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(54) **Title**: HALOGENATION OF 4,4'-METHYLENE-BIS-ANILINES

(57) **Abstract**: Described is a process for the preparation of halogenated 4,4'-methylene-bis- anilines by a direct halogenation of 4,4'-methylene-bis-anilines. High yields and a flexible control of the grade of halogenation at the aromatic rings can be achieved when treating a mixture of a 4,4'-methylene-bis-aniline and sulfuric acid with a halogen such as chlorine. The obtained halogenated 4,4'-methylene-bis-anilines and mixtures thereof can be used in the preparation of polyurethanes and epoxy resins and for adjusting the gel times thereof.

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Halogenation of 4,4′-Methylene-bis-anilines

The present invention is directed to a process for the preparation of halogenated 4,4′-methylene-bis-anilines and to the halogenated 4,4′-methylene-bis-anilines and their use in the preparation of polyurethanes and epoxy resins.

The use of chain extenders and curing agents (in the following collectively called curing agents) for the preparation of polyurethanes and epoxy resins is well known in the art. Polyurethanes, for example, may be obtained by reacting compounds having H-reactive groups such as polyether polyols or polyester polyols with a diisocyanate to form a prepolymer, which in a second step is then reacted with a curing agent to form the polyurethane. Epoxy resins, on the other hand, may be obtained by reacting epichlorohydrin with an alcohol to obtain a glycidyl derivative which then is reacted with a curing agent to obtain the cured epoxy resin.

The structure of the curing agents and the reactivity of their functional groups are often used to modify the properties of the final product or to control the reaction rate of the polymer formation and the processability of the polymer.

Commonly used curing agents for the preparation of polyurethanes (PU) and epoxy resins are chlorinated 4,4′-methylene-bis-anilines. The effect of such compounds on the properties of the polymer system substantially depends on the alkyl substituents and/or the number and/or positions of the chlorine atoms on the aromatic rings. Sterically hindered diamines such as 4,4′-methylenebis-(3-chloro-2,6-diethylaniline) (M-CDEA) are often used as a curing agent to adjust gel times. These compounds, however, do not allow to flexibly control gel times over a broad range. Other well known compounds such as 4,4′-methylenebis-(*o*-chloroaniline) (MOCA) tend to be toxic.

Chlorinated 4,4′-methylene-bis-anilines are conventionally prepared by subjecting a chlorinated aniline to a condensation reaction with formaldehyde.

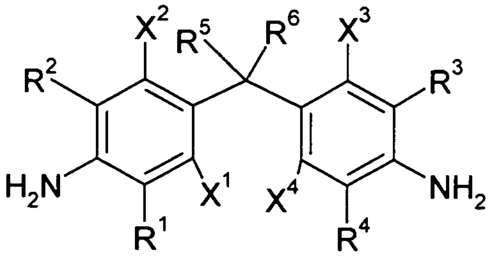
EP-A-0 171 588 discloses the preparation of chlorinated 4,4′-methylene-bis-anilines by subjecting 2-ethyl-6-chloroaniline and various 2,6-dialkylanilines to a condensation reaction with formaldehyde. The condensation reaction, however, is time consuming and often requires a high energy input. Moreover, following condensation the reaction product contains unreacted starting materials which must be removed before use as it results in endcapping of the formed polymer. While mixtures of chlorinated aromatic diamines obtained by this method can be used to vary the pot lives of polyurethane polymers, the directed preparation of specific mixtures of chlorinated 4,4'-methylene-bis-anilines is difficult. Moreover, methylene-bis-anilines having chlorine atoms in ortho-position to the amino group tend to be toxic.

EP-A-0 220 641 describes a method for preparing meta-chlorinated 4,4'-methylene-bis(2,6-dialkylanilines) by subjecting meta-chlorinated 2,6-dialkylanilines as a starting material to a condensation reaction with formaldehyde. This method, therefore, suffers from the same disadvantages as described above.

The object of the present invention, therefore, is to provide an effective and cost efficient process for the preparation of meta-halogenated 4,4'-methylene-bis-anilines and mixtures thereof.

A further object of the present invention is to provide curing compositions for the preparation of polyurethanes and epoxy resins, which can be easily prepared and which can be used to adjust the properties of the polymer system such as gel time according to the manufacturer's needs.

According to the invention, this has been achieved by a process for the preparation of halogenated aromatic amines of formula (1)

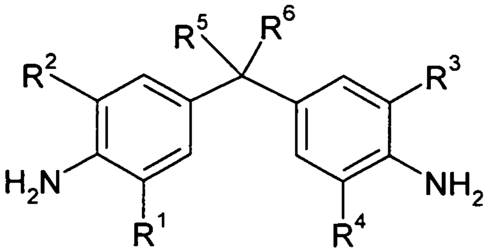


(1)

wherein R^1, R^2, R^3 and R^4 independently represent H, Cl or Br, an alkyl group or an alkoxy group, R^5 and R^6 independently represent H or an alkyl group or together with the carbon atom to which they are bound form a cyclopentane ring or a cyclohexane ring, and X^1, X^2, X^3 and X^4 independently represent H, Cl or Br, wherein at least one of X^1, X^2, X^3 and X^4 is Cl or Br, or mixtures thereof,

said process comprising:

(a) providing an aromatic amine of the formula (2)



(2)

wherein R^1, R^2, R^3, R^4, R^5 and R^6 are as defined above, in the anilinium form in a mixture with sulfuric acid; and

(b) treating the mixture of step (a) with chlorine (Cl_2) or bromine (Br_2), followed by treatment with a base to obtain the halogenated aromatic amine of the formula (1).

It has been found that the process of the invention allows selective meta-halogenation of 4,4'-methylene-bis-anilines in high yields without undesired side products.

The term alkyl as used in the definitions of R^1, R^2, R^3, R^4, R^5 and R^6 includes linear and branched alkyl groups. Preferably, the alkyl group is a C_{1-6} alkyl group, more preferably a C_{1-4} alkyl group. Preferred alkyl groups include methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl and *tert*-butyl. More preferred alkyl groups are methyl, ethyl, *n*-propyl, isopropyl and *sec*-butyl. Most preferred alkyl groups are methyl, ethyl, *n*-propyl and isopropyl.

The term alkoxy as used in the definitions of R^1, R^2, R^3, R^4, R^5 and R^6 includes linear and branched alkoxy groups. Preferably, the alkoxy group is a C_{1-6} alkoxy group, more preferably a C_{1-4} alkoxy group. Preferred alkoxy groups include methoxy, ethoxy, *n*-propoxy, isopropoxy, *n*-butoxy, *sec*-butoxy and *tert*-butoxy. More preferred alkoxy groups are methoxy, ethoxy, *n*-propoxy, isopropoxy and *n*-butoxy. Most preferred alkoxy groups are methoxy, ethoxy, *n*-propoxy and isopropoxy.

According to a preferred embodiment of the process of the invention, at least one of R^1 and R^2 and at least one of R^3 and R^4 are different from H.

