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(54) Title: PROCESS FOR THE PREPARATION OF AN ALKYLATED AMINOPLAST RESIN; RESIN THUS OBTAINABLE AND USE THEREOF

(57) Abstract: The invention relates to a process for the preparation of an alkylated aminoplast resin, comprising the step of bringing together and reacting: • a C₅ - C₃₀ alcohol; and • one or more chosen from the group consisting of: an aminoplast resin, a mixture of an amino compound and an aldehyde, and an alkylated aminoplast resin prepared from a C₁ - C₄ alcohol. The C₅ - C₃₀ alcohol is preferably chosen from the group consisting of cyclohexanol and tetrahydrofurfuryl alcohol. The invention also relates to the alkylated aminoplast resin obtainable, and to its use, for example as cross-linker in coating compositions such as powder coating compositions.



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PROCESS FOR THE PREPARATION OF AN ALKYLATED AMINOPLAST RESIN;
RESIN THUS OBTAINABLE AND USE THEREOF

5 The invention relates to a process for the preparation of an alkylated aminoplast resin; the invention furthermore relates to aminoplast resins as obtainable by the process according to the invention. Moreover the invention relates to the use of the aminoplast resins, e.g. as cross-linking agent in coating compositions.

10 Aminoplast resins as such are known. Examples of known resins are hexa(methoxymethyl)melamine (HMMM) or hexa(butoxymethyl)melamine (HBMM). It is also known to use HMMM or HBMM or mixtures thereof as a cross-linking agent in coatings such as polyester powders coatings. The disadvantage associated with the use of HMMM and/or HBMM, however, is that they have a low glass transition temperature (T_g) of about -60°C . When HMMM and/or HBMM are used in an effective
15 amount - typically 10 to 20 wt.% of a coating composition - the T_g of an HMMM- or HBMM-containing powder coating composition is lowered to undesirably low values, lying often below room temperature.

It is the objective of the present invention to reduce or even eliminate the aforementioned disadvantage.

20 The objective is achieved by an aminoplast resin, obtainable by a process comprising the steps of bringing together and reacting:

- a C_5 - C_{30} alcohol; and
- one or more compounds chosen from the group consisting of: an aminoplast resin, a mixture of an amino compound and an aldehyde, and an alkylated aminoplast
25 resin prepared from a C_1 - C_4 alcohol.

An advantage of the alkylated aminoplast resins according to the invention is that they can have a higher T_g than the known alkylated aminoplast resins, while still providing functionality that allows the alkylated aminoplast resin to be used in known fashion, e.g. as cross-linking agent.

30

The invention relates to a process for the preparation of an alkylated aminoplast resin. The term resin refers to low molecular weight oligomers having at least two reactive groups per molecule. The molecular weight of a resin usually falls in a wide range going from about 200 to about 6,000 or more. It should be noted that

products like HMMM or HBMM are relatively small but still fall within the scope of the term resin as used herein, although they are not always referred to in this way in literature. The presence of the reactive groups in a resin is important as these reactive groups form the chemical handles to connect oligomeric or polymer chains together through covalent cross-link bonds, via a chemical reaction. The process of cross-linking is also referred to as "curing" or "hardening".

The resins as prepared in the present invention are aminoplast resins. Aminoplast resins as such are known, they are understood to be resins prepared from raw materials that comprise an amino compound - i.e. a compound having at least one -NH or -NH₂ group - or mixture of amino compounds and an aldehyde or a mixture of aldehydes. The most widely used amino compounds in the preparation of aminoplast resins are urea and/or melamine. Typically in an aminoplast, the majority of the compounds reacting with the aldehyde are amino compounds. Other compounds that react with the aldehyde may be present too, however: an example of such a compound is phenol. A commonly used aldehyde in the preparation of aminoplast resins is formaldehyde. Within the context of the present invention, the term formaldehyde also encompasses compounds that can release formaldehyde such as paraformaldehyde and trioxan. Other example of aldehydes that may be used as raw materials in the process of the invention include propanal, benzaldehyde, and alkanol hemiacetals; examples of alkanol hemiacetals include methylglyoxylate methanol hemiacetal (GMHATM, DSM Fine Chemicals, Linz) and ethylglyoxylate ethanol hemiacetal (GEHATM, DSM Fine Chemicals, Linz).

In the present invention, the aminoplast resins are alkylated. The term alkylated aminoplast resins refers to resins that may be obtained by modification of at least part of the amino-aldehyde bonds in an aminoplast resin with an alcohol. A known example of an alkylated aminoplast resin is HMMM; in HMMM, the alcohol was methanol.

The process according to the invention comprises the step of bringing together raw materials and ensuring that they react.

The raw materials comprise according to the invention a C₅ - C₃₀ alcohol. Such alcohols are as such known. Examples of the said alcohols include pentanol, hexanol, cyclohexanol, tetrahydrofurfuryl alcohol (THFA), and stearyl alcohol. The term C₅ - C₃₀ alcohol may herein refer to a single compound or it may refer to a mixture of various C₅ - C₃₀ alcohols. Preferably, the hydroxy group in the C₅ - C₃₀ alcohol is attached to an aliphatic group or a cycloalkyl group; it was found that the use

of allylic (unsaturated) alcohols may lead to undesirable side effects such as discolouration. Preferably, the C₅ - C₃₀ alcohol does not comprise an aromatic ring; it was found that the -OH group in hydroxy-aromatic compounds may not be sufficiently reactive to establish the alkylation reaction; more preferably, the C₅ - C₃₀ alcohol is not phenol. The C₅ - C₃₀ alcohol is preferably a mono-hydroxy alcohol; it was found that the stability of alkylated aminoplast resins prepared with mono-hydroxy-alcohols is higher than the stability of alkylated aminoplast resins prepared with multi-hydroxy alcohols such as diols. Stability is herein qualitatively defined as the tendency of the alkylated aminoplast resin to undergo self-reaction, visible as spontaneous gel-formation.

