

20 JUL 2000

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TITLE OF THE INVENTION

Biuret polyisocyanate and process for producing
the same

BACKGROUND OF THE INVENTION5 Field of the Invention

The present invention relates to a biuret polyisocyanate. More particularly, the present invention is concerned with a biuret polyisocyanate obtained by reacting at least one diisocyanate selected from the
10 group consisting of an aliphatic diisocyanate and an alicyclic diisocyanate with a biuretizing agent, wherein the biuret polyisocyanate has a very low content of an unfavorable urea dimer which is an intermediate of the above-mentioned reaction, and exhibits a high
15 transmittance. The biuret polyisocyanate of the present invention not only exhibits an excellent stability at low temperatures, but also is free from discoloration. By virtue of these properties, the biuret polyisocyanate can be advantageously used for producing a
20 coating composition, an adhesive, a fiber treatment agent, a sealant, a waterproofing agent, a foam, an elastomer and the like. For example, when the biuret polyisocyanate of the present invention is used for producing a coating composition, the obtained coating
25 composition is capable of forming a coating which ex-

hibits excellent adhesiveness and bending resistance. The present invention is also concerned with a process for effectively and efficiently producing a biuret polyisocyanate which not only exhibits an excellent stability at low temperatures, but also is free from discoloration. By the process of the present invention, it has become possible to produce an excellent biuret polyisocyanate in high yield.

Prior Art

A polyisocyanate containing substantially no diisocyanate has been widely used for producing a coating composition, an adhesive, a sealant, a waterproofing agent, a foam, an elastomer, a fiber treatment agent and the like. A representative example of polyisocyanates for such usage is a polyisocyanate having a biuret structure (that is, a biuret polyisocyanate). A biuret polyisocyanate can be produced from a diisocyanate (as a main raw material) and a biuretizing agent, such as water, a monovalent tertiary alcohol, formic acid, hydrogen sulfide, an organic primary amine and an organic secondary amine. A number of methods for producing a biuret polyisocyanate have been proposed. For example, the following patent documents disclose the method for producing a biuret polyisocyanate: Unexam-

ined Japanese Patent Application Laid-Open Specification No. 49-134629 (corresponding to U.S. Patent No. 3,976,622), Unexamined Japanese Patent Application Laid-Open Specification No. 63-174961 (corresponding to
5 U.S. Patent No. 4,837,359), Examined Japanese Patent Application Publication No. 61-60093, Examined Japanese Patent Application Publication No. 61-26778 (corresponding to U.S. Patent No. 4,176,132), Examined Japanese Patent Application Publication No. 62-41496
10 (corresponding to U.S. Patent No. 4,290,969), Examined Japanese Patent Application Publication No. 2-62545 (corresponding to U.S. Patent No. 4,983,762), Examined Japanese Patent Application Publication No. 5-17222, and Unexamined Japanese Patent Application Laid-Open
15 Specification No. 8-225511 (corresponding to U.S. Patent No. 5,641,851).

In the production of a biuret polyisocyanate, first, an isocyanate group of a starting compound, such as a diisocyanate, reacts with a biuretizing agent to
20 thereby form a compound containing an urea bond (e.g., an "urea dimer" obtained from two diisocyanate monomers) as an intermediate. Next, the urea bond of the urea bond-containing compound and an isocyanate group react with each other to thereby form a biuret polyiso-
25 cyanate. It is known that this reaction is accompanied

by the by-production of various types of urea bond
-containing compounds, so that the obtained polyisocya-
nate becomes turbid due to the presence of the by-
produced urea bond-containing compounds. For example,
5 when a turbid polyisocyanate is used in a coating com-
position, the physical properties of the coating ob-
tained from the coating composition are likely to be-
come unsatisfactory. One method for preventing a
polyisocyanate from becoming turbid is to retain a re-
10 action mixture (which is obtained by reacting a diiso-
cyanate and a biuretizing agent) at high temperatures.
For example, such a method is described in Examined Ja-
panese Patent Application Publication No. 62-41496
(corresponding to U.S. Patent No. 4,290,969) and Exam-
15 ined Japanese Patent Application Publication No.
63-6544 (corresponding to U.S. Patent No. 4,264,519),
each of which discloses a continuous process for pro-
ducing a polyisocyanate; and Examined Japanese Patent
Application Publication No. 5-17222, Examined Japanese
20 Patent Application Publication No. 2-62545 (correspond-
ing to US Patent No. 4,983,762) and Unexamined Japanese
Patent Application Laid-Open Specification No. 8-225511
(corresponding to U.S. Patent No. 5,641,851), each of
which discloses a batchwise process for producing a
25 polyisocyanate. However, when a polyisocyanate is re-

tained at high temperatures, the polyisocyanate is sometimes likely to suffer discoloration. Further, such a method for preventing a polyisocyanate from becoming turbid has a problem in that the method causes a low productivity of the polyisocyanate and a high cost (e.g., a large investment for plant and equipment).

In the method disclosed in the above-mentioned Examined Japanese Patent Application Publication No. 62-41496 (corresponding to U.S. Patent No. 4,290,969), in an attempt to prevent the incorporation of the urea dimer and/or other urea bond-containing compounds into the polyisocyanate, a reaction mixture obtained by the reaction for producing a polyisocyanate is treated in a pipe reactor, to thereby effectively react the diisocyanate with the urea dimer and other urea bond-containing compounds. However, in this method, the treatment in the pipe reactor is performed under conditions wherein the diisocyanate concentration is as high as approximately 77 to 89 % by weight and, hence, the degree of the reduction of the urea dimer content is low. Therefore, the polyisocyanate produced by this method becomes turbid after the storage at low temperatures.

In the method disclosed in the above-mentioned Examined Japanese Patent Application Publication No.

61-60093, in order to suppress the increase in the diisocyanate concentration of a biuret polyisocyanate during the long term storage, the biuret polyisocyanate is subjected to heat treatment before the storage.

5 Specifically, in this method, the polyisocyanate is heated to increase the diisocyanate concentration thereof for the purpose of eliminating substances which cause the formation of a diisocyanate during the storage of the polyisocyanate, followed by removal of the
10 diisocyanate. However, this patent document has no description about not only the urea dimer itself, but also a recognition that the urea dimer contained in the polyisocyanate causes the turbidity of the polyisocyanate at low temperatures. Further, this patent document
15 has no teaching or suggestion about a method which not only enables a reduction in the urea dimer content of the polyisocyanate, but also prevents the discoloration of the polyisocyanate.

In general, a polyisocyanate is produced from a
20 large excess of a diisocyanate. Therefore, for obtaining a polyisocyanate as a final product, a purification step for removing the unreacted diisocyanate having a high vapor pressure is necessary. With respect to the method for removing the unreacted diisocyanate, there
25 can be mentioned an extraction with a poor solvent for

the polyisocyanate, such as a low polarity solvent or a fluid in a critical state; however, in most cases, a wiped film evaporation is employed. By wiped film evaporation, the thermal history experienced by the polyisocyanate can be suppressed, so that the heat deterioration of the polyisocyanate is suppressed. Therefore, the wiped film evaporation is suitable for removing a diisocyanate (which is a low boiling point substance) from a polyisocyanate which has a high viscosity.

In the production of a polyisocyanate in which the low boiling point substances (such as a diisocyanate) is evaporated and separated from a mixture of a polyisocyanate and a diisocyanate by wiped film evaporation, when a large amount of the above-mentioned mixture is fed to the evaporator for wiped film evaporation, the polyisocyanate (which is a high boiling point substance) may be contained in the separated low boiling point substances. This phenomenon is known as an "entrainment". The entrainment is disadvantageous not only in that the yield of the final product is lowered, but also in that, when a polyisocyanate is produced from the recovered diisocyanate, the viscosity of the polyisocyanate becomes disadvantageously high, so that it becomes necessary to change the conditions for pro-

ducing the polyisocyanate.

SUMMARY OF THE INVENTION

In this situation, the present inventors have made extensive and intensive studies with a view toward developing a biuret polyisocyanate which is free from discoloration and turbidity, particularly the turbidity which occurs during the storage at low temperatures.

As a result, it has unexpectedly been found that, when the content of an urea dimer (one of the urea bond-containing compounds) in a biuret polyisocyanate is reduced to a level not more than 0.5 % by weight, it becomes possible to prevent the polyisocyanate from becoming turbid during the storage at low temperatures.

Further, the present inventors have found that, when a biuret polyisocyanate is produced by a method in which a first reaction between a diisocyanate and a biuretizing agent is conducted to thereby obtain a first reaction mixture, and then, after adjusting the unreacted diisocyanate concentration of the first reaction mixture to a level in the range of from 3 to 20 % by weight, the first reaction mixture is subjected to a second reaction, the rate of the reduction of the urea dimer is improved.

In addition, the present inventors have also found

that the presence of a gas dissolved in the reaction mixture is causative of the entrainment.

The present invention has been completed, based on these novel findings.

5 Accordingly, it is an object of the present invention to provide a biuret polyisocyanate which is free from both discoloration and turbidity, and exhibits high stability at low temperatures.

10 It is another object of the present invention to provide a process for effectively and efficiently producing a biuret polyisocyanate which is free from both discoloration and turbidity, and exhibits high stability at low temperatures.

15 The foregoing and other objects, features and advantages of the present invention will be apparent from the following detailed description and appended claims, taken in connection with the accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWING

20 In the drawing:

Fig. 1 is a diagram showing the system employed for producing a biuret polyisocyanate in Examples 4 and 5, and Reference Examples 1 and 2.