Preferably, R^1, R^2, R^3 and R^4 independently represent H or an alkyl group and R^5 and R^6 represent H or together with the carbon atom to which they are bound form a cyclohexane ring. More preferably, at least one of R^1, R^2, R^3 and R^4 is an alkyl group, i. e., at least one of the two aromatic rings of the compounds of formulas (1) and (2) carries at least one alkyl group in ortho-position to the amino group. Even more preferably, at least one of R^1 and R^2 and at least one of R^3 and R^4 is an alkyl group, i. e., each of the two aromatic rings of the compounds of formulas (1) and (2) carries at least one alkyl group in ortho-position to the amino group, wherein these alkyl groups preferably are identical.

According to a further preferred embodiment of the invention, all of R^1, R^2, R^3 and R^4 independently represent an alkyl group. In this case, the alkyl groups of R^1 and R^2 preferably correspond to the alkyl groups R^3 and R^4, i. e., the alkyl groups of the aromatic rings of the compounds of the formula (1) and (2) are symmetrically arranged. According to a particular preferred embodiment of the invention, the alkyl groups represented by R^1, R^2, R^3 and R^4 are the same.

The number of halogen atoms represented by X^1, X^2, X^3 and X^4 in the compounds of the formula (1) may vary from 1 to 4. Preferably, if X^1 and X^2 both are Cl or Br, at least one of X^3 and X^4 is Cl or Br, respectively, and vice versa. Preferably, X^1, X^2, X^3 and X^4 independently represent H or Cl.

The sulfuric acid (H_2SO_4) used in the present process in admixture with the aromatic amines of the formula (2) preferably is a sulfuric acid having an acid concentration of at least 70% by weight, more preferably of at least 85% by weight, even more preferably of at least 90% by weight, and most preferably of at least 95% by weight. While halogenation can be carried out using a sulfuric acid having an acid concentration of below 70% by weight, yield is better at higher concentrations.

Typically, the aromatic diamine of the formula (2) is provided in the anilinium form by mixing the amino compound of the formula (2) with sulfuric acid. Following mixing of the two components, the amine will essentially be present in the form of a sulfuric acid salt, i.e., an anilinium salt, which reacts with the chlorine or bromine. Advantageously, the sulfuric acid is used in a molar excess with respect to the aromatic diamine. This allows better mixing and probably dissolution of the formed anilinium salt in the sulfuric acid. For improved yields, thus, the molar ratio of sulfuric acid to amino compound of the formula (2) in the starting mixture preferably should be at least 2:1, more preferably at least 5:1 and most preferably at least 10:1. Molar ratios of sulfuric acid to amino compound of 40:1 and more will be possible but will not improve yield. Alternatively, the compound of the formula (2) can be provided in the form of an anilinium salt, preferably a sulfuric acid salt such as an anilinium hydrogensulfate or an anilinium sulfate, which is mixed with the sulfuric acid. Preferably, to optimize yields, the mixture to be treated with the chlorine or bromine essentially consists of the amine of the formula (2) in the anilinium form and of the sulfuric acid.

Halogenation of the compound of the formula (2) is typically effected using gaseous chlorine (Cl_2) or liquid bromine (Br_2) which are introduced into or passed through the mixture with the sulfuric acid. Preferably, the process of the invention is carried out using chlorine. The reaction is typically carried out at a temperature in a range of from 5 °C to 150 °C, preferably of from 5 °C to 120 °C, and more preferably of from 5 °C to 100 °C. Lower or higher temperatures may work as well, but lower temperatures may result in a decreased reaction rate while higher temperatures do not increase yield.

The halogenation reaction is followed by treatment with a base to neutralize the sulfuric acid and to liberate the chlorinated or brominated aniline of the formula (1) from the sulfuric acid salts which are formed as intermediates. Bases which are typically used for the treatment include organic and inorganic bases such as triethylamine and alkali metal hydroxides and carbonates. Sodium or potassium hydroxide are preferred and are typically used in the form of aqueous solutions.

The liberated halogenated aromatic diamine of the formula (1) can be isolated according to known methods, for example by separating the organic layer or by extraction with a water immiscible solvent such as dichloromethane, ethyl acetate or toluene. The solvent may then be removed under reduced pressure. The halogenated aniline compounds may be purified by distillation.

Thus, the process for the preparation of halogenated aromatic amines of the formula (1) according to the present invention may further comprise the step of purifying the halogenated aromatic amine of the formula (1) obtained in above step (b).

The process of the invention may be carried out in a closed or in an open system.

According to a preferred embodiment of the invention, the halogenation reaction is carried out in a closed system, for example a sealed reaction vessel such as a sealed autoclave. A closed system has the advantage that it does not exchange matter with its surroundings during the reaction and thus allows easy control of the stoichiometry of the reactants. Typically, in the process of the invention the mixture of amino compound and sulfuric acid is charged into the reaction vessel, preferably an autoclave, and the reaction vessel is then sealed and the calculated amount of halogen is added. Due to the closed system, none of the reactants will leak so that a predetermined molar ratio of the reactants can be provided for controlling the process.

Alternatively, the halogenation reaction of the invention can be carried out in an open system which allows the flow of matter out of the system boundaries. The open system used in the process of the invention may be an open reaction vessel, for example a standard glass apparatus such as a three-necked round bottom flask, which is charged with the amino compound and the sulfuric acid before the respective halogen is added. Conveniently, if chlorine is used, the chlorine gas is passed through the reaction mixture, for example using a dip pipe.

The degree of halogenation may be controlled, for example, by adjusting the stoichiometry of the reactants, that is, the molar ratio of halogen to aromatic diamine of the formula (2). The optimum molar ratio for the desired degree of halogenation may be determined by routine experiments by the person skilled in the art.

In case of a chlorination reaction, for example, which is carried out in a closed reaction vessel, a mono-chlorinated product is obtained in high yields if chlorine (Cl_2)

and starting material of the formula (2) are used in about stoichiometric amounts, i.e., if the molar ratio of chlorine molecules (Cl_2) to starting material is in the range of from about 0.90:1 to 1.10:1, more preferably in the range of from about 0.95:1 to 1.05:1.

Under the same conditions, if the molar ratio of chlorine molecules (Cl_2) to starting material is increased to from about 1.90:1 to 2.30:1, more preferably to from about 1.95:1 to 2.2:1, the di-chlorinated product wherein one of X^1 and X^2 and one of X^3 and X^4 is Cl is obtained as the main product and in high yields.

Under the same conditions, if the molar ratio of chlorine molecules (Cl_2) to starting material is increased to from about 2.90:1 to 3.50:1, more preferably to from about 2.95:1 to 3.3:1, a tri-chlorinated product is obtained as the main product and in high yields.

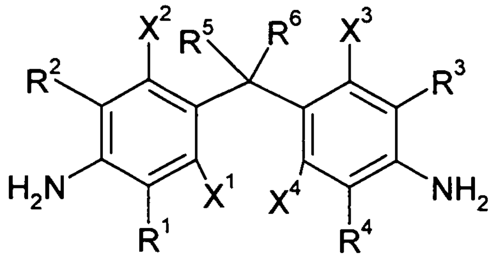
The tetra-chlorinated product can be obtained as the main product and in high yields if the molar ratio of chlorine molecules (Cl_2) to starting material is adjusted to above about 3.9:1, preferably to above about 5.0:1.