It is particularly preferred according to the invention that the C₅ - C₃₀ alcohol is cyclohexanol or THFA or a mixture thereof. It was found that the use of THFA as (part of) the C₅ - C₃₀ alcohol can lead to an alkylated aminoplast resin having a very beneficial combination of properties; one such property is an increased affinity to aqueous systems or organic solvents, so that a higher solubility in water or organic solvents can be achieved compared to alkylated aminoplast resins prepared with other alcohols, or at least with a reduced need to implement special measures to increase solubility such as acidification.

The raw materials that are brought together in the process according to the invention further comprise one or more compounds chosen from the group of:

- a mixture of an amino compound and an aldehyde;
- an aminoplast resin; and
- an alkylated aminoplast resin prepared from a C₁ - C₄-alcohol.

A selection of each of the three members of this group represents a main embodiment of the invention, whereby it is noted that the said main embodiments may be combined with each other.

In a first main embodiment of the invention, the raw materials that are brought together with the C₅ - C₃₀ alcohol comprise a mixture of an amino compound and an aldehyde; hereby a reaction mixture is formed. The amino compound and the aldehyde are thus brought into the reaction mixture essentially as such, i.e. not having reacted into an aminoplast resin. In this first main embodiment, therefore, the formation of the aminoplast resin and the - typically subsequent - formation of the alkylated aminoplast resin can take place in the same reaction space.

The forming of the reaction mixture is in this first main embodiment

designated as step a). When forming the reaction mixture in step a), not only the amino compound and the aldehyde are brought together, but also a C₅ - C₃₀ alcohol and optionally a solvent. Preferably, the amino compound comprises or even consists essentially of melamine. It is furthermore preferred that the aldehyde comprises or
5 even consists essentially of formaldehyde.

The terms 'consist essentially of', 'constitute essentially all' or equivalents have the usual meaning that no other compounds or measures are present or taken that have significant impact on the working, effects or achieved objectives of the invention.

10 It is preferred in step a) to ensure that the molar ratio between the reactants remains within certain limits.

The molar ratio between the aldehyde (D) and the amino compound (A) preferably lies within certain limits. Since the aldehyde will typically react with an -NH functionality of the amino compound, and since the amino compounds that are
15 preferably used in the process according to the invention such as melamine or urea typically comprise multiple -NH and/or NH₂ functionalities, it is preferred to express the molar ratio between D and A in terms of the amount of aldehyde molecules per -NH₂ functionality. Moreover, for practical reasons only and in view of the preferred position of melamine as amino compound, it is preferred to contemplate the ratio of an
20 aldehyde compound per three -NH₂ groups. The thus defined D/(NH₂)₃ ratio is according to the invention preferably at least 3; this has the advantage that on average each -NH₂ functionality can react with an aldehyde molecule so that a sufficiently complex resin development can take place. The D/(NH₂)₃ ratio is according to the invention preferably at most 7; this has the advantage that essentially all -NH
25 functionalities can react with an aldehyde molecule; this can ultimately lead to the highest possible degree of alkylation in the end product.

Also the molar ratio between the C₅ - C₃₀-alcohol (L) and the amino compound (A), lies preferably within certain limits. For the same reasons as given previously, it is preferred to contemplate the molar ratio between an alcohol and three
30 -NH₂ groups, the L/(NH₂)₃ ratio. The said L/(NH₂)₃ ratio is preferably at least 1. This has the advantage that a minimum sufficient degree of alkylation can take place. In many cases, it can be beneficial to use the C₅ - C₃₀-alcohol not only in its function as reactant but also in a role as solvent; it may thus be beneficial to ensure that the L/(NH₂)₃ ratio in the reaction mixture has a value that is higher than the stoichiometrically maximum
35 of 6, such as 20, 15, or 10. Nevertheless, for example in the case that it is not

necessary for the alcohol to act as solvent, it can be beneficial to limit the $L/(NH_2)_3$ ratio to at most 6, more preferably at most 4; this has the advantage that upon completion of the process of the invention it is avoided to have a high amount of residual alcohol in the reaction mixture. Furthermore, preferably, the $L/(NH_2)_3$ ratio lies between 1.5 and 3.

5 It is furthermore preferred that, while respecting the guidance given on the molar ratios $D/(NH_2)_3$ and $L/(NH_2)_3$ as given above, the molar D/L ratio can vary between 0.25 and 5; it is noted hereby that a value of D/L below 1 is mostly favourable in case the alcohol (L) is used as solvent and as reactant; otherwise, the value of D/L is preferably at least 1, preferably at least 1.5; the molar D/L ratio is preferably at most 4,
10 or 3.

The preferred ranges for the molar ratios $D/(NH_2)_3$, $L/(NH_2)_3$ and D/L as given above hold for the raw materials as they are brought together; they also hold in principle as preferred ranges for the alkylated aminoplast resin, except that excess ratios - such as a $D/(NH_2)_3$ ratio lying above 6, an $L/(NH_2)_3$ ratio lying above 6 or a D/L
15 ratio lying below 1 - are not applicable. When referring to the alkylated aminoplast resin, the said ratios should be related to the structural elements of the alkylated aminoplast resin that can be attributed to the respective raw materials (i.e. D, L, A or -NH).

In the forming of the reaction mixture in step a) according to the
20 invention, it may be beneficial - as is known - to add a solvent; preferred solvents are the C_5 - C_{30} alcohol or water.

The reaction mixture is in step b) according to the first main embodiment of the invention brought to a pH lying between 1 and 7. It was found that the formation of the alkylated aminoplast resin, and in particular the alkylation sub-step
25 in which the alcohol is incorporated into the aminoplast resin, proceeds best under acidic conditions; preferably, the reaction mixture is brought to a pH lying between 2 and 6, or between 3 and 5. If the pH of the reaction mixture is upon its formation not within the desired range, then it should be brought there by means as such known to the skilled person, e.g. by adding a (Brønstedt) acid such as sulphuric acid or formic
30 acid, or a base. Preferably, the pH is maintained within the said range throughout steps b) and c).

