



(86) Date de dépôt PCT/PCT Filing Date: 2001/11/15
(87) Date publication PCT/PCT Publication Date: 2003/05/30
(45) Date de délivrance/Issue Date: 2010/01/12
(85) Entrée phase nationale/National Entry: 2004/05/06
(86) N° demande PCT/PCT Application No.: EP 2001/013205
(87) N° publication PCT/PCT Publication No.: 2003/043963

(51) Cl.Int./Int.Cl. *C07C 29/80* (2006.01),
C07C 29/76 (2006.01), *C07C 31/22* (2006.01)

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(54) Titre : PROCEDE PERMETTANT DE SUPPRIMER LES ACETALS CONTENANT DE L'ALDEHYDE FORMIQUE
D'ALCOOLS POLYVALENTS PAR RECUISSON
(54) Title: METHOD FOR REMOVING ACETALS CONTAINING FORMALDEHYDE FROM POLYVALENT ALCOHOLS
BY MEANS OF TEMPERING

(57) **Abrégé/Abstract:**

The invention relates to a method for removing acetals containing formaldehyde from polyvalent alcohols, especially trimethylolpropane. The inventive method is characterised in that the polyvalent alcohol is liberated of low-boiling constituents after it has been produced by distillation, is then subjected to tempering and is repurified, preferably by means of distillation.

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES
PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG(19) Weltorganisation für geistiges Eigentum
Internationales Büro(43) Internationales Veröffentlichungsdatum
30. Mai 2003 (30.05.2003)

PCT

(10) Internationale Veröffentlichungsnummer
WO 03/043963 A1(51) Internationale Patentklassifikation⁷: **C07C 29/80**,
29/76, 31/22

(21) Internationales Aktenzeichen: PCT/EP01/13205

(22) Internationales Anmeldedatum:
15. November 2001 (15.11.2001)

(25) Einreichungssprache: Deutsch

(26) Veröffentlichungssprache: Deutsch

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AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR,
CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE,
GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR,
KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK,
MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU,
SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US,
UZ, VN, YU, ZA, ZW.(84) Bestimmungsstaaten (*regional*): ARIPO-Patent (GH,
GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
eurasisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ,
TM), europäisches Patent (AT, BE, CH, CY, DE, DK,
ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR),
OAPI-Patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
ML, MR, NE, SN, TD, TG).

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Veröffentlicht:

— mit internationalem Recherchenbericht

Zur Erklärung der Zweibuchstaben-Codes und der anderen
Abkürzungen wird auf die Erklärungen ("Guidance Notes on
Codes and Abbreviations") am Anfang jeder regulären Ausgabe
der PCT-Gazette verwiesen.(74) Gemeinsamer Vertreter: **BASF AKTIENGE-**
SELLSCHAFT; 67056 Ludwigschafen (DE).(54) Title: METHOD FOR REMOVING ACETALS CONTAINING FORMALDEHYDE FROM POLYVALENT ALCOHOLS
BY MEANS OF TEMPERING(54) Bezeichnung: VERFAHREN ZUM ENFERNEN VON FORMALDEHYDHALTIGEN ACETALEN AUS MEHRWERTIGEN
ALKOHOLEN DURCH TEMPERN(57) Abstract: The invention relates to a method for removing acetals containing formaldehyde from polyvalent alcohols, especially
trimethylolpropane. The inventive method is characterised in that the polyvalent alcohol is liberated of low-boiling constituents after
it has been produced by distillation, is then subjected to tempering and is repurified, preferably by means of distillation.(57) Zusammenfassung: Die vorliegende Erfindung betrifft ein Verfahren zum Entfernen von formaldehydhaltigen Acetalen aus
mehrwertigen Alkoholen, insbesondere Trimethylolpropan. Das Verfahren ist dadurch gekennzeichnet, daß der mehrwertige Al-
kohol nach seiner Herstellung durch Destillation von Leichtsiedern befreit wird, anschließend einer Temperung unterworfen und
anschließend erneut gereinigt wird, vorzugsweise durch Destillation.

WO 03/043963 A1

METHOD FOR REMOVING ACETALS CONTAINING FORMALDEHYDE FROM
POLYVALENT ALCOHOLS BY MEANS OF TEMPERING

The present invention relates to a process in which formaldehyde-containing acetals in polyhydric alcohols, which have been prepared by the condensation of formaldehyde with
10 higher aldehydes, are decomposed by heating to a suitable temperature (so-called tempering) to produce polyhydric alcohols with low acetal contents.

Polyhydric alcohols are obtained on a large scale by the condensation of formaldehyde with higher CH-acidic aldehydes or with water and acrolein or 2-alkylacroleins. This reaction has two different principal procedural variants.