If the chlorination reaction is carried out in an open reaction vessel, the mono- and di-chlorinated 4,4'-methylene-bis-anilines are obtained in high yields if chlorine is passed through the reaction mixture. The higher chlorinated compounds will be obtained only upon longer reaction times and by passing large amounts of chlorine through the reaction mixture.

The same molar ratios may be used in case of bromination. Higher concentrations of bromine, however, may be advantageous.

The process of the present invention allows a controlled halogenation of 4,4'-methylene-bis-anilines of the formula (2) in high yields and with few side products. Unreacted starting material can be recycled. The present process, thus, can be carried out in a simple manner and at low costs.

The asymmetrically or completely halogenated 4,4′-methylene-bis-anilines of the formula (1) are novel compounds which have not been described before. The present invention, therefore, also relates to compounds of the general formula (1)



(1)

wherein R^1, R^2, R^3 and R^4 independently represent H, Cl or Br, an alkyl group or an alkoxy group, R^5 and R^6 independently represent H or an alkyl group or together with the carbon atom to which they are bound form a cyclopentane ring or a cyclohexane ring, and X^1, X^2, X^3 and X^4 independently represent H, Cl or Br, wherein at least one of X^1, X^2, X^3 and X^4 is Cl or Br,

with the proviso that compounds wherein R^1, R^2, R^3 and R^4 independently are H or an alkyl group and one of X^1 and X^2 and one of X^3 and X^4 is Cl and the other one is H are excluded.

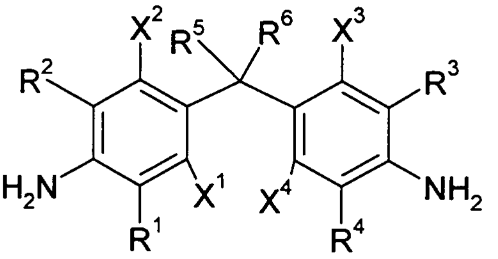
Preferred embodiments of the compounds of the formula (1) are those as defined above for the process of the invention.

Particularly preferred compounds are 3-chloro-4,4′-methylenebis-(2,6-diethylaniline), 3,3′,5-trichloro-4,4′-methylenebis-(2,6-diethylaniline), 4,4′-methylenebis-(3,5-dichloro-2,6-diethylaniline), 3-chloro-4,4′-methylenebis-(2,6-diisopropylaniline), 3,3′,5-trichloro-4,4′-methylenebis-(2,6-diisopropylaniline), 4,4′-methylenebis-(3,5-dichloro-2,6-diisopropylaniline), 3-chloro-4,4′-methylenebis-(2-isopropyl-6-methylaniline), 5-chloro-4,4′-methylenebis-(2-isopropyl-6-methylaniline), 3,5′-chloro-4,4′-methylenebis-(2-isopropyl-6-methylaniline), 3,3′,5-trichloro-4,4′-methylenebis-(2-isopropyl-6-methylaniline), 3,5,5′-trichloro-4,4′-methylenebis-(2-isopropyl-6-methylaniline) and 4,4′-methylenebis-(3,5-dichloro-2-isopropyl-6-methylaniline).

The novel compounds of the invention allow adjusting the gel times of polyurethanes and epoxy resins over a wide range. The present invention, therefore, is also directed to the use of these compounds for preparing polyurethanes and epoxy resins and, in particular, for adjusting the gel times of polyurethanes or epoxy resins.

The process of the invention can also be used to prepare mixtures of halogenated compounds of the formula (1) which can be used in the preparation of polyurethanes and epoxy resins. Depending on the starting material used in the process of the invention and on the reaction conditions, the compounds present in the mixture may differ in the number of chlorine or bromine substituents and/or in the type of alkyl substituents on the aromatic ring.

The present invention, therefore, is further directed to a curing composition comprising two or more compounds of the formula (1)



(1)

wherein R^1, R^2, R^3 and R^4 independently represent H, Cl or Br, an alkyl group or an alkoxy group, R^5 and R^6 independently are H or an alkyl group or together with the carbon atom to which they are bound form a cyclopentane ring or a cyclohexane ring, and X^1, X^2, X^3 and X^4 independently represent H, Cl or Br, wherein at least one of X^1, X^2, X^3 and X^4 is Cl or Br, wherein at least two of the compounds present in said composition differ in the number of halogen atoms represented by X^1, X^2, X^3 and X^4 and/or in at least one of R^1, R^2, R^3, R^4, R^5 and R^6.

Preferred compounds of the formula (1) which may be comprised in the curing compositions of the invention are those defined above for the process of the invention.

Particularly preferred compounds being comprised by the curing composition of the present invention are 3-chloro-4,4′-methylenebis-(2,6-diethylaniline), 4,4′-methylenebis-(3-chloro-2,6-diethylaniline), 3,3′,5-trichloro-4,4′-methylenebis-(2,6-di-ethylaniline), 4,4′-methylenebis-(3,5-dichloro-2,6-diethylaniline), 3-chloro-4,4′-methylenebis-

(2,6-diisopropylaniline), 4,4′-methylenebis-(3-chloro-2,6-diisopropylaniline), 3,3′,5-trichloro-4,4′-methylenebis-(2,6-diisopropylaniline), 4,4′-methylenebis-(3,5-dichloro-2,6-diisopropylaniline), 3-chloro-4,4′-methylenebis-(2-isopropyl-6-methylaniline), 5-chloro-4,4′-methylenebis-(2-isopropyl-6-methylaniline), 4,4′-methylenebis-(3-chloro-2-isopropyl-6-methylaniline), 4,4′-methylenebis-(5-chloro-2-isopropyl-6-methylaniline), 3,5′-chloro-4,4′-methylenebis-(2-isopropyl-6-methylaniline), 3,3′,5-trichloro-4,4′-methylenebis-(2-isopropyl-6-methylaniline), 3,5,5′-trichloro-4,4′-methylenebis-(2-isopropyl-6-methylaniline) and 4,4′-methylenebis-(3,5-dichloro-2-isopropyl-6-methylaniline).

It has been found that compositions comprising compounds differing in the number of halogen atoms, for example chlorine atoms, represented by X^1, X^2, X^3 and X^4 and/or in at least one of R^1, R^2, R^3, R^4, R^5 and R^6, preferably at least one of R^1, R^2, R^3 and R^4, can be used to tailor the gel times of polyurethanes and epoxy resins according to the manufactures needs, as the number of halogen atoms and the type of alkyl groups present in the individual compounds are essential factors determining the gel times of the polymers. Specifically, it has been found that the gel time increases with an increasing number of halogen atoms.

The mixtures of the invention are obtainable by the process of the invention, or they can be formed by mixing the individual compounds.