In order for the reaction step to take place efficiently and effectively, the reaction mixture should not only be brought to within a certain pH range, but also to within a certain temperature range. The first main embodiment according to the
35 invention comprises, therefore, a step c) wherein the reaction mixture is brought to a

temperature lying between 80°C and 130°C. The implementation of step c) will usually necessitate a heating of the reaction mixture. This heating may be achieved by means that are as such known, such as a heat exchanger.

Once the reaction mixture has been brought to within the said
5 temperature range, the formation of the alkylated aminoplast resin can take place. For this to happen, the reaction mixture should remain within the said temperature range for a desired amount of time. The amount of time necessary will depend on factors that are as such known to the skilled person. Crucial factors herein are the actual
10 temperature, the actual pH and the desired constitution of the alkylated aminoplast resin. The influence of the actual temperature is, as is known, that an increase of temperature will lead to a shortening of the time needed to achieve the desired result. The influence of the actual pH is, as is known, that a lowering of the pH will lead to a shortening of the time needed to achieve the desired result. Nevertheless, a too low pH
15 such as a pH lying below 1 is less favourable, because it was found that then undesired side-reactions - such as the protonating of an -NH functionality of an amino compound or spontaneous self-condensation leading to gel formation - may arise or may increase to significant levels; moreover, a very low pH is unfavourable in case step d) - to be discussed in more detail below - is executed, as a very high amount of a
20 base must then be added. Also of influence of the time needed to execute step c) is the desired constitution of the alkylated aminoplast resin: the higher the desired molecular weight of the alkylated aminoplast resin, the longer step c) will need to be carried out. In practice this may mean that the length of time needed to carry out step c) may vary between wide limits, for example between 5 or 10 minutes and 180 or even 240
25 minutes. The actual optimal time needed to carry out step c) may be easily determined via routine experiments in which the factors as identified above such as temperature and pH are varied and in which the development of the alkylated aminoplast resin is monitored via the taking of sample at regular intervals and analysing them by means of tests that are as such known such as but not limited to cloud point measurement, water
tolerance measurement, infrared analysis, NMR analysis.

30 In the first main embodiment of the invention, steps a), b) and c) may be carried out in sequence or they may be carried out simultaneously.

Upon completion of step c), it may be desirable to stop the reaction and / or to isolate the alkylated aminoplast resin as formed. This may be achieved by implementing the preferred steps d) and possibly also e) and f). In step d), the pH of
35 the reaction mixture is brought to a value lying between 9 and 13. This may be

achieved by means known as such, such as by adding a base like (aqueous) sodium hydroxide. The most important effect of the pH increase is that the formation or further formation of the alkylated aminoplast resin is effectively brought to a standstill. It may now be possible to use the alkylated aminoplast resin; it may, however, also be
5 desirable to isolate the alkylated aminoplast resin from unreacted raw materials, in particular the C₅ - C₃₀ alcohol. In this case, it is preferred to bring in a step e) the temperature of the reaction mixture to a value such that volatile components such as the C₅ - C₃₀ alcohol can be boiled off, followed by a step f) in which substantially all of the volatile components such as the C₅ - C₃₀ alcohol are boiled off and which the
10 alkylated aminoplast is thus recovered. The temperature to which the reaction mixture is brought in step e) is preferably at or above the boiling point of the C₅ - C₃₀ alcohol at the prevailing pressure. It may be favourable of necessary to operate step f) in vacuum, in order to facilitate the boiling off of the alcohol and/or to avoid degradation of the alkylated aminoplast resin. Volatile components are defined as those compounds that
15 can be separated from the alkylated aminoplast resin through heating and/or distillation and/or exposure to vacuum without leading to significant degradation of the alkylated aminoplast resin.

In a second main embodiment of the invention, a reaction system is
20 formed that at first does not comprise the C₅ - C₃₀ alcohol. Rather, an aminoplast resin is formed first, then followed by an alkylation step. The second main embodiment of the invention thus comprises the steps of:

- i. bringing an amino compound - preferably comprising melamine - together with an aldehyde and optionally a solvent, to form a reaction system;
- 25 ii. bringing the pH of the reaction system to between 7 and 10;
- iii. bringing the temperature of the reaction system to between 60°C and reflux and letting the reaction system remain within the said temperature range for a desired amount of time, whereby an aminoplast resin is formed;
- iv. bringing the pH of the reaction system to between 1 and 7 and adding a C₅ -
30 C₃₀-alcohol to the reaction system;
- v. letting the reaction system remain within the temperature range of 70°C and reflux for a desired amount of time, whereby the alkylated aminoplast resin is formed.

Steps (i) to (iii) are steps that are as such known in processes for the
35 preparation of aminoplast resins, and may be executed according to customary

industrial practice, while taking account of the features of the present embodiment. The interpretation of terms is as in the previous main embodiment, unless noted otherwise.

In step (i), an amino compound and the aldehyde are brought into the reaction mixture essentially as such, i.e. not having reacted into an aminoplast resin.

- 5 The amino compound preferably comprises melamine, or even consists essentially of melamine. The aldehyde as used may comprises formaldehyde, and preferably even consists essentially of it. It may, however, also be possible to use another aldehyde such as one of the aldehydes mentioned earlier in this description. Also in this second main embodiment, the $D/(NH_2)_3$ ratio is preferably at least 3 and preferably at most 7.
- 10 The solvent in step (i) is preferably water.