One of these is the so-called Cannizzaro process, which is
20 further subdivided into the inorganic and the organic Cannizzaro processes. In the inorganic variant an excess of formaldehyde is reacted with the appropriate alkanal in the presence of stoichiometric amounts of an inorganic base such as NaOH or $\text{Ca}(\text{OH})_2$. In the second stage, the dimethylolbutanal formed in the first stage reacts with the excess formaldehyde in a disproportionation reaction to give trimethylolpropane and the formate of the base used, i.e. either sodium or calcium formate. The accumulation of these salts constituted a disadvantage because they are difficult to separate from the reaction product
30 and, moreover, one equivalent of formaldehyde is lost.

In the organic Cannizzaro process a tertiary alkylamine is used instead of an inorganic base. This affords higher yields than with an inorganic base. Trialkylammonium formate is obtained as an unwanted by-product, so once again one equivalent of formaldehyde is lost.

The disadvantages of the Cannizzaro process are avoided in the so-called hydrogenation process. Here, formaldehyde is reacted
40 with the appropriate aldehyde in the presence of catalytic amounts of an amine, enabling the reaction to be stopped at the alkylolated aldehyde stage. After separation of the formaldehyde, the reaction mixture, which apart from said alkylolated aldehyde also contains small amounts of the corresponding polyhydric alcohol and small amounts of acetals of the alcohols formed, is

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subjected to a hydrogenation to give the desired polyhydric alcohol.

A particularly effective process for the preparation of alcohols obtainable by the condensation of aldehydes with formaldehyde is described in WO 98/28253. This process affords high yields combined with the accumulation of small amounts of coupling products. The procedure involves reacting the higher aldehyde with 2 to 8 times the amount of formaldehyde in the presence of a tertiary amine and separating the resulting reaction mixture into two solutions, one containing said completely methylolated alkanal and the other containing unreacted starting material. The latter solution is recycled into the reaction. The separation is effected by distillation or by simply separating the aqueous phase from the organic phase. The solution containing the product is subjected to a catalytic and/or thermal treatment in order to convert incompletely alkylolated alkanals to the desired completely methylolated compounds. By-product formed in this process is separated off by distillation and the resulting bottom product is subjected to catalytic hydrogenation to give the polyhydric alcohols.

Examples of important alcohols prepared by the processes described are neopentyl glycol, pentaerythritol, trimethylolethane, trimethylolbutane and, in particular, trimethylolpropane (TMP).

Alcohols prepared by both the Cannizzaro process and the hydrogenation process have to be separated by distillation from components that are more or less volatile than the alcohol (so-called low or high boilers respectively), and also from components boiling in the same range as the alcohol (so-called medium boilers). Low boilers are especially water, methanol and, in the case where an amine is used as catalyst, the free amine.

The high and medium boilers are often compounds which are derived from the polyhydric alcohol prepared and which have been formed therefrom by reaction with e.g. formaldehyde, methanol or another molecule of the alcohol prepared.

In order to use the polyhydric alcohol, it is particularly important for the alcohol to have a low content of formaldehyde-containing acetals.