According to a preferred embodiment of the invention, the composition comprises at least two compounds which differ in the number of the halogen atoms represented by X^1, X^2, X^3 and X^4. Preferably, the composition comprises at least two compounds wherein the number of halogen atoms differs by one. For example, if the number of halogen atoms, for example chlorine atoms, in a first compound is 1, the number of halogen (chlorine) atoms in a second compound is 2. Such mixtures may be obtained when a single 4,4′-methylene-bis-aniline of the formula (2) is used as the starting material for the halogenation reaction according to the process of the invention and by properly adjusting the molar ratio of halogen to aromatic amine in the reaction mixture. If the alkyl substituents in the starting material are different, isomeric mixtures of halogenated compounds may be obtained as well.

According to a further embodiment of the invention, the composition comprises at least two compounds which differ in at least one of the substituents R^1, R^2, R^3 and R^4 on the aromatic ring and/or on at least one of the substituents R^5 and R^6. Such compositions may be obtained when two or more 4,4'-methylene-bis-anilines of the formula (2) are used as the starting material for the chlorination reaction according to the process of the invention. Mixtures wherein the compounds differ in the number of halogen atoms and, in addition, in the other substituents R^1 to R^6 can be prepared as well by using two or more different 4,4'-methylene-bis-anilines of the formula (2) as the starting material and properly adjusting the molar ratio of halogen to aromatic amine in the reaction mixture.

The process of the invention allows to flexibly control the equivalents of halogen atoms in the mixture of halogenated 4,4'-methylene-bis-anilines and to gradually adjust the molar ratio of chlorine atoms to amino groups. The mixtures thus obtained can therefore be used for preparing polyurethanes and epoxy resins and, in particular, for flexibly adjusting the gel times of polyurethanes or epoxy resins in a low, medium or upper range.

The compositions of the invention can be used to flexibly control gel times of polyurethanes and epoxy resins according to the manufactures needs. In the absence of halogen atoms in ortho-position to the amino group, no toxicity problems occur. Moreover, the compounds and mixtures obtained by the present process, unlike other curing agents such as di(methylthio)toluenediamines, have no adverse effect on the appearance of the final polymer product.

Further advantages of the present invention will be obvious from the following description of specific non-limiting examples which illustrate the present invention.

Examples

The following examples illustrate the chlorination of 4,4'-methylene-bis-(dialkylanilines) in the presence of sulfuric acid according to the process of the invention using a sealed autoclave to allow precise control of the stoichiometry of the chlorination reaction. All examples use sulfuric acid having a concentration of 96% by weight. Gas chromatography (GC) was carried out using an Agilent 6850 apparatus and a dimethylpolysiloxane-coated capillary as the separation column (30 m × 0.32 mm × 0.35 µm).

Example 1

11.8 g (38.0 mmol) of 4,4′-methylene-bis-(2,6-diethylaniline) and 58.6 g (574 mmol) of sulfuric acid (96% by weight) were introduced into an autoclave made of Hastelloy® HC22. The autoclave was cooled to 15 °C and flushed with nitrogen to check leak-tightness. Following release of the nitrogen, 2.7 g (38.1 mmol) of chlorine gas were introduced into the mixture. The reaction was stirred at 15 °C for 1 h and then poured into 50 g of ice. The suspension was neutralized with 440 g of 10% aqueous sodium hydroxide and then extracted with 210 g of toluene. Following phase separation, the organic layer was dried over anhydrous magnesium sulfate and evaporated under reduced pressure to give 14.7 g of a crude product. According to gas chromatography the crude product contained 55.3% of 3-chloro-4,4′-methylenebis-(2,6-diethylaniline), 25.8% of 4,4′-methylenebis-(3-chloro-2,6-diethylaniline) and 18.2% of unreacted 4,4′-methylenebis-(2,6-diethylaniline).

Example 2

Example 1 was repeated with a reaction temperature of 30 °C and a reaction time of 3 h. The crude product obtained contained (according to GC) 54.2% of 3-chloro-4,4′-methylene-bis-(2,6-diethylaniline), 27.0% of 4,4′-methylenebis-(3-chloro-2,6-diethylaniline) and 15.4% of unreacted 4,4′-methylenebis-(2,6-diethylaniline).

Example 3

10.0 g (32.2 mmol) of 4,4′-methylenebis-(2,6-diethylaniline) and 48.8 g (478 mmol) of sulfuric acid (96% by weight) were introduced into an autoclave made of Hastelloy® HC22. The autoclave was heated to 30 °C and flushed with nitrogen to check leak-tightness. Following release of the nitrogen, 4.5 g (63.5 mmol) of chlorine gas were introduced into the mixture. The reaction was stirred at 30 °C for 4.5 h and then poured into 50 g of ice. The suspension was neutralized with 420 g of 10% aqueous sodium hydroxide and then extracted with 200 g of toluene. Following phase separation, the organic layer was dried over anhydrous magnesium sulfate and evaporated under reduced pressure to give 12.0 g of a crude product containing (according to GC) 91.7% of 4,4′-methylenebis-(3-chloro-2,6-diethylaniline) and 5.5% of 3-chloro-4,4′-methylenebis-(2,6-diethylaniline).

[$C_{21}H_{28}Cl_2N_2$]:

^{1}H NMR ($CDCl_3$, 400 MHz): δ: 1.14 (t, J = 7.5 Hz, 6H, CH_3), 1.18 (t, J = 7.5 Hz, 6H, CH_3), 2.42 (q, J = 7.5 Hz, 4H, CH_2), 2.79 (q, J = 7.5 Hz, 4H, CH_2), 3.64 (br s, 4H, NH_2), 4.03 (br s, 2H, CH_2), 6.61 (s, 2H, 5-Ar-H).

GC (dimethylpolysiloxane, 30 m × 0.32 mm × 0.35 µm; 90 °C, 30 K/min → 200 °C, 20 K/min → 260 °C, 2 K/min → 280 °C): t_R = 13.4 min.

Example 4

Example 2 was repeated with a molar ratio of chlorine to 4,4′-methylenebis-(2,6-diethylaniline) of 3.5 : 1. The crude product obtained contained (according to GC) 51.3% of 3,3′,5-trichloro-4,4′-methylenebis-(2,6-diethylaniline), 32.9% of 4,4′-methylenebis-(3,5-dichloro-2,6-diethylaniline) and 15.9% of 4,4′-methylenebis-(3-chloro-2,6-diethylaniline).

Example 5

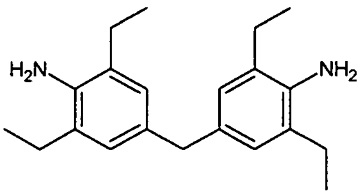
7.2 g (23.2 mmol) of 4,4′-methylenebis-(2,6-diethylaniline) and 70.2 g (687 mmol) of sulfuric acid (96% by weight) were introduced into an autoclave made of Hastelloy® HC22. The autoclave was heated to 30 °C and flushed with nitrogen to check leak-tightness. Following release of the nitrogen, 12.3 g (173.5 mmol) of chlorine gas were introduced into the mixture. The reaction was stirred at 30 °C for 3 h and then poured into 100 g of ice. The suspension was neutralized with 660 g of 10% aqueous sodium hydroxide and then extracted with 400 g of dichloromethane. Following phase separation, the organic layer was dried over anhydrous magnesium sulfate and evaporated under reduced pressure to give 9.6 g of a crude product containing (according to GC) 99.1% of 4,4′-methylenebis-(3,5-dichloro-2,6-diethylaniline).