The desired amount of time as needed for the execution of step (iii) is primarily determined by the desired characteristics of the aminoplast resin that is formed. As is known, a prolonged reaction time in step (iii) will lead to an increase of molecular weight of the aminoplast resin; said increase can go so far that the cloud

15 point is reached, or even that the water tolerance is reduced to 2, 1 or even 0. It was found that an increase of molecular weight in step (iii) can lead to an increase in glass transition temperature T_g of the alkylated aminoplast resin that will be subsequently formed in step (v). As is known, the cloud point of a resin is defined as the point at which 1 drop of the resin added to a large amount of water at 20°C no longer directly

20 dissolves but shows turbidity. As is also known, the water tolerance of a resin is defined as the amount of water in gram that can be added at 20°C to 1 gram of resin before the resin turns turbid.

In case the molar $D/(NH_2)_3$ ratio in step (i) was lower than 6, it can be beneficial to introduce, during or subsequent to step (iii) and prior to the execution of

25 steps (iv) and further as discussed below, a D-mixing step (iiia) and a D-binding step (iiib). In D-mixing step (iiia), the aminoplast resin is brought together with an amount of an aldehyde compound D, such that the overall molar $D/(NH_2)_3$ ratio in the reaction system increases with at least 0.3, preferably at least 0.5 or 1, and with at most such that the overall $D/(NH_2)_3$ ratio in the reaction system is brought to 8. In D-binding step

30 (iiib), then, the reaction system is brought to conditions such that the free aldehyde can react with the aminoplast resin so that an aldehyde-enriched aminoplast resin is formed. The conditions in step (iiib) can be similar or even the same as in step (iii). The aldehyde as introduced into the reaction system in step (iiia) may be the same aldehyde as introduced in step (i) or it may be a different aldehyde.

35 Subsequent to the formation of the aminoplast resin or aldehyde-

enriched aminoplast resin, the pH of the reaction system is decreased and the alkylation step is done; this is reflected in steps (iv) and (v) of the invention. The amount of C₅ - C₃₀-alcohol to be added is also in this second main embodiment laid down preferably via the molar ratio between the C₅ - C₃₀-alcohol (L) and the amino
5 compound (A) via the -NH functionality. The L/(NH₂)₃ ratio is preferably at least 1, and preferably at most 4, and more preferably lies between 1.5 and 3. The preferences for the D/L ratio are as given for the previous main embodiment.

The desired amount of time as needed for the execution of step (v) is primarily determined by the time needed for the alkylation to have progressed
10 sufficiently far. Although it is usually preferred to progress the alkylation as far as the prevailing reaction conditions will allow, it is also possible to progress to only a fraction of this, e.g. to 50% or 75% of maximum alkylation.

Upon completion of step (v) of the second main embodiment, it may be desirable to stop the alkylation reaction; it may also be desirable to recover the
15 alkylated aminoplast resin that has been formed from the reaction system. The invention thus further comprises the preferred steps of:

- vi. bringing the pH of the reaction system to between 9 and 13;
- vii. bringing the temperature of the reaction system to a value such that volatile components can be boiled off; and
- 20 viii. boiling off substantially all of the volatile components and recovering the alkylated aminoplast resin.

The execution of steps (vi), (vii) and (viii) is done analogous to the execution of steps d), e) and f).

25 In a third main embodiment of the invention, a reaction composition is formed in a step α). The reaction composition differs from the earlier defined reaction mixture and reaction system in that the raw materials as brought together do not comprise an amino compound as such to any significant extent, and neither an aldehyde as such to any significant extent. Rather, they are brought into the reaction
30 composition in reacted form, in particular in the form of an alkylated aminoplast resin prepared from a C₁ - C₄-alcohol. The amount of amino compound and aldehyde in unreacted form in the reaction composition is preferably limited to less than 15, 10 or 5 wt.%, preferably less than 2 wt.% or 1 wt.% of the total amount of amino compound or aldehyde, i.e. including the amounts that were used to prepare the alkylated aminoplast
35 resin prepared from a C₁ - C₄ alcohol. Preferably, HMMM or HBMM are used as

alkylated aminoplast resin prepared from a C₁ - C₄ alcohol. It is generally favourable to use an alkylated aminoplast resin prepared from melamine as amino compound. In another preferred embodiment, isopropanol was used as the C₁ - C₄ alcohol. The third main embodiment of the invention thus constitutes essentially a re-alkylation process

5 and comprises the steps of:

- α) bringing an alkylated aminoplast resin prepared from a C₁ - C₄-alcohol together with a C₅ - C₃₀-alcohol and optionally a solvent such as for example water, to form a reaction composition;
- β) bringing the pH of the reaction composition to between 1 and 7;
- 10 γ) bringing the reaction composition to a temperature lying between 60°C and 130°C and letting the reaction composition remain within the said temperature range for a desired amount of time, whereby the alkylated aminoplast resin is formed.

Steps α), β) and γ) may be executed according to customary
15 industrial practice, while taking account of the features of the present embodiment. The interpretation of terms is as in the previous main embodiments, unless noted otherwise. In a preferred embodiment the alkylated aminoplast resin prepared from a C₁ - C₄-alcohol is HMMM and/or HBMM.

The desired amount of time as needed to complete step γ) of the
20 invention is primarily determined by the time needed to reach a sufficient degree of re-alkylation. Although it is usually preferred to progress the re-alkylation as far as the prevailing reaction conditions will allow, it is also possible to progress to only a fraction of this, e.g. to 50% or 75% of maximum re-alkylation.

Upon completion of step γ) of the third main embodiment, it may be
25 desirable to stop the re-alkylation reaction; it may also be desirable to recover the alkylated aminoplast resin that has been formed from the reaction composition. The invention thus further comprises the preferred steps of:

- δ) bringing the pH of the reaction composition to between 9 and 13;
- ε) bringing the temperature of the reaction system to a value such that volatile
30 components can be boiled off; and;
- ζ) boiling off substantially all of the volatile components and recovering the alkylated aminoplast resin.