25 Description of Reference Numerals

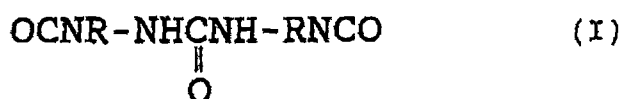
- 1: Introduction pipe for a biuretizing agent
2: Introduction pipe for a raw material
3, 6: Agitator
3A, 6A: Heating jacket
5 4: First reactor
5, 8, 12: Pipe
7: Second reactor
9, 10, 11: Pipe reactor
9A, 10A, 11A: Jacket
10 13, 15, 17: Exhaust pipe
14, 16, 18: Condenser
19: Intermediate tank
20: Degassing apparatus
21, 24: Wiped film evaporator
15 22, 25, 26: Withdrawal pipe
23: Heating vessel

DETAILED DESCRIPTION OF THE INVENTION

According to the present invention, there is
20 provided a biuret polyisocyanate obtained by reacting
at least one diisocyanate selected from the group con-
sisting of an aliphatic diisocyanate and an alicyclic
diisocyanate with a biuretizing agent,

the biuret polyisocyanate having the following
25 characteristics (1) and (2):

(1) the biuret polyisocyanate contains urea bond
-containing compounds including an urea dimer which are
the intermediate products of the reaction between the
diisocyanate and the biuretizing agent, wherein the
urea dimer is represented by the following formula (I):



wherein, each R independently represents an
aliphatic group or an alicyclic group derived
from the diisocyanate, and

the biuret polyisocyanate has an urea dimer content of
not more than 0.5 % by weight, based on the total
weight of the biuret polyisocyanate and the urea bond
-containing compounds including the urea dimer, wherein
the urea dimer content is defined as the percent of the
area of a peak ascribed to the urea dimer in a gel per-
meation chromatogram of the biuret polyisocyanate con-
taining the unreacted diisocyanate and the urea bond
-containing compounds, based on the total area of all
peaks, exclusive of a peak ascribed to the unreacted
diisocyanate, in the gel permeation chromatogram; and

(2) the biuret polyisocyanate exhibits a transmit-
tance of at least 90 % as measured at 430 nm using a

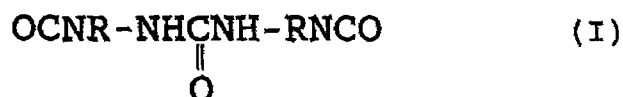
cell having a length of 2 cm.

For easy understanding of the present invention,
the essential features and various embodiments of the
present invention are enumerated below.

1. A biuret polyisocyanate obtained by reacting at
least one diisocyanate selected from the group consist-
ing of an aliphatic diisocyanate and an alicyclic di-
isocyanate with a biuretizing agent,

the biuret polyisocyanate having the following
characteristics (1) and (2):

(1) the biuret polyisocyanate contains urea bond-
-containing compounds including an urea dimer which are
the intermediate products of the reaction between the
diisocyanate and the biuretizing agent, wherein the
urea dimer is represented by the following formula (I):



wherein, each R independently represents an
aliphatic group or an alicyclic group derived
from the diisocyanate, and
the biuret polyisocyanate has an urea dimer content of

not more than 0.5 % by weight, based on the total weight of the biuret polyisocyanate and the urea bond-containing compounds including the urea dimer, wherein the urea dimer content is defined as the percent of the area of a peak ascribed to the urea dimer in a gel permeation chromatogram of the biuret polyisocyanate containing the unreacted diisocyanate and the urea bond-containing compounds, based on the total area of all peaks, exclusive of a peak ascribed to the unreacted diisocyanate, in the gel permeation chromatogram; and

(2) the biuret polyisocyanate exhibits a transmittance of at least 90 % as measured at 430 nm using a cell having a length of 2 cm.

2. A process for producing a biuret polyisocyanate, which comprises:

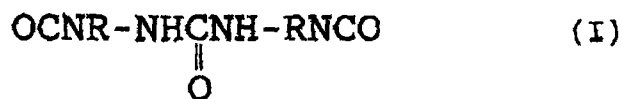
(a) conducting a first reaction between at least one diisocyanate selected from the group consisting of an aliphatic diisocyanate and an alicyclic diisocyanate and a biuretizing agent, wherein the molar ratio of the diisocyanate to the biuretizing agent is from 4 to 40, thereby obtaining a first reaction mixture containing the unreacted diisocyanate and a biuret polyisocyanate;

(b) adjusting the concentration of the unreacted diisocyanate in the first reaction mixture to a level

in the range of from 3 to 20 % by weight, based on the total weight of the unreacted diisocyanate and the biuret polyisocyanate;

(c) heating the first reaction mixture, which has been adjusted with respect to the unreacted diisocyanate concentration in step (b), at a temperature of from 110 to 160 °C to thereby perform a second reaction, thus producing a biuret polyisocyanate having the following characteristics (1) and (2):

(1) the biuret polyisocyanate contains urea bond-containing compounds including an urea dimer which are the intermediate products of the first reaction, wherein the urea dimer is represented by the following formula (I):



wherein, each R independently represents an aliphatic group or an alicyclic group derived from the diisocyanate, and

the biuret polyisocyanate has an urea dimer content of not more than 0.5 % by weight, based on the total weight of the biuret poly-

isocyanate and the urea bond-containing compounds including the urea dimer, wherein the urea dimer content is defined as the percent of the area of a peak ascribed to the urea dimer in a gel permeation chromatogram of the biuret polyisocyanate containing the unreacted diisocyanate and the urea bond-containing compounds, based on the total area of all peaks, exclusive of a peak ascribed to the unreacted diisocyanate, in the gel permeation chromatogram, and

(2) the biuret polyisocyanate exhibits a transmittance of at least 90 % as measured at 430 nm using a cell having a length of 2 cm; and

(d) isolating the biuret polyisocyanate from the second reaction mixture obtained in step (c).

3. The process according to item 2, wherein, in step (d), the isolation of the biuret polyisocyanate is performed by removing the unreacted diisocyanate from the second reaction mixture.

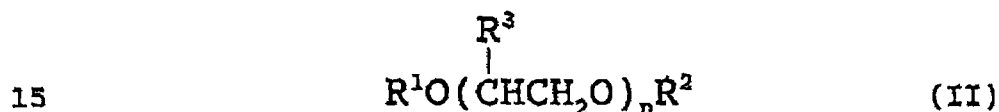
4. The process according to item 2 or 3, wherein the at least one diisocyanate is a hexamethylene-1,6-diiso-

diisocyanate.

5. The process according to any one of items 2 to 4, wherein the biuretizing agent is water.

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6. The process according to item 5, wherein, in step (a), the first reaction between the diisocyanate and water is performed in the presence of at least one solvent selected from the group consisting of a compound represented by the following formula (II) and an alkyl phosphate:



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wherein each of R^1 and R^2 independently represents an alkyl or an acyl group having 1 to 4 carbon atoms, R^3 represents a methyl group or a hydrogen atom, and n represents an integer of 1 or 2.

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7. The process according to any one of items 2 to 6, wherein, in step (b), the adjustment of the unreacted diisocyanate concentration of the first reaction mixture is performed by wiped film evaporation.

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8. The process according to item 7, wherein the first reaction mixture is degassed before being subjected to wiped film evaporation.

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9. The process according to any one of items 3 to 8, wherein, in step (d), the removal of the unreacted diisocyanate from the second reaction mixture is performed by wiped film evaporation.

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10. The process according to item 9, wherein the second reaction mixture is degassed before being subjected to the wiped film evaporation.

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11. The process according to any one of items 2 to 10, wherein step (a) comprises continuously conducting the following substeps (i) and (ii):

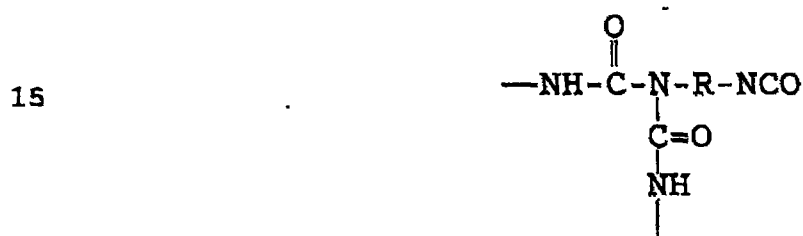
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(i) agitating a mixture of the diisocyanate and the biuretizing agent to conduct a reaction between the diisocyanate and the biuretizing agent in a homogeneous system of the mixture, thereby obtaining an intermediate reaction mixture; and

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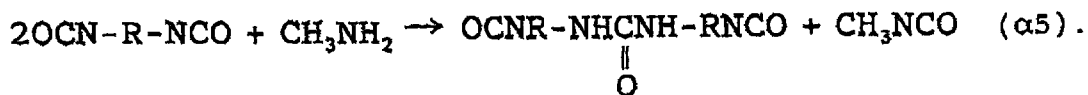
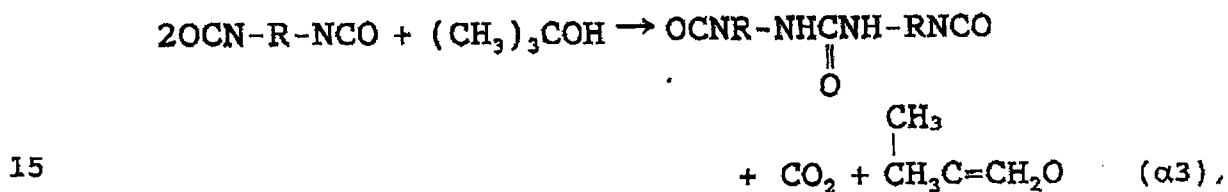
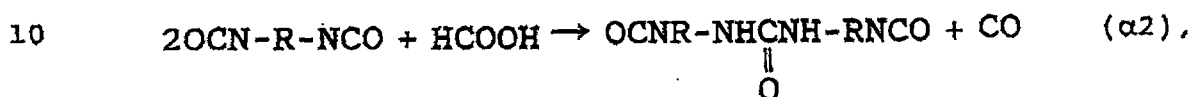
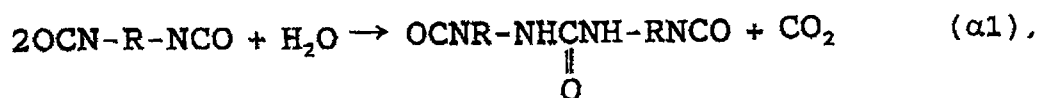
(ii) feeding the intermediate reaction mixture to a pipe reactor to thereby conduct a further reaction between the diisocyanate and the biuretizing agent in a