[$C_{21}H_{26}Cl_4N_2$]:

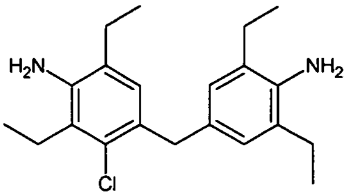
^1H NMR (($(CD_3)_3SO$), 400 MHz): δ: 1.24 (t, $J = 7.5$ Hz, 12H, CH_3), 2.86 (q, $J = 7.5$ Hz, 8H, CH_2), 3.91 (br s, 4H, NH_2), 4.72 (br s, 2H, CH_2).

GC (dimethylpolysiloxane, 30 m × 0.32 mm × 0.35 µm; 90 °C, 30 K/min → 200 °C, 20 K/min → 260 °C, 2 K/min → 280 °C): $t_R = 18.5$ min.

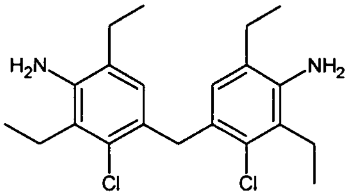
The results of examples 1 to 5 are summarized in Table 1, wherein the terms M-DEA, M-DEA-Cl, M-CDEA, M-DEA-Cl3 und M-DEA-Cl4 represent the following compounds:



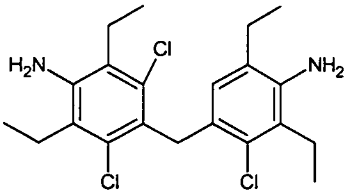
4,4'-methylenebis(2,6-diethylaniline)
M-DEA



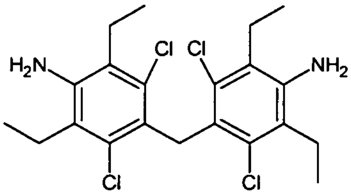
3-chloro-4,4'-methylenebis(2,6-diethylaniline)
M-DEA-Cl



4,4'-methylenebis(3-chloro-2,6-diethylaniline)
M-CDEA



3,3',5-trichloro-4,4'-methylenebis(2,6-diethylaniline)
M-DEA-Cl3



4,4'-methylenebis(3,5-dichloro-2,6-diethylaniline)
M-DEA-Cl4

Table 1

Example	Molar ratio Cl_2:M-DEA	Reaction temperature (°C)	Time (h)	Proportion in product mixture [1]				
				M-DEA	M-DEA-Cl	M-CDEA	M-DEA-Cl3	M-DEA-Cl4
1	1:1	15	1	18.2%	55.3%	25.8%	0.0%	0.0%
2	1:1	30	3	15.4%	54.2%	27.0%	0.0%	0.0%
3	2:1	30	4.5	0.3%	5.5%	91.7%	1.2%	0.0%
4	3.5:1	30	3	0.0%	0.0%	15.9%	51.3%	32.9%
5	7.5:1	30	3	0.0%	0.0%	0.0%	0.00%	99.1%

(1) The proportions of the compounds in the product mixture are calculated on the basis of the areas of the respective peaks in a gas chromatogram.

Examples 1 to 5 demonstrate that by controlling the stoichiometry of the reaction, i. e. the molar ratio of chlorine (Cl_2) to M-DEA, high yields of chlorinated methylene-bis-anilines having a specific grade of chlorination could be obtained. A comparison of examples 1 and 2 further shows that the same selectivities and yields were obtained even at a reduced reaction temperature of 15 °C and a reduced reaction time of 1 h.

Example 6

Example 3 was repeated under identical conditions except that 4,4′-methylene-bis(2,6-diisopropylaniline) was used as the starting material. After a reaction time of 3 h and usual work up a crude product was obtained containing a mixture of products of the chlorinated starting material with 4,4′-methylenebis-(3-chloro-2,6-diisopropyl-aniline) being the major product with a content of 73.0% (according to GC).

GC (dimethylpolysiloxane, 30 m × 0.32 mm × 0.35 µm; 100 °C, 30 K/min → 300 °C): t_R = 7.6 min.

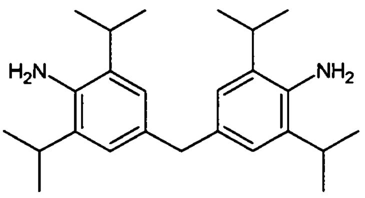
Example 7

Example 5 was repeated under identical conditions except that 4,4′-methylene-bis-(2,6-diisopropylaniline) was used as the starting material. After a reaction time of

4 h and usual work up a crude product was obtained containing a mixture of products of the chlorinated starting material with 4,4'-methylenebis-(3,5-dichloro-2,6-diisopropylaniline) being the major product with a content of 72.7% (according to GC).

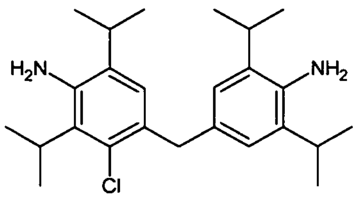
GC (dimethylpolysiloxane, 30 m × 0.32 mm × 0.35 µm; 100 °C, 30 K/min → 300° C): t_R = 8.9 min.

The results of examples 6 and 7 are summarized in Table 2, wherein the terms M-DIPA, M-DIPA-Cl, M-DIPA-Cl2, M-DIPA-Cl3 and M-DIPA-Cl4 represent the following compounds:



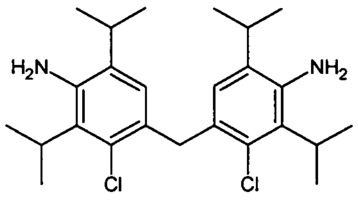
4,4'-methylenebis(2,6-diisopropylaniline)

M-DIPA



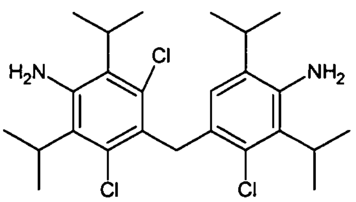
3-chloro-4,4'-methylenebis(2,6-diisopropylaniline)

M-DIPA-Cl



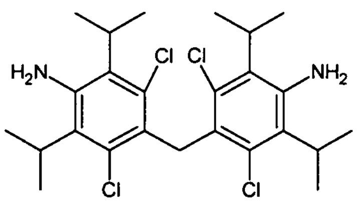
4,4'-methylenebis(3-chloro-2,6-diisopropylaniline)

M-DIPA-Cl2



3,3',5-trichloro-4,4'-methylenebis(2,6-diisopropylaniline)

M-DIPA-Cl3



4,4'-methylenebis(3,5-dichloro-2,6-diisopropylaniline)

M-DIPA-Cl4

Table 2

Example	Molar ratio Cl_2:M-DIPA	Reaction temperature (°C)	Time (h)	Proportion in product mixture (1)				
				M-DIPA	M-DIPA-Cl	M-DIPA-Cl2	M-DIPA-Cl3	M-DIPA-Cl4
6	2:1	30	3	7.4%	0.0%	73.0%	18.0%	0.0%
7	7.5:1	30	4	0.0%	0.0%	0.0%	13.8%	72.7%

(1) The proportions of the compounds in the product mixture are calculated on the basis of the areas of the respective peaks in a gas chromatogram.