The execution of steps δ), ε) and ζ) is done analogous to the execution of steps d), e) and f) and (vi), (vii) and (viii).

As indicated earlier, it can be possible to combine in certain ways the main embodiments with each other, whereby further main embodiments of the invention are defined. An example of such a combination is the use of an alkylated aminoplast resin as formed in step c) of the invention as raw material in step a), partly or wholly instead of the alkylated aminoplast resin prepared from a C₁ - C₄ alcohol. Similarly, it is possible to use the alkylated aminoplast resin as formed in step (v) of the invention to partly or wholly replace the alkylated aminoplast resin prepared from a C₁ - C₄ alcohol in step a).

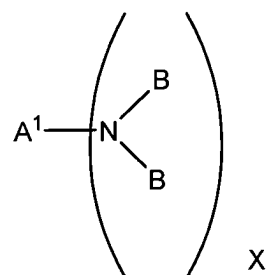
For all main embodiments certain combinations of compounds are particularly preferred, such as the choice of melamine as amino compound, the choice of cyclohexanol or THFA as the C₅ - C₃₀ alcohol, and the choice of formaldehyde as aldehyde. It may, however, be preferred to operate under formaldehyde-free conditions. In such a case one of the alternative aldehydes as mentioned earlier such as propanal, benzaldehyde or GMHA is preferred, in combination with melamine as amino compound and cyclohexanol or THFA as the C₅ - C₃₀ alcohol.

The main embodiments as described above relate to processes for the preparation of alkylated aminoplast resins. In preparing the alkylated aminoplast resins, it was found that the molar D/(NH₂)₃ ratio is of influence on the glass transition temperature T_g of the alkylated aminoplast resin; it was found that a lower D/(NH₂)₃ ratio - however preferably within the ranges as given - can lead to an increase of the T_g; care must be taken, however, that in such cases the stability of the alkylated aminoplast resin has not suffered too much. Stability is herein qualitatively defined as the tendency of the alkylated aminoplast resin to undergo self-reaction, visible as spontaneous gel-formation. Likewise it was found that a reduction of the molar L/(NH₂)₃ ratio is of influence on the glass transition temperature T_g of the alkylated aminoplast resin; it was found that a lower L/(NH₂)₃ ratio - however preferably within the ranges as given - can lead to an increase of the T_g; care must also here be taken, however, that in such cases the stability of the alkylated aminoplast resin has not suffered too much. It was found that the specific type of alcohol is of influence on the stability of the alkylated aminoplast resin; generally speaking, C₅ - C₃₀ alcohols lead to more stable alkylated aminoplast resins than C₁ - C₄ alcohols.

Surprisingly, it is possible according to the invention to prepare alkylated aminoplast resins that have a high T_g - that can lie at 10, 15, or 20°C or even at 25, 30, 40°C or higher - and that have a good stability, whereby the alkylated aminoplast resins still have the reactivity needed for certain uses such as the use as

cross-linker in e.g. coating compositions.

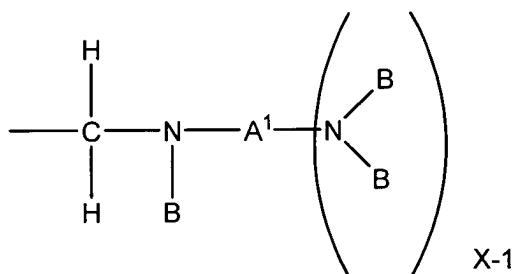
The invention thus further relates to alkylated aminoplast resins that are obtainable according to any one of the above-described main embodiments. In certain cases it may be possible to express the alkylated aminoplast resin according to the invention by means of the following formula (I):



(I)

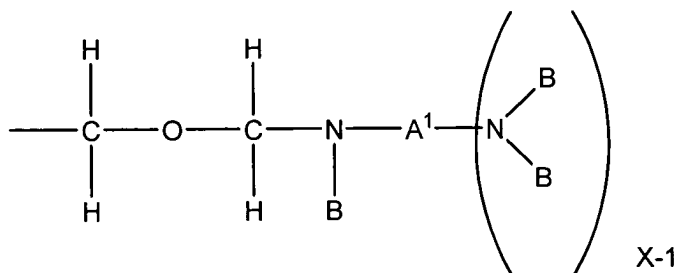
wherein:

- A¹ is the core of an amino compound A¹-(-NH₂)_x;
- x is at least 2;
- B is H, CH₂OR₁, a group according to formula (II), or a group according to formula (III), whereby:
 - R₁ is H or the C₅ - C₃₀ alcohol minus a -OH group
 - formula (II) is:



(II)

- formula (III) is:



(III)

whereby:

- at least 30% or 40%, preferably 50%, 60%, or even 70% or 80% of all B groups are CH_2OR_1 such that R_1 is the $\text{C}_5 - \text{C}_{30}$ alcohol minus a -OH group;
- the resin as a whole comprises at most 1.5 or 1.3, preferably at most 1.0, 0.8, 0.7 or even at most 0.6, 0.5 or 0.4 -NH groups per 'A¹' moiety, and
- the weight-average molecular weight of the resin lies between 200 and 10,000; preferably, the said weight-average molecular weight of the resin lies between 300 and 9,500, more preferably between 400 or 500 or 1,000 and 9,000.

10 The alkylated aminoplast resins according to the invention are suitable for a wide range of applications; one such application is their use as cross-linker; the cross-linking ability is favourable in e.g. resins, adhesive compositions, or coating compositions. Due to the possibility of creating according to the invention alkylated aminoplast resins having a high T_g - lying e.g. around room temperature or
15 above - they are in particular suitable as cross-linking agent in powder coating compositions. The invention thus further relates to coating compositions, in particular powder coating compositions, comprising the alkylated aminoplast resin according to the invention. The amount of alkylated aminoplast resin that is comprised in the powder coating composition may vary within wide limits; preferably, the said amount lies
20 between 1 and 30 wt.%, based on the powder coating composition as a whole. In an alternative embodiment of the invention, the alkylated aminoplast resin is not only used as cross-linker but moreover as integral coating element in a coating composition. In such a case, the amount of alkylated aminoplast resin as comprised in a coating composition may be up to 40, 60, 70, 80, 90 or even 95, 99 or essentially 100 wt.%.