5 The polyisocyanate of the present invention is a biuret structure-containing polyisocyanate which is obtained by reacting at least one diisocyanate selected from the group consisting of an aliphatic diisocyanate and an alicyclic diisocyanate with a biuretizing agent. Illustratively stated, the polyisocyanate of the present invention is a polyisocyanate containing a biuret structure represented by the following formula:



In the present invention, such a biuret structure
-containing polyisocyanate is referred to as a "biuret
polyisocyanate". The reaction between the diisocyanate
and the biuretizing agent for obtaining the biuret
polyisocyanate comprises a reaction between two isocya-
nate groups and a biuretizing agent to form an urea
bond, and a reaction between the formed urea bond and

an isocyanate group to form a biuret structure. There is no particular limitation with respect to the reaction for forming an urea bond. As examples of such a reaction, there can be mentioned reactions represented by the following formulae (α1) to (α5):



A urea bond-containing dimer of the diisocyanate, which is produced in the reactions shown above, is the "urea

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The process for producing the biuret polyisocyanate involves not only the urea dimer-forming reaction, such as the reactions of formulae (α1) to (α5) above, but also various side reactions which form urea bond-containing compounds other than the urea dimer. Examples of such urea bond-containing compounds (other than the urea dimer) include a compound represented by the following formula:



wherein n is an integer of 2 or more,

5 and a compound having a structure wherein at least one of the terminal isocyanate groups of the biuret polyisocyanate shown in formula (β) above is converted into an urea bond.

It is known that the presence of the urea dimer in
 10 the biuret polyisocyanate is one of the causes of the turbidity of the biuret polyisocyanate, but the present inventors have for the first time found that, by decreasing the urea dimer content of the biuret polyisocyanate, it becomes possible to prevent the biuret
 15 polyisocyanate from becoming turbid during the storage at low temperatures (this occurrence of turbidity during the storage at low temperatures has been considered to be due to the increase in the concentration of diisocyanate in the biuret polyisocyanate). The urea dimer
 20 mer content of the biuret polyisocyanate of the present invention is reduced to a level of not more than 0.5 % by weight, preferably not more than 0.3 % by weight, based on the total weight of the biuret polyisocyanate and the urea bond-containing compounds including the
 25 urea dimer. When the urea dimer content of the biuret

polyisocyanate exceeds 0.5 % by weight, the biuret polyisocyanate becomes turbid when it is stored at about 5 °C or less.

5 The urea dimer content of the biuret polyisocyanate is defined as the percent of the area of a peak ascribed to the urea dimer in a gel permeation chromatogram of the biuret polyisocyanate containing the unreacted diisocyanate and the urea bond-containing compounds, based on the total area of all peaks, exclusive
10 of a peak ascribed to the unreacted diisocyanate (and also exclusive of a peak ascribed to the reaction solvent when the reaction solvent is used), in the gel permeation chromatogram. In the present invention, the gel permeation chromatogram used to determine the urea
15 dimer content is a gel permeation chromatogram obtained by subjecting a biuret polyisocyanate to gel permeation chromatography under the conditions described in the Examples of the present specification.

20 Further, the biuret polyisocyanate of the present invention exhibits a transmittance of at least 90 % as measured at 430 nm using a cell having a length of 2 cm. Such high transmittance means that the biuret polyisocyanate is not discolored. In a conventional method for producing a biuret polyisocyanate, a biuret polyisocyanate is heated for a long time to prevent the
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polyisocyanate from being turbid during the storage (especially, during the low temperature storage), so that the polyisocyanate is likely to suffer discoloration. On the other hand, in the production of the biuret polyisocyanate of the present invention, the urea dimer contained in the biuret polyisocyanate, which causes the turbidity of the biuret polyisocyanate, is eliminated without heating the polyisocyanate for a long time, so that the biuret polyisocyanate of the present invention exhibits high transmittance.

With respect to the process for producing the biuret polyisocyanate of the present invention, it is preferred to employ the process of the present invention. By the process of the present invention, it becomes possible to produce a biuret polyisocyanate which is substantially free of not only the urea dimer but also other urea bond-containing compounds and which exhibits high transmittance. Such a biuret polyisocyanate exhibits excellent stability at low temperatures and is free from both discoloration and turbidity.

The process of the present invention comprises the following steps (a), (b), (c) and (d):

(a) conducting a first reaction between at least one diisocyanate selected from the group consisting of an aliphatic diisocyanate and an alicyclic diisocyanate

and a biuretizing agent, wherein the molar ratio of the diisocyanate to the biuretizing agent is from 4 to 40, thereby obtaining a first reaction mixture containing the unreacted diisocyanate and a biuret polyisocyanate;

5 (b) adjusting the concentration of the unreacted diisocyanate in the first reaction mixture to a level in the range of from 3 to 20 % by weight, based on the total weight of the unreacted diisocyanate and the biuret polyisocyanate;

10 (c) heating the first reaction mixture, which has been adjusted with respect to the unreacted diisocyanate concentration in step (b), at a temperature of from 110 to 160 °C to thereby perform a second reaction, thus producing a biuret polyisocyanate of the present invention; and

15 (d) isolating the biuret polyisocyanate from the second reaction mixture obtained in step (c).

The diisocyanate used as a raw material in the process of the present invention is at least one diisocyanate selected from the group consisting of an

20 aliphatic diisocyanate and an alicyclic diisocyanate. As an aliphatic diisocyanate, a C₄-C₃₀ aliphatic diisocyanate is preferred, and as an alicyclic diisocyanate, a C₈-C₃₀ alicyclic diisocyanate is preferred. Specific

25 examples of diisocyanates include tetramethylene-1,4

-diisocyanate, pentamethylene-1,5-diisocyanate, hexamethylene-1,6-diisocyanate, 2,2,4-trimethylhexamethylene-1,6-diisocyanate, lysine diisocyanate, isophorone diisocyanate, 1,3-bis(isocyanatemethyl)cyclohexane and 4,4'-dicyclohexylmethane diisocyanate. Such diisocyanates can be used individually or in combination. Among them, hexamethylene-1,6-diisocyanate (hereinbelow, frequently referred to simply as "HMDI") and isophorone diisocyanate (hereinbelow, frequently referred to simply as "IPDI"), which have been widely used in industry, are preferred, and HMDI is most preferred.

Examples of biuretizing agents used in the process of the present invention include water, a monovalent tertiary alcohol, formic acid, hydrogen sulfide, an organic primary monoamine and an organic primary diamine. Among them, water is preferred because the use of water not only enables the production of a low viscosity polyisocyanate, but also does not cause the by-production of a flammable gas, a toxic gas, a monoisocyanate and the like.

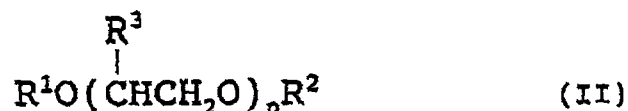
In step (a) of the process of the present invention, the diisocyanate and the biuretizing agent, which are subjected to the first reaction, are used in a molar ratio (of the diisocyanate to the biuretizing

agent) of at least 4, preferably at least 5, and not more than 40, preferably not more than 30, more preferably not more than 20. When the molar ratio of the diisocyanate to the biuretizing agent is less than 4, the viscosity of the produced polyisocyanate becomes disadvantageously high, and such a high viscosity polyisocyanate cannot be used for obtaining an excellent coating composition, and the like. Illustratively stated, a high viscosity polyisocyanate has a low compatibility with a polyol (which is a main agent of a coating composition using a polyisocyanate as a curing agent), so that, when a coating composition is prepared using such a high viscosity polyisocyanate, the solids content of the coating composition becomes low. When the molar ratio of the diisocyanate to the biuretizing agent is more than 40, the yield of the polyisocyanate is lowered, which is disadvantageous from the viewpoint of productivity and economy.

In the process of the present invention, when water is used as a biuretizing agent, it is preferred to conduct the first reaction between a diisocyanate and water in the presence of a solvent. It is preferred to use a reaction solvent capable of dissolving both the diisocyanate and water, since a homogenous reaction system can be obtained under reaction conditions used

in the process of the present invention, so that the formation of by-products, such as urea bond-containing compounds, can be suppressed. Therefore, when a solvent is used in step (a), it is preferred that the solvent is used in an amount which is sufficient to form a homogeneous reaction system.

With respect to the solvent used in step (a), it is preferred that the solubility of water (as a biuretizing agent) in the solvent is 0.5 % by weight or more. When the solubility of water is lower than 0.5 % by weight, a large amount of solvent must be added to the reaction system. The use of a large amount of a solvent necessitates extra costs for separating and recovering the solvent after the reaction and, hence, is economically disadvantageous. In addition, from the viewpoint of ease in separating and recovering the unreacted diisocyanate, it is preferred that the boiling point of the solvent is lower than that of the diisocyanate. Specifically, the solvent preferably used in the present invention is at least one solvent selected from the group consisting of a compound represented by the following formula (II) and an alkyl phosphate:



5 wherein each of R^1 and R^2 independently represents an alkyl or an acyl group having 1 to 4 carbon atoms, R^3 represents a methyl group or a hydrogen atom, and n represents an integer of 1 or 2.

10 Both the compound represented by formula (II) above and the alkyl phosphate do not react with an isocyanate group. In addition, both of the above compounds are hydrophilic, so they can be favorably used in a reaction system where the biuretizing agent is water.