Similar to Examples 1 to 5 above, Examples 6 and 7 demonstrate that use of 4,4′-methylenebis-(2,6-diisopropylaniline) as the starting material also results in high yields of chlorinated methylene-bis-anilines having a specific grade of chlorination when controlling the stoichiometry of the reaction, i.e. the molar ratio of chlorine (Cl_2) to M-DIPA.

Example 8

Example 3 was repeated under identical conditions except that 4,4′-methylene-bis-(2-isopropyl-6-methylaniline) was used as the starting material and the reaction time was 3 h. The crude product obtained was a mixture of products of the chlorinated starting material with 4,4′-methylenebis-(3-chloro-6-isopropyl-2-methylaniline) being the major product with a content of 80.0% (according to GC).

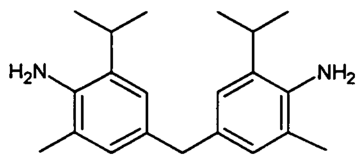
GC (dimethylpolysiloxane, 30 m × 0.32 mm × 0.35 µm; 70 °C, 25 K/min → 260 °C, 5 K/min → 270 °C, 25 K/min → 300 °C): t_R = 12.8 min.

Example 9

Example 5 was repeated under identical conditions except that 4,4′-methylene-bis-(2-isopropyl-6-methylaniline) was used as the substrate and the molar ratio of chlorine (Cl_2) to starting material was 7:1. After a reaction time of 3 h, a crude product was obtained containing a mixture of products of the chlorinated starting material with 4,4′-methylene-bis-(3,5-dichloro-6-isopropyl-2-methylaniline) being the major product with a content of 81.9% (according to GC).

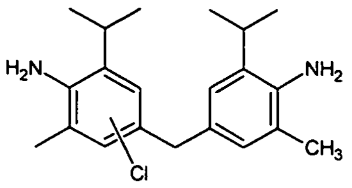
GC (dimethylpolysiloxane, 30 m × 0.32 mm × 0.35 µm; 70 °C, 25 K/min → 260 °C, 5 K/min → 270 °C, 25 K/min → 300 °C): t_R = 15.1 min.

The results of examples 8 and 9 are summarized in Table 3, wherein the terms M-MIPA, M-MIPA-Cl, M-MIPA-Cl2, M-MIPA-Cl3 and M-MIPA-Cl4 represent the following compounds with M-MIPA-Cl, M-MIPA-Cl2 and M-MIPA-Cl3 including the various isomers of the mono-, di- and trichloroanilines:

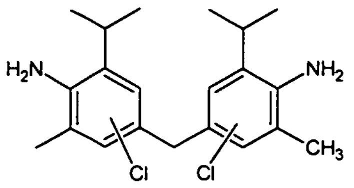


4,4'-methylenebis(2-isopropyl-6-methylaniline)

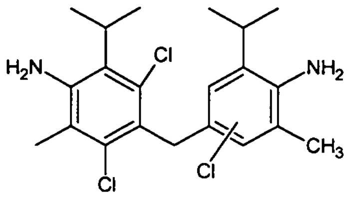
M-MIPA



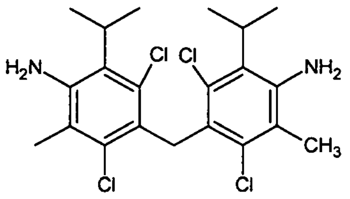
M-MIPA-Cl



M-MIPA-Cl2



M-MIPA-Cl3



4,4'-methylenebis-(3,5-dichloro-2-isopropyl-6-methylaniline)

M-MIPA-Cl4

Table 3

Example	Molar ratio Cl_2 : M-MIPA	Reaction temperature (°C)	Time (h)	Proportion in product mixture [(1)]				
				M-MIPA	M-MIPA-Cl	M-MIPA-Cl2	M-MIPA-Cl3	M-MIPA-Cl4
8	2:1	30	3	4.8%	0.0%	80.0%	3.2%	0.0%
9	7:1	30	3	0.0%	0.0%	0.0%	0.0%	81.9%

(1) The proportions of the compounds in the product mixture are calculated on basis of the areas of the respective peaks in a gas chromatogram.

Again, examples 8 and 9 demonstrate that by controlling the stoichiometry of the chlorination reaction high yields of chlorinated 4,4'-methylenebis-(2,6-dialkylanilines) having specific grade of chlorination can be achieved.

Examples 1 to 9 demonstrate that the process of the invention allows the preparation of product mixtures containing high proportions of a specific chlorinated methylene-bis-aniline. By modifying the reaction conditions such as reaction temperature, reaction time and, in particular, the molar ratio of Cl_2 to starting material (like M-DEA, M-DIPA and M-MIPA), however, it is possible to also obtain mixtures containing two or more different reaction products in considerable amounts.

Preparation of polyurethanes and epoxy resins

Mixtures of chlorinated 4,4′-methylenebis-(2,6-dialkylanilines) obtained in the above examples were used in the preparation of polyurethanes and epoxy resins and gel times were determined as described below.

Preparation of polyurethanes

For the preparation of polyurethanes, a polyether diol based on polypropylene glycol with an OH number of 26 to 29 and an average molecular weight of 3800 g/mol (available under the trade name Voranol® EP 1900) was mixed with the mixtures of chlorinated 4,4′-methylene-bis-(2,6-dialkylanilines) obtained in the above examples at 80 °C in the equivalent ratios given in Table 4 below. 4,4′-Methylenebis-(3-chloro-2,6-diethylaniline) (M-CDEA), which is a common curing agent in the preparation of polyurethanes and epoxy resins, was used for comparison under the same conditions. After 10 to 15 minutes at 80 °C, a homogenous viscous solution was obtained. The viscous solution was cooled to room temperature and then prepolymerised diphenylmethane diisocyanate (MDI) with an isocyanate value of 10.2% (available under the trade name Suprasec® 2008, Huntsman Corporation, US) was added in the equivalent ratios given below. The equivalent ratio of reactive amino (NH_2) groups to reactive hydroxyl (OH) groups was of from 75:25 to 25:75. The final equivalent ratio of reactive NCO groups to the sum of reactive NH_2 and OH groups was 95:100 in all examples. The gel time was measured at 25 °C after having obtained a homogenous mixture using a GELNORM® Gel Timer (Gel Instrumente AG, Thalwil, Switzerland) according to DIN 16945 Page 1 and DIN 16916. The results are summarized in Table 4.