25 As is known, a powder coating composition usually contains a catalyst, the role of the catalyst being to facilitate the cross-linking activity of the cross-linking agent. Often and preferably an acid is chosen as catalyst, in an effective amount; such effective amounts lie often in the range of 0.1 to 2 wt.%. An example of an acid that is often chosen in cross-linking practice is paratoluenesulfonic acid
30 (PTSA). In doing so, however, the catalysing functionality of the acid should be contemplated in function of the temperature. In practice, a powder coating composition comprising a cross-linking agent and a catalyst is prepared at somewhat elevated temperatures of for example about 50 to 80°C. It is important that a catalyst should not be very active at such temperatures. On the other hand, it is very favourable if a

catalyst becomes very active at temperatures which are only slightly higher than this, e.g. at about 100 - 120°C. In order to find a compromise between non-activity at somewhat elevated temperatures with high activity at temperatures slightly above that, the catalyst often comprises a combination of an acid and a blocking agent. Such combinations are as such known. An example of a class of components that is often chosen as blocking agents is the class of epoxy compounds. A preferred embodiment of the invention thus relates to a powder coating composition comprising an alkylated aminoplast resin according to the present invention and furthermore comprising as catalyst an acid and an epoxy compound, whereby the weight ratio between the acid and the epoxy compound lies between 10:90 and 70:30. Particularly preferred is a catalyst comprising paratoluenesulfonic as acid and a cycloaliphatic epoxide, preferably 3,4-epoxy cyclohexyl methyl-3,4 epoxy cyclohexane carboxylate.

The invention will be elucidated by means of the Examples as given below, without being limited thereto.

Example 1

Example 1 was carried out according to the first main embodiment of the invention, whereby the amino compound was melamine, paraformaldehyde was used as formaldehyde and the C₅ - C₃₀ alcohol was tetrahydrofurfuryl alcohol.

Steps a) and b) were executed in combination as follows: an oil heated 1.5 litre glass reactor equipped with a distillation setup was charged with 106.7 gram melamine, 171.3 gram paraformaldehyde (91-92% pure) and 1037.0 gram tetrahydrofurfuryl alcohol, and put under nitrogen. The oil temperature was set on 110°C. After 55 minutes the temperature of the reaction mixture was 94°C and the reaction mixture became clear. The oil temperature was set at 115°C. After 10 minutes 21.7 gram of a 2 Molar formic acid solution in tetrahydrofurfuryl alcohol was added and a vacuum of 400 mBar was applied.

Step c) was then executed. Over the course of 95 minutes the pressure was gradually reduced to 26 mBar. After 60 minutes the vacuum was stopped. Then, step d) was done through the addition of 68.5 gram of a 5% sodium hydroxide solution in tetrahydrofurfuryl alcohol. In the following steps e) and f), first a total 400 gram of liquid was removed. The clear reaction product still contains a lot of solvent. On a rotation evaporator the solvent was removed under vacuum; starting at 120°C, the temperature was gradually increased over a period of 100 minutes to 170°C and was then kept at 170°C for 15 minutes. Finally, 310 gram of alkylated aminoplast

resin was recovered.

Subsequent testing of the alkylated aminoplast resin yielded the following properties:

- Glass transition temperature T_g was 22°C as determined via DSC
- 5 - Number-averaged molecular weight (M_n) was 1478; weight-averaged molecular weight (M_w) was 7490 (measured in GPC with polystyrene standard)
- The molar ratio of D/(NH₃)₃ of the alkylated aminoplast resin, i.e. equalling the ratio of formaldehyde to melamine building blocks as incorporated into the resin, was 3.6; this was determined via a ¹³C-NMR measurement on the alkylated aminoplast
- 10 resin.
- The molar L/(NH₂)₃ ratio of the alkylated aminoplast resin, i.e. equalling the ratio of tetrahydrofurfuryl alcohol to melamine building blocks as incorporated into the resin, was 2.1; this was determined via a ¹³C-NMR measurement on the alkylated aminoplast resin.

15

Example 2

Example 2 was carried out according to the second main embodiment of the invention, whereby the amino compound was melamine and the C₅ - C₃₀ alcohol was cyclohexanol.

20

Preparation of an aminoplast resin:

An oil heated 1,5 litre glass reactor equipped with reflux condenser was charged with 100.8 gram melamine, 335,2 gram 50,14% formaldehyde in water and 53 gram water. The pH of the formaldehyde solution was adjusted before addition

25 to the reactor to pH 9,0 with a 2 molar sodium hydroxide solution. The temperature of the reaction system was set on 60 °C. As soon as the reaction system became clear the reactor was discharged. The reaction system was left at room temperature for 16 hours.

30 *Preparation, recovery and property-determination of the alkylated aminoplast resin:*

An oil heated 1,5 litre glass reactor equipped with a dean stark set up was charged with 206 gram of the reaction system - comprising the aminoplast resin. To the reaction system was added 592 gram cyclohexanol; the reaction system was then put under nitrogen atmosphere. The oil temperature was set on 84°C. After 70

35 minutes the reaction mixture became clear and the pH was lowered to 4.6 with fuming

hydrochloric acid (step (iv)). The oil temperature was set at 109°C. After 10 minutes the temperature of the reaction mixture was 92°C. After 140 minutes a vacuum of 600 mBar was applied and within 50 minutes lowered to 70 mBar. After 80 minutes the vacuum was stopped and the pH was set on 12.5 (step (vi)) with a saturated sodium hydroxide solution in methanol. Via the dean stark 130 gram of water was removed.