15 Examples of compounds represented by formula (II) above include compounds which are used as ethylene glycol-type solvents and compounds which are used as propylene glycol-type solvents. Examples of ethylene glycol-type solvents include ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, ethylene glycol mono-*n*-propyl ether acetate, ethylene glycol monoisopropyl ether acetate, ethylene glycol mono-*n*-butyl ether acetate, ethylene glycol diacetate, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol di-*n*-propyl ether, ethylene glycol diisopropyl ether, ethylene glycol di-*n*-butyl ether,

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ethylene glycol methyl ethyl ether, ethylene glycol methyl isopropyl ether, ethylene glycol methyl n-butyl ether, ethylene glycol ethyl n-propyl ether, ethylene glycol ethyl isopropyl ether, ethylene glycol ethyl n-butyl ether, ethylene glycol n-propyl n-butyl ether, ethylene glycol isopropyl n-butyl ether, diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, diethylene glycol mono-n-propyl ether acetate, diethylene glycol monoisopropyl ether acetate, diethylene glycol mono-n-butyl ether acetate, diethylene glycol diacetate, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol di-n-propyl ether, diethylene glycol diisopropyl ether, diethylene glycol di-n-butyl ether, diethylene glycol methyl ethyl ether, diethylene glycol methyl isopropyl ether, diethylene glycol methyl n-propyl ether, diethylene glycol methyl n-butyl ether, diethylene glycol ethyl isopropyl ether, diethylene glycol ethyl n-propyl ether, diethylene glycol ethyl n-butyl ether, diethylene glycol n-propyl n-butyl ether, and diethylene glycol isopropyl n-butyl ether. Among these compounds, preferred are ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, ethylene glycol diacetate, and diethylene glycol dimethyl ether.

Examples of propylene glycol-type solvents include propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol mono-n-propyl ether acetate, propylene glycol monoisopropyl ether acetate, propylene glycol mono-n-butyl ether acetate, propylene glycol diacetate, propylene glycol dimethyl ether, propylene glycol diethyl ether, propylene glycol di-n-propyl ether, propylene glycol diisopropyl ether, propylene glycol di-n-butyl ether, propylene glycol methyl ethyl ether, propylene glycol methyl isopropyl ether, propylene glycol methyl n-butyl ether, propylene glycol ethyl n-propyl ether, propylene glycol ethyl isopropyl ether, propylene glycol ethyl n-butyl ether, propylene glycol n-propyl n-butyl ether, propylene glycol isopropyl n-butyl ether, dipropylene glycol monomethyl ether acetate, dipropylene glycol monoethyl ether acetate, dipropylene glycol mono-n-propyl ether acetate, dipropylene glycol monoisopropyl ether acetate, dipropylene glycol mono-n-butyl ether acetate, dipropylene glycol diacetate, dipropylene glycol dimethyl ether, dipropylene glycol diethyl ether, dipropylene glycol di-n-propyl ether, dipropylene glycol diisopropyl ether, dipropylene glycol di-n-butyl ether, dipropylene glycol methyl ethyl ether, dipropylene glycol methyl isopropyl ether, dipropylene glycol methyl n-propyl ether, dipro-

pylene glycol methyl n-butyl ether, dipropylene glycol ethyl isopropyl ether, dipropylene glycol ethyl n-propyl ether, dipropylene glycol ethyl n-butyl ether, dipropylene glycol n-propyl n-butyl ether and dipropylene glycol isopropyl n-butyl ether. Among these compounds, preferred are propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol diacetate and dipropylene glycol dimethyl ether.

Examples of alkyl phosphates include trimethyl phosphate, triethyl phosphate, tripropyl phosphate and tributyl phosphate. Among these alkyl phosphates, preferred are trimethyl phosphate and triethyl phosphate.

The above-mentioned solvents can be used individually or in combination. From the viewpoint of suppressing the increase in the diisocyanate concentration of the obtained polyisocyanate during the long term storage, the use of a mixed solvent is preferred in the process of the present invention. Specifically, when an ethylene glycol-type solvent and an alkyl phosphate are used in combination, it is preferred that the weight ratio of the ethylene glycol-type solvent to the alkyl phosphate is in the range of from 3/7 to 9/1. It is preferred that a mixed solvent as mentioned above is used in an amount of from 20 to 50 % by weight, based

on the total weight of the diisocyanate as a raw material and the mixed solvent.

In the process of the present invention, an OH-acidic compound, such as di(2-ethylhexyl) phosphate described in Unexamined Japanese Patent Application Laid-Open Specification No. 8-225511 (corresponding to U.S. Patent No. 5,641,851), may be added to the reaction system. When an OH-acidic compound is added to the reaction system, the rate of the biuretizing reaction is increased, and it becomes possible to suppress the increase in the diisocyanate concentration of the polyisocyanate during the long term storage.

In step (a) of the process of the present invention, the first reaction is conducted between a diisocyanate and a biuretizing agent, thereby obtaining a first reaction mixture containing the unreacted diisocyanate and a biuret polyisocyanate. In the first reaction, the urea bond-containing compounds including the urea dimer are formed by the reaction between the isocyanate group of the diisocyanate and the biuretizing agent, and in turn the urea bonds in the urea bond-containing compounds are converted into the biuret structures by a reaction between the urea bond-containing compounds and the isocyanate groups, thereby obtaining a biuret polyisocyanate. It is preferred

that the first reaction is conducted at a temperature of from 70 to 200 °C, more preferably from 90 to 180 °C. When the first reaction is conducted at a temperature lower than 70 °C, it becomes difficult to advance the
5 above-mentioned reaction. On the other hand, when the first reaction is conducted at a temperature higher than 200 °C, the polyisocyanate is likely to suffer discoloration.

The first reaction between the diisocyanate and
10 the biuretizing agent in step (a) may be performed in either a batchwise manner or a continuous manner. However, from the viewpoint of productivity and the like, it is preferred to conduct the first reaction in a continuous manner. Specifically, it is preferred that
15 step (a) is performed by the continuous method described in Examined Japanese Patent Application Publication No. 62-41496, which comprises continuously conducting the following substeps (i) and (ii):

(i) agitating a mixture of a diisocyanate and a
20 biuretizing agent to conduct a reaction between the diisocyanate and the biuretizing agent in a homogeneous system of the mixture, thereby obtaining an intermediate reaction mixture; and

(ii) feeding the intermediate reaction mixture to
25 a pipe reactor to thereby conduct a further reaction

between the diisocyanate and the biuretizing agent in a piston flow, thereby obtaining a first reaction mixture. When the reaction is conducted using a pipe reactor in a piston flow, the whole of the reaction mixture
5 resides in the pipe reactor, and thus, the urea bond-containing compounds easily react with the isocyanate groups. As a result, the content of the urea bond-containing compounds can be remarkably decreased.

The reaction in substep (i) can be conducted using,
10 for example, an agitation vessel-type reactor, under the reaction conditions described above for step (a). In the subsequent substep (ii) conducted in a pipe reactor, the reaction is generally conducted under an atmospheric pressure at 80 to 180 °C, preferably 90 to
15 160 °C. The reaction time (that is, residence time) is generally 30 to 240 minutes, preferably 30 to 120 minutes, and the flow rate of the reaction mixture is generally 0.5 to 5 m/hr, preferably 0.5 to 2 m/hr.

In step (b) of the process of the present invention,
20 tion, the concentration of the unreacted diisocyanate in the first reaction mixture obtained in step (a) is adjusted to a specific level. The unreacted diisocyanate concentration is the amount (% by weight) of the unreacted diisocyanate, based on the total weight of
25 the unreacted diisocyanate and the polyisocyanate

(which contains the urea bond-containing compounds including the urea dimer). Step (b) is conducted so as to adjust the unreacted diisocyanate concentration of the first reaction mixture to a level in the range of from 3 to 20 % by weight, preferably 3 to 15 % by weight, more preferably 3 to 10 % by weight. When the diisocyanate concentration is outside the above-mentioned range, the rate of the reduction of the urea dimer is lowered in the second reaction conducted in the subsequent step (c). The process of the present invention has been developed, based on a surprising finding that the rate of the reduction of the urea dimer increases when the second reaction is conducted in a reaction system where the unreacted diisocyanate concentration is in the above-mentioned specific range. As explained in detail above, the urea bond in the urea dimer is reacted with an isocyanate group to convert the urea bond into a biuret bond, thereby eliminating the urea dimer contained in the polyisocyanate. In general, it was conventionally considered that the higher the isocyanate group concentration of the reaction system, the faster the reduction rate of the urea dimer content, so that the urea dimer content of a polyisocyanate can be rapidly reduced when the reaction is conducted in a reaction system having a high unre-

acted diisocyanate concentration. However, according to the studies of the present inventors, it has been found that, in the reaction system having a low unreacted diisocyanate concentration of from 3 to 20 % by weight, the rate of the reduction of the urea dimer is high, as compared to that in the reaction system having a high unreacted diisocyanate concentration exceeding 20 % by weight.

In general, since the first reaction mixture contains a large amount of the unreacted diisocyanate, an excess of the unreacted diisocyanate is removed from the first reaction mixture. However, when the unreacted diisocyanate concentration of the first reaction mixture is lower than the above-mentioned range, a diisocyanate is added to the first reaction mixture, thereby adjusting the unreacted diisocyanate concentration of the reaction mixture to a desired level. The removal of the unreacted diisocyanate for the adjustment of the unreacted diisocyanate concentration of the first reaction mixture can be performed by extraction with a poor solvent for the polyisocyanate, such as a low polarity solvent or a fluid in a critical state, or by distillation. However, in the process of the present invention, it is preferred that the removal of the unreacted diisocyanate is performed by distillation by

means of wiped film evaporation. In the wiped film evaporation, the contents in the evaporator are forcibly treated so as to form a thin film, thereby facilitating the evaporation of the diisocyanate (which has a low boiling point), so that the diisocyanate can be efficiently separated from the polyisocyanate.