Table 4:

Amine or amine mixture	Equivalent ratio NH_2:OH[1]	Equivalent ratio NCO:(NH_2+OH)[1]	Gel time at 25 °C [s]
Mixtures of compounds according to the present invention			
Amine mixture obtained in example 1	75:25	95:100	25
	50:50	95:100	28
	25:75	95:100	120
Amine mixture obtained in example 5	75:25	95:100	1700
	50:50	95:100	2650
	25:75	95:100	7600
Amine mixture obtained in example 6	75:25	95:100	110
	50:50	95:100	270
	25:75	95:100	7980
Amine mixture obtained in example 8	75:25	95:100	58
	50:50	95:100	150
	25:75	95:100	800
Comparative Compound			
M-CDEA	75:25	95:100	110
	50:50	95:100	250
	25:75	95:100	358

(1) The equivalents of reactive NH_2 groups used for calculating the equivalent ratios were calculated on the basis of the proportions of the chlorinated 4,4′-methylenebis-(2,6-dialkylanilines) in the product mixtures given in Tables 1 to 3 wherein the proportions in Tables 1 to 3 were equated with the mass ratios of the respective compounds.

As may be seen from the results shown in Table 4, the mixtures of the present invention allow adjusting gel times of a polyurethane system over a wide range. Within the given equivalent ratios, the mixture obtained in example 1 allows a precise adjustment of gel times in a lower range of up to about 120 s. The mixture of example 8 allows adjusting the gel times in a mid range of about 58 to 800 s. Use of the mixture of example 5 allows gel times in an upper range of about 1700 to 7600 s. An even wider range spanning gel times of from about 110 s up to about 7980 s can be achieved using the mixture of example 6. The process of the invention and the mixtures obtainable therewith thus can be used to adjust the gel times of polyurethanes to the manufacturer's needs by varying the number of chlorine substituents on the aromatic rings. Such a precise control of gel times over a wide range is not possible with individual curing agents such as M-CDEA alone.

From the results it may further be seen that the type of alkyl substituent at position 2 and 6 of the aromatic rings also has an effect on the gel times. For instance, when more bulky substituents like isopropyl are used (see example 6) the use of the resultant product mixtures allows long gel times of up to about 7980 s when preparing polyurethanes. In contrast thereto, when part of the isopropyl substituents are replaced by methyl (see example 8) the gel times are in a mid range of up to about 800 s.

Thus, the present invention provides a possibility to effectively adjust the gel time of polyurethanes, which is particularly advantageous in the preparation of polyurethane elastomers and high performance polyurethanes. The present invention also avoids the use of toxic compounds such as MOCA and of compounds which may affect the appearance of the final product.

Preparation of epoxy resins

For the preparation of epoxy resins the mixtures of chlorinated 4,4'-methylene-bis-(2,6-dialkylanilines) obtained with the process of the present invention were mixed with Epikote® 828 (epoxy resin produced from Bisphenol A and epichlorohydrin available from Resolution Performance Products, OH, USA) in an equivalent ratio of reactive amino groups to reactive epoxy groups of 1:1.

Gel times were measured at 150 °C using the same equipment and method as described above for the polyurethane systems. The gel times achieved by using the mixtures of the present invention and the comparative compound M-CDEA are listed in Table 5.

Table 5:

Amine or amine mixture	Equivalent ratio Amino:Epoxy(1)	Gel time at 150 °C [s]
Mixtures of compounds according to the present invention		
Amine mixture obtained in example 1	1:1	65
Amine mixture obtained in example 5	1:1	139(2)
Amine mixture obtained in example 6	1:1	265
Amine mixture obtained in example 8	1:1	103
Comparative compound		
M-CDEA	1:1	128

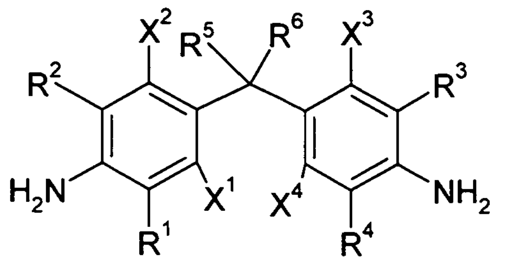
(1) The equivalents of reactive NH_2 groups used for calculating the equivalent ratios were calculated on the basis of the proportions of the chlorinated 4,4′-methylenebis-(2,6-dialkylanilines) in the product mixtures given in Tables 1 to 3 wherein the proportions in Tables 1 to 3 were equated with the mass ratios of the respective compounds.

(2) Gel time measured at 180 °C as melting point too high.

As may be seen from the results shown in Table 5, the mixtures of the present invention allow adjusting gel times of epoxy resins within a wide range including the value obtainable with the comparative compound M-CDEA. Thus, the present invention provides a possibility to effectively adjust the gel time of epoxy resins over a wide range and at the same time to avoid the use of toxic compounds such as MOCA and of compounds which may affect the appearance of the final product.

Claims

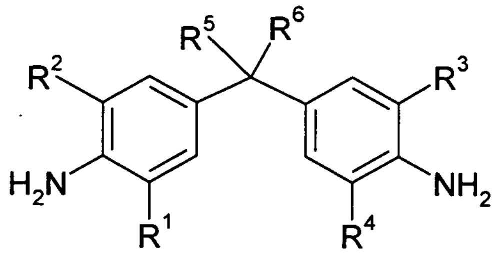
1. A process for the preparation of halogenated aromatic amines of the formula (1)



(1)

wherein R^1, R^2, R^3 and R^4 independently represent H, Cl or Br, an alkyl group or an alkoxy group, R^5 and R^6 independently represent H or an alkyl group or together with the carbon atom to which they are bound form a cyclopentane ring or a cyclohexane ring, and X^1, X^2, X^3 and X^4 independently represent H, Cl or Br, wherein at least one of X^1, X^2, X^3 and X^4 is Cl or Br, or mixtures thereof, said process comprising:

(a) providing an aromatic amine of the formula (2)



(2)

wherein R^1, R^2, R^3, R^4, R^5 and R^6 are as defined above, in the anilinium form in a mixture with sulfuric acid; and

(b) treating the mixture of step (a) with chlorine (Cl_2) or bromine (Br_2), followed by treatment with a base to obtain the halogenated aromatic amine of the formula (1).

2. The process of Claim 1, wherein R^1, R^2, R^3 and R^4 independently are an alkyl group and R^5 and R^6 are H or together with the carbon atom to which they are bound form a cyclohexane ring.

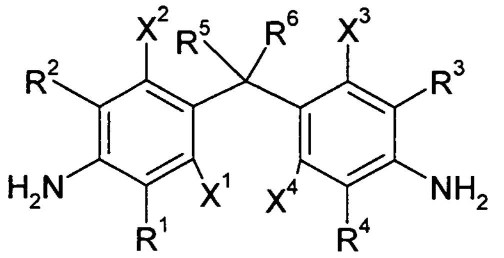
3. The process of Claim 1 or Claim 2, wherein X^1, X^2, X^3 and X^4 independently represent H or Cl.