On a rotation evaporator any excess solvent or volatile components were removed under vacuum at 120°C and in 100 minutes the temperature was gradually increased to 150°C leaving it at 150°C for 15 minutes. The alkylated aminoplast resin was thus recovered.

Subsequent testing of the alkylated aminoplast resin yielded the following properties:

- Glass transition temperature T_g was 48°C (measured in DSC)
- Number-averaged molecular weight (M_n) was 1193; weight-averaged molecular weight (M_w) was 2511 (measured in GPC with polystyrene standard)
- The molar ratio of $D/(NH_3)_3$ of the alkylated aminoplast resin, i.e. equalling the ratio of formaldehyde to melamine building blocks as incorporated into the resin, was 4.7; this was determined via a ^{13}C -NMR measurement on the alkylated aminoplast resin.
- The molar $L/(NH_2)_3$ ratio of the alkylated aminoplast resin, i.e. equalling the ratio of cyclohexanol to melamine building blocks as incorporated into the resin, was 2.1; this was determined via a ^{13}C -NMR measurement on the alkylated aminoplast resin.

Example 3

Example 3 was carried out as example 2, with however the following differences:

- instead of lowering the pH to 4.6 in step (iv), it was lowered to 2.9;
- the final recovery of the alkylated aminoplast resin in step (viii) was done via precipitation from acetone at -20°C followed by filtration and drying under vacuum.

Subsequent testing of the alkylated aminoplast resin yielded the following properties:

- Glass transition temperature T_g was 47°C (measured in DSC)
- Number-averaged molecular weight (M_n) was 2784; weight-averaged molecular weight (M_w) was 5833 (measured in GPC with polystyrene standard)
- The molar ratio of $D/(NH_3)_3$ of the alkylated aminoplast resin, i.e. equalling the ratio

of formaldehyde to melamine building blocks as incorporated into the resin, was 5.0; this was determined via a ^{13}C -NMR measurement on the alkylated aminoplast resin.

- 5 - The molar $\text{L}/(\text{NH}_2)_3$ ratio of the alkylated aminoplast resin, i.e. equalling the ratio of cyclohexanol to melamine building blocks as incorporated into the resin, was 3.0; this was determined via a ^{13}C -NMR measurement on the alkylated aminoplast resin.

Example 4

10 *Use of an alkylated aminoplast resin as cross-linker*

20 parts of the alkylated aminoplast resin as prepared in Example 1, 80 parts of UralacTM P1580 powder (an OH-functional saturated carboxylated polyester coating resin; supplier: DSM[®] Resins), 0.5 part of a catalysing compound consisting of 1 part paratoluene sulfonic acid and 3 parts AEPD (2-amino-2-ethyl-1,3-propanediol), 15 0.75 part of benzoin as anti-foaming agent, 50 parts titanium white (KronosTM 2160), and 1.5 part of ResiflowTM PV5 as flowing agent (supplier: Worlée-Chemie) were fed to a twin-screw extruder and extruded at 85°C. The extrudate was milled, and subsequently sieved so as to obtain a powder coating composition having no particles bigger than 90 µm.

20 A layer of the powder coating composition, which had a T_g lying above room temperature, was sprayed electrostatically onto an aluminium sheet. The layer had a thickness of about 52 µm. In order to investigate at what temperature a curing of the coating could be achieved - including cross-linking as achieved by the alkylated aminoplast resin according to the invention - the powder-covered aluminium 25 sheet was put into a gradient oven during 40 minutes. The oven had a gradient from 100°C to 150°C.

The aluminium sheet as taken out of the gradient oven was put to an acetone double rub test. In this test, a cloth is drenched in acetone and then rubbed to and fro over the coating. One to and fro movement counts as one double rub. In 30 executing the test, it is counted how many times the cloth can be swiped over the coating until the coating has dissolved, whereby the requirement for satisfactory performance is achieved if the coating withstands at least 100 double rubs. This requirement was met at curing temperatures of 120°C and higher, thereby proving that sufficient curing of the powder coating composition had indeed been achieved at those 35 temperatures.

Example 5

Example 5 was carried out as example 4, except that 20 parts of the alkylated aminoplast resin as prepared in Example 2 were used.

5 A layer of the powder coating composition, which had a T_g lying above room temperature, was sprayed electrostatically onto an aluminium sheet. The layer had a thickness of about 45 μm . The powder-covered aluminium sheet was put into a gradient oven during 20 minutes. The oven had a gradient from 100°C to 150°C.

10 The aluminium sheet as taken out of the gradient oven was put to an acetone double rub test, whereby the requirement to withstand at least 100 double rubs was met at curing temperatures of 140°C and higher, thereby proving that sufficient curing of the powder coating composition had indeed been achieved at those temperatures.

15 Example 6

Example 6 was carried out as example 4, except that 20 parts of the alkylated aminoplast resin as prepared in Example 3 were used.

20 A layer of the powder coating composition, which had a T_g lying above room temperature, was sprayed electrostatically onto an aluminium sheet. The layer had a thickness of about 37 μm . The powder-covered aluminium sheet was put into a gradient oven during 30 minutes. The oven had a gradient from 100°C to 200°C.

25 The aluminium sheet as taken out of the gradient oven was put to an acetone double rub test, whereby the requirement to withstand at least 100 double rubs was met at curing temperatures of 180°C and higher, thereby proving that sufficient curing of the powder coating composition had indeed been achieved at those temperatures.