In the process of the present invention, it is preferred that the first reaction mixture is degassed before being subjected to the wiped film evaporation. When the polyisocyanate is produced using water as a biuretizing agent, carbon dioxide (CO_2) gas is generated as a by-product gas. Conventionally, the CO_2 gas was considered to be substantially insoluble in the reaction mixture, but actually, a part of the by-produced CO_2 gas is dissolved in the reaction mixture. The amount of the gas dissolved in the reaction mixture varies depending on the reaction conditions, but is generally in the range of from 0.05 to 0.4 Nml/ml (wherein "Nml" means ml as measured under the normal temperature and pressure conditions (0°C , 1 atm)). When the first reaction mixture containing the gas dissolved therein is fed to the wiped film evaporator which is operated under a vacuum condition, the following unfavorable phenomenon occurs. The gas dissolved in the first reaction mixture vaporizes and expands in the

wiped film evaporator and causes a part of the first reaction mixture to be scattered onto a cooling apparatus (used for condensing a vapor composed of the unreacted diisocyanate). The thus scattered first reaction mixture adheres to the cooling apparatus. When the separation and recovery of the unreacted diisocyanate is performed using such a cooling apparatus, the adhered first reaction mixture is caused to be mixed with the recovered unreacted diisocyanate. This phenomenon markedly occurs when the amount of the first reaction mixture fed to the wiped film evaporator is large, leading to a lowering of the yield of the biuret polyisocyanate to disadvantage. In addition, the biuret polyisocyanate contained in the recovered diisocyanate causes the polyisocyanate prepared from the recovered diisocyanate to have a high viscosity, thereby unfavorably affecting the physical properties of the polyisocyanate.

The above-mentioned unfavorable phenomenon also markedly occurs during the reaction for producing the biuret polyisocyanate, when the biuretizing agent (such as water) used is a compound which generates a by-product gas (such as carbon dioxide). However, the amount of the biuret polyisocyanate contained in the recovered diisocyanate varies depending on the reaction

conditions, but may sometimes be as much as several weight percent, based on the weight of the recovered diisocyanate.

In a preferred mode of the process of the present invention, in view of the above-mentioned finding about the phenomena caused by the by-product gas, the first reaction mixture is degassed to remove the gas dissolved therein before being subjected to the wiped film evaporation, so as to prevent the incorporation of the polyisocyanate into the recovered diisocyanate. The degassing of the first reaction mixture can be performed, for example, by the following method. The system used for the production of the polyisocyanate is provided with a degassing apparatus having the same degree of vacuum as in the wiped film evaporator. The first reaction mixture is fed to the degassing apparatus at the upper portion thereof, so that the first reaction mixture is degassed as it falls from the upper portion of the degassing apparatus. When the degassing of the first reaction mixture is incomplete at the time the first reaction mixture has reached the surface of the liquid phase at the lower portion of the degassing apparatus, the liquid phase becomes foaming at the surface thereof, so that the first reaction mixture is degassed. In this method, it is not preferred to feed

the first reaction mixture directly to the lower portion of the degassing apparatus containing the liquid phase, since the degassing of the first reaction mixture may become incomplete. The degassing apparatus may be equipped with a stirrer. However, since the degassing apparatus is operated under vacuum conditions, the structure of the degassing apparatus becomes complicated when it is equipped with a stirrer. Therefore, the use of such a complicated apparatus may increase a cost.

It is preferred that the temperature of the first reaction mixture to be subjected to the wiped film evaporation is not higher than the boiling point of the first reaction mixture. When the temperature of the first reaction mixture is higher than the boiling point of the first reaction mixture, an unfavorable entrainment is likely to occur when it is fed to the wiped film evaporator.

The removal of the diisocyanate from the first reaction mixture can be performed in a single stage using a single wiped film evaporator, or alternatively, in two stages using two wiped film evaporators connected in series. When the wiped film evaporation is conducted in two stages, the degassing of the first reaction mixture can be performed prior to each stage.

In step (c) of the process of the present invention, the first reaction mixture is heated so as to conduct a second reaction for decreasing the urea dimer content of the biuret polyisocyanate, thus obtaining the biuret polyisocyanate of the present invention. In the second reaction, the urea dimer formed in the first reaction is reacted with the isocyanate group to convert the urea bond into the biuret structure, thereby eliminating the urea dimer. In step (c), the first reaction mixture which has been adjusted with respect to the unreacted diisocyanate concentration is heated at 110 to 160 °C, preferably 110 to 140 °C. When the reaction temperature is lower than 110 °C, the rate of the reduction of the urea dimer is disadvantageously lowered. When the reaction temperature is higher than 160 °C, the biuret polyisocyanate is likely to suffer discoloration. The heating in step (c) is conducted so that the urea dimer content of the resultant biuret polyisocyanate becomes not more than 0.5 % by weight, but it is important that the heating is conducted so that the biuret polyisocyanate also exhibits a transmittance of at least 90 % as measured at 430 nm using a cell having a length of 2 cm. When the transmittance is less than 90 %, this means that the final polyisocyanate is discolored. In order to obtain a biuret

polyisocyanate which exhibits a transmittance of at least 90 %, the heating is conducted at a temperature within the above-mentioned range for 5 to 90 minutes, preferably 5 to 60 minutes, more preferably 5 to 30 minutes. When the heating time is shorter than the above-mentioned range, the reduction of the urea dimer becomes unsatisfactory. When the heating time is longer than the above-mentioned range, the transmittance of the biuret polyisocyanate is lowered and, hence, the biuret polyisocyanate suffers discoloration.

Step (c) can be conducted in either a batchwise manner or a continuous manner. Since the reduction of the urea dimer proceeds like the zeroth-order reaction, the reaction times (residence times) for the batchwise reaction and the continuous reaction in step (c) may be substantially the same. The reaction time employed in step (c) is preferably 5 to 90 minutes, more preferably, 5 to 60 minutes, most preferably 5 to 30 minutes.

In step (d), the biuret polyisocyanate obtained in step (c) is isolated from the second reaction mixture. It is preferred that the isolation of the biuret polyisocyanate is performed by removing the unreacted diisocyanate from the second reaction mixture. The removal of the unreacted diisocyanate in step (d) can be performed by extraction with a poor solvent for the

polyisocyanate, such as a low polarity solvent or a fluid in a critical state, or by distillation, but it is preferred to remove the unreacted diisocyanate by wiped film evaporation in the same manner as described for the adjustment of the unreacted diisocyanate concentration in step (b). In addition, as in the case of step (b), it is preferred that the second reaction mixture is degassed before being subjected to the wiped film evaporation.

10 The process of the present invention for producing the biuret polyisocyanate in a continuous manner is described in detail below, referring to the system shown in Fig. 1.

15 In the production of a biuret polyisocyanate using the system shown in Fig. 1, a feedstock diisocyanate is continuously fed to first reactor 4 through inlet pipe 2 at a constant flow rate. Simultaneously with the feeding of the feedstock, a biuretizing agent is continuously fed to first reactor 4 through inlet
20 pipe 1 at a constant flow rate. First reactor 4 is a complete mixing-type agitation vessel equipped with agitator 3 and heating jacket 3A. In first reactor 4, a reaction between the diisocyanate and the biuretizing agent is conducted, thereby obtaining a first intermediate reaction mixture. The gas generated during the
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reaction is removed through exhaust pipe 13 and condenser 14. The first intermediate reaction mixture is fed to second reactor 7 through pipe 5. Second reactor 7 is also a complete mixing-type agitation vessel
5 equipped with agitator 6 and heating jacket 6A. A further reaction is conducted in second reactor 7, thereby obtaining a second intermediate reaction mixture, and the gas generated during the reaction is removed through exhaust pipe 15 and condenser 16 (corresponding
10 to substep (i) of step (a)). The second intermediate reaction mixture is fed through pipe 8 to a serially connected pipe reactors 9, 10 and 11. Pipe reactors 9, 10 and 11 are equipped with jackets 9A, 10A and 11A, respectively. Still a further reaction is conducted in
15 the pipe reactors, thereby obtaining a first reaction mixture (corresponding to substep (ii) of step (a)). A small amount of gas generated during the reaction is removed through exhaust pipe 17 and condenser 18. The first reaction mixture is continuously withdrawn from
20 the pipe reactors and is introduced into intermediate tank 19 through pipe 12. Next, the first reaction mixture is fed to degassing apparatus 20 to degas the first reaction mixture. The degassed first reaction mixture is fed to wiped film evaporator 21, in which the
25 unreacted diisocyanate concentration in the first reac-

tion mixture is adjusted (corresponding to step (b)). The unreacted diisocyanate which is removed to adjust the unreacted diisocyanate concentration of the first reaction mixture is recovered through withdrawal
5 pipe 22, and the first reaction mixture which has been adjusted with respect to the unreacted diisocyanate concentration is fed to heating vessel 23. In heating vessel 23, the first reaction mixture is heated to perform a second reaction, to thereby obtain a second re-
10 action mixture (corresponding to step (c)). Subsequently, the second reaction mixture is fed to wiped film evaporator 24, in which the unreacted diisocyanate in the second reaction mixture is removed through withdrawal pipe 25, to thereby isolate the biuret polyiso-
15 cyanate from the second reaction mixture. The isolated biuret polyisocyanate is withdrawn from withdrawal pipe 26 (corresponding to step (d)).