4. The process of any one of Claims 1 to 3, wherein the reaction is carried out in a closed system.

5. The process of any one of Claims 1 to 3, wherein the reaction is carried out in an open system.

6. The process of any one of Claims 1 to 5, wherein the sulfuric acid has a sulfuric acid concentration of at least 85% by weight, preferably at least 95% by weight.

7. A compound of the general formula (1)



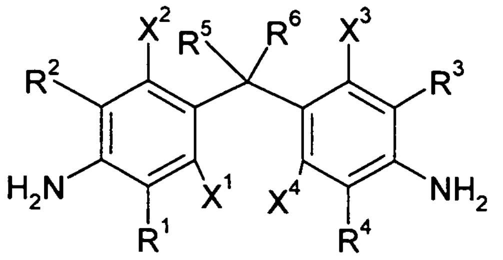
(1)

wherein R^1, R^2, R^3 and R^4 independently represent H, Cl or Br, an alkyl group or an alkoxy group, R^5 and R^6 independently represent H or an alkyl group or together with the carbon atom to which they are bound form a cyclopentane ring or a cyclohexane ring, and X^1, X^2, X^3 and X^4 independently represent H or Cl or Br, wherein at least one of X^1, X^2, X^3 and X^4 is Cl or Br,
with the proviso that compounds wherein R^1, R^2, R^3 and R^4 independently are H or an alkyl group and one of X^1 and X^2 and one of X^3 and X^4 is Cl and the other one is H are excluded, and at least one of R^1, R^2, R^3 and R^4 is an alkyl group.

8. The compound of Claim 7, wherein R^1, R^2, R^3 and R^4 independently are an alkyl group and R^5 and R^6 are H or together with the carbon atom to which they are bound form a cyclohexane ring.

9. The compound of Claim 7 or Claim 8, wherein X^1, X^2, X^3 and X^4 independently represent H or Cl.

10. A composition comprising two or more compounds of the formula (1)



(1)

wherein R^1, R^2, R^3 and R^4 independently represent H, Cl or Br, an alkyl group or an alkoxy group, R^5 and R^6 independently represent H or an alkyl group or together with the carbon atom to which they are bound form a cyclopentane ring or a cyclohexane ring, and X^1, X^2, X^3 and X^4 independently represent H, Cl or Br, wherein at least one of X^1, X^2, X^3 and X^4 is Cl or Br, wherein at least two of the compounds present in said composition differ in the number of halogen atoms represented by X^1, X^2, X^3 and X^4 and/or in at least one of R^1, R^2, R^3, R^4, R^5 and R^6, and at least one of R^1, R^2, R^3 and R^4 is an alkyl group.

11. The composition of Claim 10, obtainable by the process of any one of Claims 1 to 6.

12. The composition of Claim 10 or Claim 11, wherein R^1, R^2, R^3 and R^4 independently are an alkyl group and R^5 and R^6 are H or together with the carbon atom to which they are bound form a cyclohexane ring.

13. The composition of any one of Claims 10 to 12, wherein X^1, X^2, X^3 and X^4 independently represent H or Cl.

14. Use of a compound of any one of Claims 7 to 9 or of a composition of Claims 10 to 13 as a curing agent in the preparation of polyurethanes or epoxy resins.

15. Use of a compound of any one of Claims 7 to 9 or of a composition of Claims 10 to 13 for adjusting the gel time of polyurethanes or epoxy resins.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/004423

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G18/10 C08G18/32 C08G18/38 C07C209/68 C07C209/74
C07C211/51 C07C213/00 C07C217/80 C08G59/50
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 950 792 A (ALTHAUS HANS [CH] ET AL) 21 August 1990 (1990-08-21) column 2, line 36 - column 3, line 11 claims 1,2,3,4	1-6
A	WO 97/21749 A1 (LONZA AG [CH]; DAUM ULRICH [CH]; FEEKEN ARNO [DE]; JARRE WOLFGANG [DE]) 19 June 1997 (1997-06-19) the whole document	1-6
X	US 3 752 768 A (THOMPSON J ET AL) 14 August 1973 (1973-08-14) column 1, lines 10-15 column 3, lines 13-16 column 5, lines 49-60	7-15

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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search 30 January 2012	Date of mailing of the international search report 06/02/2012
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Bezard, Stéphane

International application No
PCT/EP2011/004423

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 207 377 A (ALLIED CHEM [US]) 30 September 1970 (1970-09-30) page 1, lines 14-15 example V -----	7-9,14
X	GB 1 044 509 A (US RUBBER CO) 5 October 1966 (1966-10-05) page 2, lines 30-32 page 2, lines 38-39; example Formula II -----	7-9,14, 15

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2011/004423

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-6

   "a process for the preparation of halogenated aromatic amines of the formula (1), wherein R1, R2, R3 and R4 independently represent H, Cl, Br, an alkyl group or an alkoxy group, R5 and R6 independently represent H or an alkyl group or together with the carbon atom to which they are bound form a cyclopentane ring or a cyclohexane ring, and X1, X2, X3 and X4 independently represent H, Cl or Br, wherein at least one of X1, X2, X3 and X4 is Cl or Br, or mixtures thereof, said process comprising:
   (a) providing an aromatic amine of the formula (2), wherein R1, R2, R3, R4, R5 and R6 are as defined above, in the anilinium form in a mixture with sulfuric acid; and
   (b) treating the mixture of step (a) with chlorine (Cl2) or bromine (Br2), followed by treatment with a base to obtain the halogenated aromatic amine of the formula (1)".

   ---

2. claims: 7-9(completely); 14, 15(partially)

   "a compound of the general formula (1) wherein R1, R2, R3 and R4 independently represent H, Cl, Br, an alkyl group or an alkoxy group, R5 and R6 independently represent H or an alkyl group or together with the carbon atom to which they are bound form a cyclopentane ring or a cyclohexane ring, and X1, X2, X3 and X4 independently represent H, Cl or Br, wherein at least one of X1, X2, X3 and X4 is Cl or Br, with the provisio that compounds wherein R1, R2, R3 and R4 independently are H or an alkyl group and one of X1 and X2 and one of X3 and X4 is Cl and the other one is H are excluded".

   ---

3. claims: 10-13(completely); 14, 15(partially)

   "a composition comprising two or more compounds of the formula (1), wherein R1, R2, R3 and R4 independently represent H, Cl, Br, an alkyl group or an alkoxy group, R5 and R6 independently represent H or an alkyl group or together with the carbon atom to which they are bound form a cyclopentane ring or a cyclohexane ring, and X1, X2, X3 and X4 independently represent H, Cl or Br, wherein at least one of X1, X2, X3 and X4 is Cl or Br, wherein at least two of the compounds present in said composition differ in the number of halogen atoms represented by X1, X2, X3 and X4 and/or in at least one of R1, R2, R3, R4, R5 and R6".

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2011/004423

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