CLAIMS

1. Process for the preparation of an alkylated aminoplast resin, comprising the step of bringing together and reacting:
 - 5 • a C₅ - C₃₀-alcohol; and
 - one or more compounds chosen from the group consisting of: an aminoplast resin, a mixture of an amino compound and an aldehyde, and an alkylated aminoplast resin prepared from a C₁ - C₄-alcohol.
2. Process according to claim 1, wherein the molar ratio between the C₅ -
10 C₃₀-alcohol and the amino compound in the alkylated aminoplast resin lies between 1:1 and 4:1.
3. Process according to claim 1 or 2, wherein the molar ratio between the aldehyde and three NH₂-groups of the amino compound in the alkylated aminoplast resin lies between 3:1 and 6:1.
- 15 4. Process according to any one of claims 1 - 3, comprising the steps of:
 - a) bringing an amino compound together with an aldehyde and a C₅ - C₃₀-alcohol and optionally a solvent, to form a reaction mixture;
 - b) bringing the pH of the reaction mixture to between 1 and 7;
 - c) bringing the reaction mixture to a temperature lying between 80°C and
20 130°C and letting the reaction mixture remain within the said temperature range for a desired amount of time, whereby the alkylated aminoplast resin is formed.
5. Process according to claim 4, further comprising the steps of:
 - d) bringing the pH of the reaction mixture to between 9 and 13;
 - 25 e) bringing the temperature of the reaction mixture to a value such that volatile components can be boiled off; and
 - f) boiling off substantially all of the volatile components and recovering the alkylated aminoplast resin.
6. Process according to claim 4 or 5, wherein the amino compound comprises
30 melamine and/or urea, the aldehyde comprises formaldehyde and the C₅ - C₃₀ alcohol is used as solvent.
7. Process according to any one of claims 1 - 3, comprising the steps of:
 - i. bringing an amino compound together with an aldehyde and a solvent, to form a reaction system;

- ii. bringing the pH of the reaction system to between 7 and 10;
iii. bringing the temperature of the reaction system to between 60°C and reflux and letting the reaction system remain within the said temperature range for a desired amount of time, whereby an aminoplast resin is
5 formed;
iv. bringing the pH of the reaction system to between 1 and 7 and adding a C₅ - C₃₀-alcohol to the reaction system;
v. letting the reaction system remain within the temperature range of 70°C and reflux for a desired amount of time, whereby the alkylated
10 aminoplast resin is formed.
8. Process according to claim 7, further comprising the steps of:
vi. bringing the pH of the reaction system to between 9 and 13;
vii. bringing the temperature of the reaction system to a value such that volatile components can be boiled off; and
15 viii. boiling off substantially all of the volatile components and recovering the alkylated aminoplast resin.
9. Process according to claim 7 or 8, wherein the amino compound comprises melamine and/or urea, the aldehyde comprises formaldehyde and water is used as solvent.
- 20 10. Process according to any one of claims 7 - 9, comprising during or subsequent to step (iii) and prior to the execution of steps (iv):
- an aldehyde-mixing step (iiia), in which the aminoplast resin is brought together with an amount of an aldehyde, such that the overall molar aldehyde/(NH₂)₃ ratio in the reaction system increases with at least 0.3,
25 and such that the overall molar aldehyde/(NH₂)₃ ratio in the reaction system is brought to at most 8; and
 - an aldehyde-binding step (iiib), in which the reaction system is brought to conditions such that the free aldehyde can react with the aminoplast resin so that an aldehyde-enriched aminoplast resin is formed.
- 30 11. Process according to any one of claims 1 - 3, comprising the steps of:
α) bringing an alkylated aminoplast resin prepared from a C₁ - C₄-alcohol together with a C₅ - C₃₀-alcohol and optionally a solvent, to form a reaction composition;
β) bringing the pH of the reaction composition to between 1 and 7;

- y) bringing the reaction composition to a temperature lying between 60°C and 130°C and letting the reaction composition remain within the said temperature range for a desired amount of time, whereby the alkylated aminoplast resin is formed.
- 5 12. Process according to claim 11, further comprising the steps of:
- δ) bringing the pH of the reaction composition to between 9 and 13;
- ε) bringing the temperature of the reaction system to a value such that volatile components can be boiled off; and;
- 10 ζ) boiling off substantially all of the volatile components and recovering the alkylated aminoplast resin.
13. Process according to claim 11 or 12, wherein the alkylated aminoplast resin prepared from a C₁ - C₄ alcohol comprises HMMM and/or HBMM.
14. Process according to any one of claims 1 - 13, wherein the C₅ - C₃₀-alcohol is chosen from the group consisting of cyclohexanol and tetrahydrofurfuryl
- 15 alcohol.
15. Process according to any one of claims 1 - 14, wherein the molar ratio between the C₅ - C₃₀-alcohol and the amino compound lies between 1.5:1 and 3:1.
16. Process according to any one of claims 11 - 13, wherein in step α) the
- 20 alkylated aminoplast resin prepared from a C₁ - C₄-alcohol is replaced at least partly by an alkylated aminoplast resin obtainable according to any one of claims 4 - 10.
17. Alkylated aminoplast resin, obtainable according to any one of claims 1 - 16.
18. Use of the alkylated aminoplast resin according to claim 17 as cross-linker.
- 25 19. Coating composition, comprising the alkylated aminoplast resin according to claim 17.
20. Coating composition according to claim 19, wherein the coating composition is a powder coating composition.
21. Powder coating composition according to claim 20, comprising a catalyst,
- 30 wherein the catalyst comprises an acid.
22. Powder coating composition according to claim 21, wherein the catalyst comprises a blocked acid.
23. Powder coating composition according to claim 21 or 22, wherein the catalyst comprises an acid and an epoxy compound, whereby the weight ratio between
- 35 the acid and the epoxy compound lies between 10:90 and 70:30.

24. Powder coating composition according to claim 23, wherein the acid is paratoluenesulfonic acid and wherein the epoxy compound is a cycloaliphatic epoxide, preferably 3,4-epoxy cyclohexyl methyl-3,4 epoxy cyclohexane carboxylate.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/005242

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G12/42 C09D5/03 C09D161/32

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 C09D

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2007/005242

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

International application No

PCT/EP2007/005242

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