The biuret polyisocyanate obtained by the process of the present invention not only has a very low con-
20 tent with respect to the urea dimer (which is causative of the turbidity of the biuret polyisocyanate, which occurs during the storage at low temperatures), but also is colorless, transparent. Specifically, the urea dimer content of the biuret polyisocyanate is not more
25 than 0.5 % by weight, preferably not more than 0.3 % by

weight, and the transmittance of the biuret polyisocyanate is at least 90 %. In addition, the biuret polyisocyanate obtained by the process of the present invention contains substantially no diisocyanate, and
5 generally, has an unreacted diisocyanate concentration of not more than 5 % by weight, preferably not more than 2 % by weight, more preferably not more than 1 % by weight.. With respect to the biuret polyisocyanate, the isocyanate group content is generally 3 to 25 % by
10 weight; the number average molecular weight is generally 550 to 1000; and the viscosity is generally 500 to 50,000 mPa's at 25 °C.

BEST MODE FOR CARRYING OUT THE INVENTION

Hereinbelow, the present invention will be described in more detail with reference to the following Examples, Comparative Examples and Reference Examples, but they should not be construed as limiting the scope of the present invention.

In the following Examples, Comparative Examples and Reference Examples, various properties were measured as follows.

(1) Urea dimer content:

The urea dimer content of a biuret polyisocyanate is defined as the amount (% by weight) of an urea dimer represented by formula (I) above, based on the total weight of the biuret polyisocyanate and the urea bond-containing compounds including the urea dimer.

A sample of a biuret polyisocyanate for the measurement of the urea dimer content thereof is prepared by dissolving the biuret polyisocyanate in tetrahydrofuran (THF) so that the final concentration of the biuret polyisocyanate in THF becomes 0.5 % by weight. For measurement of the urea dimer content of a biuret polyisocyanate in a reaction mixture, the reaction mixture as such is used as a sample.

The sample of a biuret polyisocyanate is subjected to gel permeation chromatography (GPC) under conditions as mentioned below, thereby obtaining a chromatogram. The urea dimer content is determined as the percent of the area of a peak ascribed to the urea dimer (i.e., a peak having a retention time corresponding to the molecular weight of 310 when the diisocyanate is hexamethylene-1-6-diisocyanate (HMDI)), based on the total area of all peaks, exclusive of a peak ascribed to the unreacted diisocyanate in the obtained chromatogram.

GPC was conducted under the following conditions:
Chromatoprocessor: HLC-8120GPC (manufactured and sold by TOSOH Corporation, Japan),
Columns: TSKgel Super H1000, TSKgel Super H2000 and TSKgel Super H3000 (each of which is manufactured and sold by TOSOH Corporation, Japan), connected in series,
Carrier: THF (flow rate: 0.6 ml/min), and
Detector: refractive index detector.

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(2) Transmittance:

The transmittance of a biuret polyisocyanate is measured by means of a visible and UV spectrophotometer ("UV-160", manufactured and sold by Shimadzu Corporation, Japan) at 430 nm, using a cell having a length of

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2 cm.

(3) Unreacted diisocyanate concentration:

5 The unreacted diisocyanate concentration of a reaction mixture or a biuret polyisocyanate is defined as the amount (% by weight) of unreacted diisocyanate, based on the total weight of the unreacted diisocyanate and the biuret polyisocyanate (containing urea bond -containing compounds including the urea dimer).

10 A sample of the reaction mixture or biuret polyisocyanate is prepared in substantially the same manner as described in item (1) above. The sample of the reaction mixture or polyisocyanate is subjected to GPC under the conditions as described in item (1) above,
15 thereby obtaining a chromatogram. The diisocyanate concentration is determined as the percent of the area of a peak ascribed to the diisocyanate (i.e., a peak having a retention time corresponding to the molecular weight of 168 when the diisocyanate is HMDI), based on
20 the total area of all peaks in the obtained chromatogram.

(4) Number average molecular weight:

25 A sample of a polyisocyanate for the measurement of the number average molecular weight thereof is pre-

pared by dissolving the biuret polyisocyanate in tetrahydrofuran (THF) so that the final concentration of the polyisocyanate in THF becomes 0.25 % by weight. The prepared sample is subjected to GPC to thereby determine the number average molecular weight thereof. The GPC is conducted under the conditions as described in item (1) above.

(5) Isocyanate group content:

The isocyanate group content is defined as the content (% by weight) of isocyanate groups in a biuret polyisocyanate.

For measuring the isocyanate group content, 5 to 10 g of a biuret polyisocyanate is accurately weighed and used as a sample. 20 ml of toluene and 20 ml of a 2 N solution of n-dibutylamine in toluene are added to the biuret polyisocyanate. The resultant mixture is allowed to stand at room temperature for 15 minutes, to thereby conduct a reaction.

The resultant reaction mixture is subjected to back titration by means of an automatic titration apparatus (model APB-410, manufactured and sold by KYOTO DENSHI Co., Ltd., Japan) using 1 N hydrochloric acid. The volume of 1 N hydrochloric acid necessary for neutralizing the unreacted n-dibutylamine in the reaction

mixture (i.e., titer of sample titration) is determined.

In addition, titration is conducted in substantially the same manner as mentioned above, except that the biuret polyisocyanate is not used. The volume of
5 1 N hydrochloric acid necessary for neutralizing the unreacted n-dibutylamine in the reaction mixture (i.e., titer of blank titration) was determined.

The amount of isocyanate groups is determined in accordance with the formula below:

10 The isocyanate group content (% by weight) =

$$\frac{[(\text{titer (ml) of blank titration}) - (\text{titer (ml) of sample titration}) \times 42 / (\text{weight (g) of sample} \times 1,000)] \times 100}{1}$$

15 (6) Viscosity:

The viscosity of a biuret polyisocyanate is measured using an E-type viscometer (model VISCONIC ED, manufactured and sold by TOKIMEC Co., Ltd., Japan) at
25 °C.

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(7) Storage stability of a biuret polyisocyanate at
5 °C:

A biuret polyisocyanate is placed in a colorless, transparent glass container and tightly sealed after
25 purging the container with nitrogen gas. The resultant

glass container is placed at 5 °C for 1 day. The biuret polyisocyanate in the glass container is examined with the naked eye to determine whether the polyisocyanate became turbid or not.

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Example 1

A flask provided with a stirrer, a thermometer, a reflux condenser and a nitrogen gas feeding pipe was purged with nitrogen gas. 700 Parts by weight of hexamethylene-1,6-diisocyanate (HMDI), a mixed solvent of 150 parts by weight of trimethyl phosphate and 150 parts by weight of methyl cellosolve acetate, and 15 parts by weight of water as a biuretizing agent (molar ratio of HMDI/water = 5/1) were charged to the flask. The resultant mixture was stirred for 1 hour while maintaining a temperature of the flask at 160 °C, to thereby effect a first reaction. The unreacted diisocyanate concentration of the first reaction mixture was 65 % by weight.

In order to adjust the unreacted diisocyanate concentration of the first reaction mixture, the first reaction mixture was fed into a wiped film evaporator at a feeding rate of 500 g/hr, and subjected to wiped film evaporation at 160 °C and under a degree of vacuum of 655 Pa. As a result, the unreacted diisocyanate con-

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centration of the first reaction mixture became 5 % by weight. The urea dimer content and transmittance of the biuret polyisocyanate in the first reaction mixture were 1.5 % by weight and 94 %, respectively.

5 The first reaction mixture, which had been adjusted with respect to the unreacted diisocyanate concentration, was heated in a nitrogen atmosphere at a temperature of 140 °C for 30 minutes, to thereby perform a second reaction. With respect to the biuret polyisocyanate in the second reaction mixture, the urea dimer content was not more than 0.2 % by weight and the transmittance was 93 %.

 Subsequently, the second reaction mixture was fed to a wiped film evaporator (degree of vacuum: 67 Pa, temperature: 160 °C) to thereby isolate a biuret polyisocyanate therefrom by removing the unreacted diisocyanate in the second reaction mixture. With respect to the isolated biuret polyisocyanate, the number average molecular weight was 690; the isocyanate group content was 22.9 % by weight; the unreacted diisocyanate concentration was 0.3 % by weight; and the urea dimer content was not more than 0.2 % by weight. The transmittance and viscosity of the biuret polyisocyanate were 93 % and 3,700 mPa's at 25 °C, respectively. Further, the biuret polyisocyanate did not become turbid

even after being subjected to storage stability testing at 5 °C.

Example 2

5 A first reaction was effected in substantially the same manner as in Example 1 except that the amount of water charged to the flask as a biuretizing agent was 9.4 parts by weight (molar ratio of HMDI/water = 8/1). The unreacted diisocyanate concentration of the first
10 reaction mixture was 70 % by weight.

 In order to adjust the unreacted diisocyanate concentration of the first reaction mixture, the first reaction mixture was subjected to wiped film evaporation under substantially the same conditions as in Example 1.
15 As a result, the unreacted diisocyanate concentration of the first reaction mixture became 4 % by weight. The urea dimer content and transmittance of the biuret polyisocyanate in the first reaction mixture were 1.1 % by weight and 95 %, respectively.

20 The first reaction mixture, which had been adjusted with respect to the unreacted diisocyanate concentration, was heated in a nitrogen atmosphere at a temperature of 110 °C for 60 minutes, to thereby perform a second reaction. With respect to the biuret polyisocyanate in the second reaction mixture, the urea dimer
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content was not more than 0.2 % by weight and the transmittance was 95 %.

Subsequently, the second reaction mixture was subjected to wiped film evaporation to thereby isolate a biuret polyisocyanate therefrom by removing the unreacted diisocyanate in the second reaction mixture.

With respect to the isolated biuret polyisocyanate, the number average molecular weight was 635; the isocyanate group content was 23.8 % by weight; the unreacted diisocyanate concentration was 0.3 % by weight; and the urea dimer content was not more than 0.2 % by weight.

The transmittance and viscosity of the biuret polyisocyanate were 94 % and 1,600 mPa's at 25 °C, respectively. Further, the biuret polyisocyanate did not become turbid even after being subjected to storage stability testing at 5 °C.

Example 3

A first reaction was effected in substantially the same manner as in Example 2. The unreacted diisocyanate concentration of the first reaction mixture was 70 % by weight.

