably between 1h-4h, the compounded terminator is added to terminate the reaction.

11. A light colored modified isocyanate mixture containing carbodiimide and/or uretonimine groups obtained by the preparation method according to any one of claims 1-10, its NCO content is 20-32wt%, preferably 28-30wt%, the viscosity is 10-200cp, preferably 20-60cp, the color number is 20-40 APHA.