The first reaction mixture was subjected to wiped film evaporation under substantially the same conditions as in Example 2, followed by adding HMDI to the

first reaction mixture, thereby adjusting the unreacted diisocyanate concentration of the first reaction mixture to 10 % by weight.

5 The first reaction mixture, which had been adjusted with respect to the unreacted diisocyanate concentration, was heated in a nitrogen atmosphere at a temperature of 125 °C for 30 minutes, to thereby perform a second reaction. With respect to the biuret polyisocyanate in the second reaction mixture, the urea dimer
10 content was not more than 0.2 % by weight and the transmittance was 95 %.

Subsequently, the second reaction mixture was subjected to wiped film evaporation to thereby isolate a biuret polyisocyanate therefrom by removing the unreacted diisocyanate in the second reaction mixture.
15 With respect to the isolated biuret polyisocyanate, the number average molecular weight was 635; the isocyanate group content was 23.7 % by weight; the unreacted diisocyanate concentration was 0.3 % by weight; and the
20 urea dimer content was not more than 0.2 % by weight. The transmittance and viscosity of the biuret polyisocyanate were 94 % and 1,600 mPa·s at 25 °C, respectively. Further, the biuret polyisocyanate did not become turbid even after being subjected to storage sta-
25 bility testing at 5 °C.

Comparative Example 1

A first reaction was effected in substantially the same manner as in Example 2. The unreacted diisocyanate concentration of the first reaction mixture was 70 %
5 by weight.

The first reaction mixture was subjected to wiped film evaporation under substantially the same conditions as in Example 2, followed by adding HMDI to the
10 first reaction mixture, thereby adjusting the unreacted diisocyanate concentration of the first reaction mixture to 50 % by weight.

The first reaction mixture, which had been adjusted with respect to the unreacted diisocyanate concentration, was heated in a nitrogen atmosphere at a temperature of 125 °C for 30 minutes, to thereby perform a
15 second reaction. With respect to the biuret polyisocyanate in the second reaction mixture, the urea dimer content was 0.5 % by weight and the transmittance was
20 95 %.

Subsequently, the second reaction mixture was subjected to wiped film evaporation to thereby isolate a biuret polyisocyanate therefrom by removing the unreacted diisocyanate in the second reaction mixture.
25 With respect to the isolated biuret polyisocyanate, the

number average molecular weight was 635; the isocyanate group content was 23.8 % by weight; the unreacted diisocyanate concentration was 0.3 % by weight; and the urea dimer content was 1.0 % by weight. The transmittance and viscosity of the biuret polyisocyanate were 92 % and 1,600 mPa's at 25 °C, respectively. However, the biuret polyisocyanate became turbid after being subjected to storage stability testing at 5 °C.

10 Comparative Example 2

A first reaction was effected in substantially the same manner as in Example 2. The unreacted diisocyanate concentration of the first reaction mixture was 70 % by weight.

15 In order to adjust the unreacted diisocyanate concentration of the first reaction mixture, the first reaction mixture was subjected to wiped film evaporation under substantially the same conditions as in Example 2.

The first reaction mixture, which had been adjusted with respect to the unreacted diisocyanate concentration, was heated in a nitrogen atmosphere at a temperature of 100 °C for 15 minutes, to thereby perform a second reaction. With respect to the biuret polyisocyanate in the second reaction mixture, the urea dimer content was 0.8 % by weight and the transmittance was

20
25

95 %.

Subsequently, the second reaction mixture was subjected to wiped film evaporation to thereby isolate a biuret polyisocyanate therefrom by removing the unreacted diisocyanate in the second reaction mixture.

With respect to the isolated biuret polyisocyanate, the number average molecular weight was 635; the isocyanate group content was 23.8 % by weight; the unreacted diisocyanate concentration was 0.3 % by weight; and the urea dimer content was 0.8 % by weight. The transmittance and viscosity of the biuret polyisocyanate were 95 % and 1,600 mPa·s at 25 °C, respectively. However, the biuret polyisocyanate became turbid after being subjected to storage stability testing at 5 °C.

Comparative Example 3

A first reaction was effected in substantially the same manner as in Example 2. The unreacted diisocyanate concentration of the first reaction mixture was 70 % by weight.

In order to adjust the unreacted diisocyanate concentration of the first reaction mixture, the first reaction mixture was subjected to wiped film evaporation under substantially the same conditions as in Example 2.

The first reaction mixture, which had been adjust-

ed with respect to the unreacted diisocyanate concentration, was heated in a nitrogen atmosphere at a temperature of 150 °C for 120 minutes, to thereby perform a second reaction. With respect to the biuret polyisocyanate in the second reaction mixture, the urea dimer content was not more than 0.2 % by weight and the transmittance was 88 %.

Subsequently, the second reaction mixture was subjected to wiped film evaporation to thereby isolate a biuret polyisocyanate therefrom by removing the unreacted diisocyanate in the second reaction mixture.

With respect to the isolated biuret polyisocyanate, the number average molecular weight was 635; the isocyanate group content was 23.8 % by weight; the unreacted diisocyanate concentration was 0.3 % by weight; and the urea dimer content was not more than 0.2 % by weight. The viscosity of the biuret polyisocyanate was 1,600 mPa·s at 25 °C. Further, the biuret polyisocyanate did not become turbid even after being subjected to storage stability testing at 5 °C. However, the transmittance of the biuret polyisocyanate was 87 %, that is, the biuret polyisocyanate suffered discoloration.

Comparative Example 4

A flask provided with a stirrer, a thermometer, a reflux condenser and a nitrogen gas feeding pipe was purged with nitrogen gas. 700 Parts by weight of HMDI, a mixed solvent of 150 parts by weight of trimethyl phosphate and 150 parts by weight of methyl cellosolve acetate, and 15 parts by weight of water as a biuretizing agent (molar ratio of HMDI/water = 5/1) were charged to the flask. The resultant mixture was stirred for 1 hour while maintaining a temperature of the flask at 160 °C, to thereby effect a first reaction. The unreacted diisocyanate concentration of the first reaction mixture was 65 % by weight.

In order to adjust the unreacted diisocyanate concentration of the first reaction mixture, the first reaction mixture was fed into a wiped film evaporator at a feeding rate of 500 g/hr, and subjected to wiped film evaporation at 160 °C and under a degree of vacuum of 655 Pa, and then, at 160 °C and under a degree of vacuum of 67 Pa. As a result, the unreacted diisocyanate concentration of the first reaction mixture became 0.5 % by weight. The urea dimer content and transmittance of the biuret polyisocyanate in the first reaction mixture were 1.5 % by weight and 94 %, respectively.

The first reaction mixture, which had been adjust-

ed with respect to the unreacted diisocyanate concentration, was heated in a nitrogen atmosphere at a temperature of 110 °C for 30 minutes, to thereby perform a second reaction. With respect to the biuret polyisocyanate in the second reaction mixture, the number average molecular weight was 690; the isocyanate group content was 22.9 % by weight; the unreacted diisocyanate concentration was 0.5 % by weight; and the urea dimer content was 1.2 % by weight. The transmittance and viscosity of the biuret polyisocyanate were 94 % and 3,700 mPa's at 25 °C, respectively. However, the biuret polyisocyanate became turbid after being subjected to storage stability testing at 5 °C.

Example 4

Example 4 was conducted using the system shown in Fig. 1. All procedures were performed in a nitrogen atmosphere unless otherwise specified.

Hexamethylene-1,6-diisocyanate (HMDI) and a reaction solvent (a 1:1 mixed solvent of methyl cellosolve acetate and trimethyl phosphate) were continuously fed to first reactor 4 through inlet pipe 2 at flow rates of 1,000 parts by weight per hour and 500 parts by weight per hour, respectively. As a biuretizing agent, water was continuously fed to first reactor 4 through

inlet pipe 1 at a flow rate of 7.1 parts by weight per hour (molar ratio of HMDI/water = 15/1). A first reaction was continuously performed consecutively in first reactor 4, second reactor 7, and pipe reactors 9, 10 and 11. Illustratively stated, the reaction in first reactor 4 was performed at 120 °C and at a residence time of 90 minutes; the reaction in second reactor 7 was performed at 150 °C and at a residence time of 60 minutes; and the reaction in the pipe reactors 9, 10 and 11 was performed at 160 °C and at a residence time of 60 minutes, thereby obtaining a first reaction mixture.

The obtained first reaction mixture (amount of gas dissolved therein: 0.25 NmL/mL) was fed to degassing apparatus 20 at its upper portion (a gaseous phase), wherein degassing apparatus 20 was maintained at 30 °C under a degree of vacuum of 655 Pa, to thereby degas the first reaction mixture. The degassed first reaction mixture was withdrawn through the lower portion (a liquid phase) of degassing apparatus 20. The content of the unreacted diisocyanate in the first reaction mixture was 83 % by weight.

The degassed first reaction mixture was fed to wiped film evaporator 21 (degree of vacuum: 655 Pa, temperature: 160 °C), and the unreacted diisocyanate

concentration in the first reaction mixture was adjusted by wiped film evaporation, so that the diisocyanate concentration of the first reaction mixture became 5 % by weight. The urea dimer content and transmittance of the biuret polyisocyanate in the first reaction mixture were 1.0 % by weight and 93 %, respectively. The unreacted diisocyanate and the reaction solvent were recovered in the form of a mixture thereof through withdrawal pipe 22. The amount of the biuret polyisocyanate contained in the recovered mixture was not more than 0.5 % by weight.

The first reaction mixture, which had been adjusted with respect to the unreacted diisocyanate concentration, was fed to heating vessel 23, and heated at 130 °C for 30 minutes, to thereby perform a second reaction. With respect to the biuret polyisocyanate in the obtained second reaction mixture, the urea dimer content was not more than 0.2 % by weight and the transmittance was 91 %.

Subsequently, the second reaction mixture was fed to wiped film evaporator 24 (degree of vacuum: 67 Pa, temperature: 160 °C) and the unreacted diisocyanate in the second reaction mixture was removed from withdrawal pipe 25, to thereby isolate the biuret polyisocyanate from the second reaction mixture. The isolated biuret

polyisocyanate was withdrawn from withdrawal pipe 26.

With respect to the obtained biuret polyisocyanate, the number average molecular weight was 600; the isocyanate group content was 24.7 % by weight; the unreacted diisocyanate concentration was 0.5 % by weight; and the urea dimer content was not more than 0.2 % by weight. The transmittance and viscosity of the biuret polyisocyanate were 91 % and 900 mPa·s at 25 °C, respectively. Further, the biuret polyisocyanate did not become turbid even after being subjected to storage stability testing at 5 °C.

Example 5

A first reaction was continuously performed in substantially the same manner as in Example 4 except that the flow rate of water was 10.7 parts by weight per hour (molar ratio of HMDI/water = 10/1). The content of the unreacted diisocyanate in the obtained first reaction mixture was 73 % by weight.

The first reaction mixture was subjected to wiped film evaporation under substantially the same conditions as in Example 4 to adjust the unreacted diisocyanate concentration of the first reaction mixture. Next, a second reaction was performed in substantially the same manner as in Example 4. With respect to the biu-

ret polyisocyanate in the second reaction mixture, the urea dimer content was not more than 0.2 % by weight and the transmittance was 94 %.

Subsequently, the unreacted diisocyanate in the second reaction mixture was removed in substantially the same manner as in Example 4, to thereby isolate the biuret polyisocyanate from the second reaction mixture. With respect to the obtained biuret polyisocyanate, the number average molecular weight was 615; the isocyanate group content was 24.4 % by weight; the unreacted diisocyanate concentration was 0.4 % by weight; and the urea dimer content was not more than 0.2 % by weight. The transmittance and viscosity of the biuret polyisocyanate were 94 % and 1,700 mPa·s at 25 °C, respectively. Further, the biuret polyisocyanate did not become turbid even after being subjected to storage stability testing at 5 °C.

With respect to the mixture of the unreacted diisocyanate and the reaction solvent recovered during the first wiped film evaporation, the amount of the biuret polyisocyanate contained therein was not more than 0.5 % by weight.

Reference Example 1

A biuret polyisocyanate was produced in substan-

tially the same manner as in Example 5 except that the degassing step was not conducted. With respect to the produced biuret polyisocyanate, the number average molecular weight was 615; the isocyanate group content was 24.4 % by weight; and the unreacted diisocyanate concentration was 0.5 % by weight. The viscosity of the biuret polyisocyanate was 1,700 mPa·s at 25 °C.

With respect to the mixture of the unreacted diisocyanate and the reaction solvent recovered during the first wiped film evaporation, the amount of the biuret polyisocyanate contained therein was as large as 4 % by weight.

Reference Example 2

A biuret polyisocyanate was produced in substantially the same manner as in Reference Example 1 (i.e., the degassing apparatus was not used) except that the mixture of the unreacted diisocyanate and the reaction solvent recovered during the first wiped film evaporation in Reference Example 1 was used as a diisocyanate (raw material). With respect to the produced biuret polyisocyanate, the number average molecular weight was 665; the isocyanate group content was 23.6 % by weight; and the unreacted diisocyanate concentration was 0.5 % by weight. The viscosity of the biuret polyisocyanate

was as high as 2,010 mPa·s at 25 °C.

With respect to the mixture of the unreacted di-
isocyanate and the reaction solvent recovered during
the first wiped film evaporation, the amount of the
5 biuret polyisocyanate contained therein was as large as
4 % by weight.

Industrial Applicability

The biuret polyisocyanate of the present invention not only exhibits an excellent stability at low temperatures, but also is free from turbidity and discoloration. By virtue of these properties, the biuret polyisocyanate can be advantageously used for producing a coating composition, an adhesive, a fiber treatment agent, a sealant, a waterproofing agent, a foam, an elastomer and the like. For example, when the biuret polyisocyanate of the present invention is used for producing a coating composition, the obtained coating composition is capable of forming a coating which exhibits excellent adhesiveness and bending resistance. In addition, by the process of the present invention, it has become possible to effectively and efficiently produce a biuret polyisocyanate which not only exhibits an excellent stability at low temperatures, but also is free from turbidity and discoloration. Further, by the use of the process of the present invention, it has become possible to recycle the unreacted diisocyanate recovered after the reaction for producing a polyisocyanate.

CLAIMS

1. A biuret polyisocyanate obtained by reacting at least one diisocyanate selected from the group consisting of an aliphatic diisocyanate and an alicyclic diisocyanate with a biuretizing agent,

said biuret polyisocyanate having the following characteristics (1) and (2):

(1) said biuret polyisocyanate contains urea bond-containing compounds including an urea dimer which are the intermediate products of the reaction between the diisocyanate and the biuretizing agent, wherein said urea dimer is represented by the following formula (I):



wherein, each R independently represents an aliphatic group or an alicyclic group derived from said diisocyanate, and said biuret polyisocyanate has an urea dimer content of not more than 0.5 % by weight, based on the total weight of said biuret polyisocyanate and said urea bond-containing compounds including said urea dimer, wherein said urea dimer content is defined as the per-



cent of the area of a peak ascribed to said urea dimer
in a gel permeation chromatogram of said biuret poly-
isocyanate containing the unreacted diisocyanate and
said urea bond-containing compounds, based on the total
5 area of all peaks, exclusive of a peak ascribed to said
unreacted diisocyanate, in said gel permeation chroma-
togram; and

(2) said biuret polyisocyanate exhibits a trans-
mittance of at least 90 % as measured at 430 nm using a
10 cell having a length of 2 cm.

2. A process for producing a biuret polyisocyanate,
which comprises:

(a) conducting a first reaction between at least
15 one diisocyanate selected from the group consisting of
an aliphatic diisocyanate and an alicyclic diisocyanate
and a biuretizing agent, wherein the molar ratio of
said diisocyanate to said biuretizing agent is from 4
to 40, thereby obtaining a first reaction mixture con-
20 taining the unreacted diisocyanate and a biuret poly-
isocyanate;

(b) adjusting the concentration of the unreacted
diisocyanate in said first reaction mixture to a level
in the range of from 3 to 20 % by weight, based on the
25 total weight of the unreacted diisocyanate and said



biuret polyisocyanate;

(c) heating said first reaction mixture, which has been adjusted with respect to the unreacted diisocyanate concentration in step (b), at a temperature of from 110 to 160 °C to thereby perform a second reaction, thus producing a biuret polyisocyanate having the following characteristics (1) and (2):

(1) said biuret polyisocyanate contains urea bond-containing compounds including an urea dimer which are the intermediate products of said first reaction, wherein said urea dimer is represented by the following formula (I):



wherein, each R independently represents an aliphatic group or an alicyclic group derived from said diisocyanate, and said biuret polyisocyanate has an urea dimer content of not more than 0.5 % by weight, based on the total weight of said biuret polyisocyanate and said urea bond-containing compounds including said urea dimer, wherein



said urea dimer content is defined as the percent of the area of a peak ascribed to said urea dimer in a gel permeation chromatogram of said biuret polyisocyanate containing the unreacted diisocyanate and said urea bond-containing compounds, based on the total area of all peaks, exclusive of a peak ascribed to said unreacted diisocyanate, in said gel permeation chromatogram, and

(2) said biuret polyisocyanate exhibits a transmittance of at least 90 % as measured at 430 nm using a cell having a length of 2 cm; and

(d) isolating said biuret polyisocyanate from said second reaction mixture obtained in step (c).

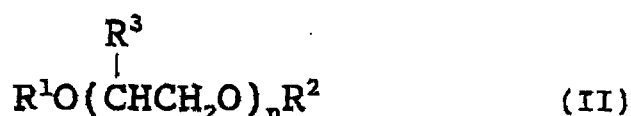
3. The process according to claim 2, wherein, in step (d), the isolation of said biuret polyisocyanate is performed by removing the unreacted diisocyanate from said second reaction mixture.

4. The process according to claim 2 or 3, wherein said at least one diisocyanate is a hexamethylene-1,6-diisocyanate.



5. The process according to any one of claims 2 to 4, wherein said biuretizing agent is water.

6. The process according to claim 5, wherein, in step (a), the first reaction between said diisocyanate and water is performed in the presence of at least one solvent selected from the group consisting of a compound represented by the following formula (II) and an alkyl phosphate:



wherein each of R^1 and R^2 independently represents an alkyl or an acyl group having 1 to 4 carbon atoms, R^3 represents a methyl group or a hydrogen atom, and n represents an integer of 1 or 2.

7. The process according to any one of claims 2 to 6, wherein, in step (b), the adjustment of the unreacted diisocyanate concentration of the first reaction mixture is performed by wiped film evaporation.

8. The process according to claim 7, wherein said



first reaction mixture is degassed before being subjected to wiped film evaporation.

5 9. The process according to any one of claims 3 to 8, wherein, in step (d), the removal of the unreacted diisocyanate from said second reaction mixture is performed by wiped film evaporation.

10 10. The process according to claim 9, wherein said second reaction mixture is degassed before being subjected to the wiped film evaporation.

15 11. The process according to any one of claims 2 to 10, wherein step (a) comprises continuously conducting the following substeps (i) and (ii):

(i) agitating a mixture of the diisocyanate and the biuretizing agent to conduct a reaction between said diisocyanate and said biuretizing agent in a homogeneous system of said mixture, thereby obtaining an intermediate reaction mixture; and

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(ii) feeding said intermediate reaction mixture to a pipe reactor to thereby conduct a further reaction between said diisocyanate and said biuretizing agent in a piston flow, thereby obtaining a first reaction mixture.

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