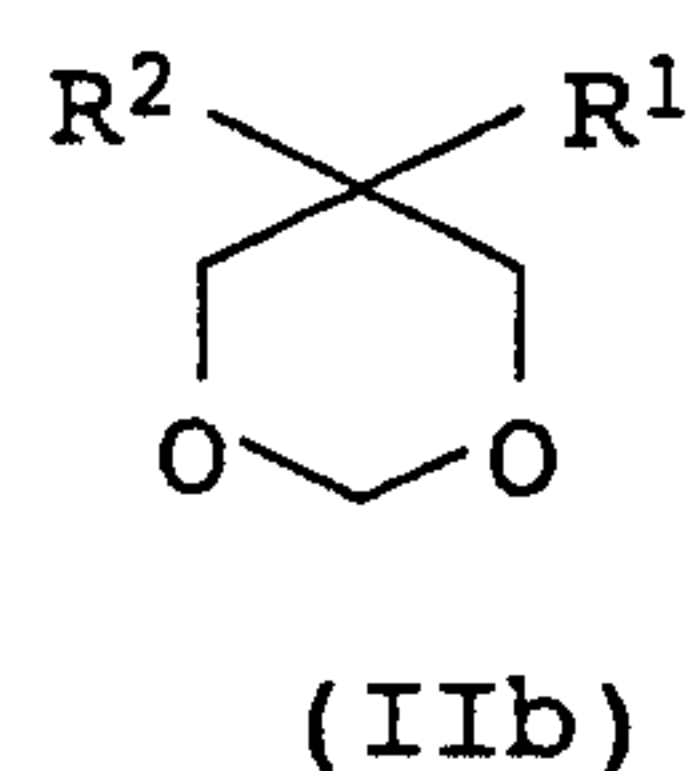
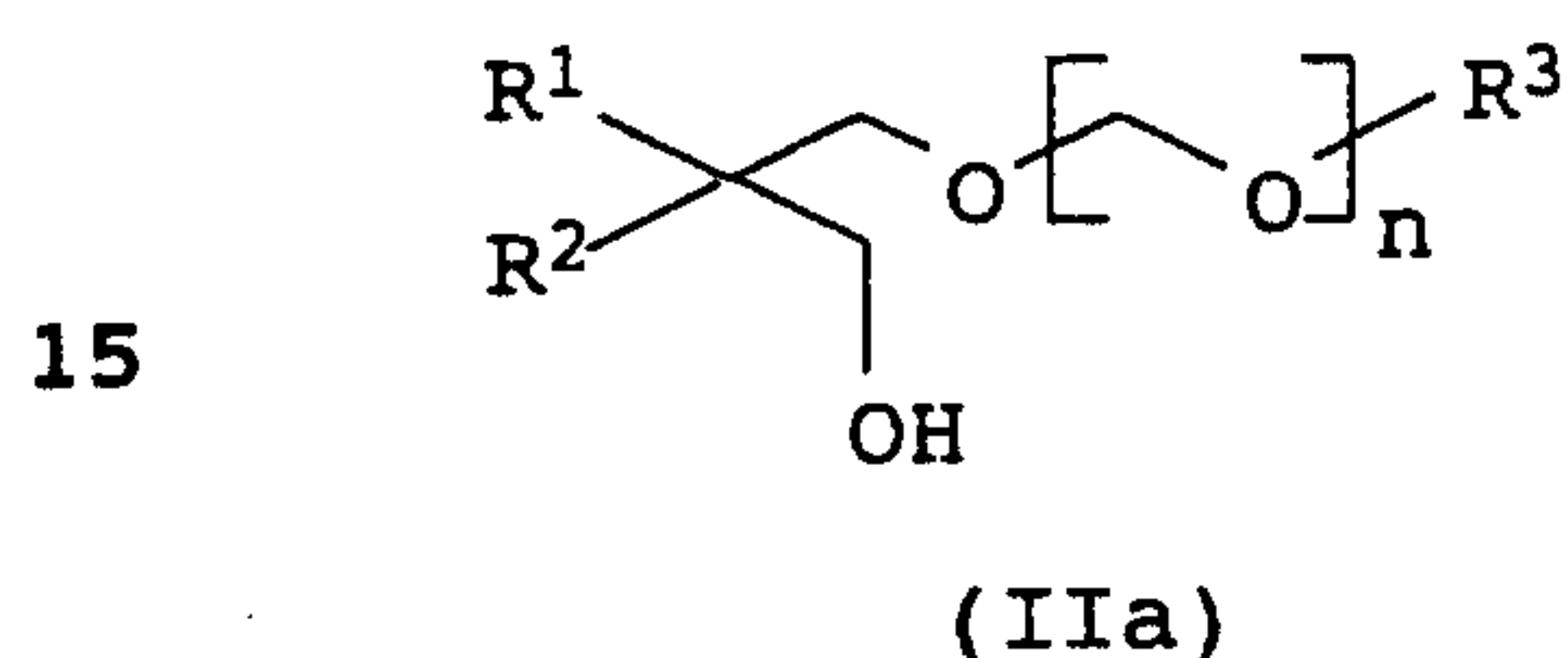
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Formaldehyde-containing acetals are understood as meaning any compounds that are derived from formaldehyde and contain the structural element



They can also be called formals.

The preparation of polyhydric alcohols produces
10 formaldehyde-containing acetals of general formula (IIa) or (IIb):



in which

20

R^1, R^2 independently of one another are hydrogen, C_1 - to C_{10} -alkyl, C_1 - to C_{10} hydroxyalkyl, carboxyl or C_1 - to C_4 -alkoxycarbonyl, preferably C_1 - to C_{10} -alkyl or C_1 - to C_{10} -hydroxyalkyl,

25

R^3 is hydrogen, C_1 - to C_{10} -alkyl, preferably C_1 - to C_8 -alkyl and particularly preferably C_1 - to C_5 -alkyl, or C_1 - to C_{10} -hydroxyalkyl, preferably C_1 - to C_8 alkyl and particularly preferably C_1 - to C_5 -alkyl, and

30

n is an integer from 1 to 4, preferably from 1 to 3 and particularly preferably 1 or 2,

it being possible for each of the alkyl radicals to be branched
35 or unbranched.

Examples of R^1 and R^2 are hydrogen, methyl, ethyl, isopropyl, n-propyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-decyl, hydroxymethyl, carboxyl,
40 methoxycarbonyl, ethoxycarbonyl or n-butoxycarbonyl, particularly hydrogen, hydroxymethyl, methyl or ethyl and particularly preferably hydroxymethyl, methyl or ethyl.

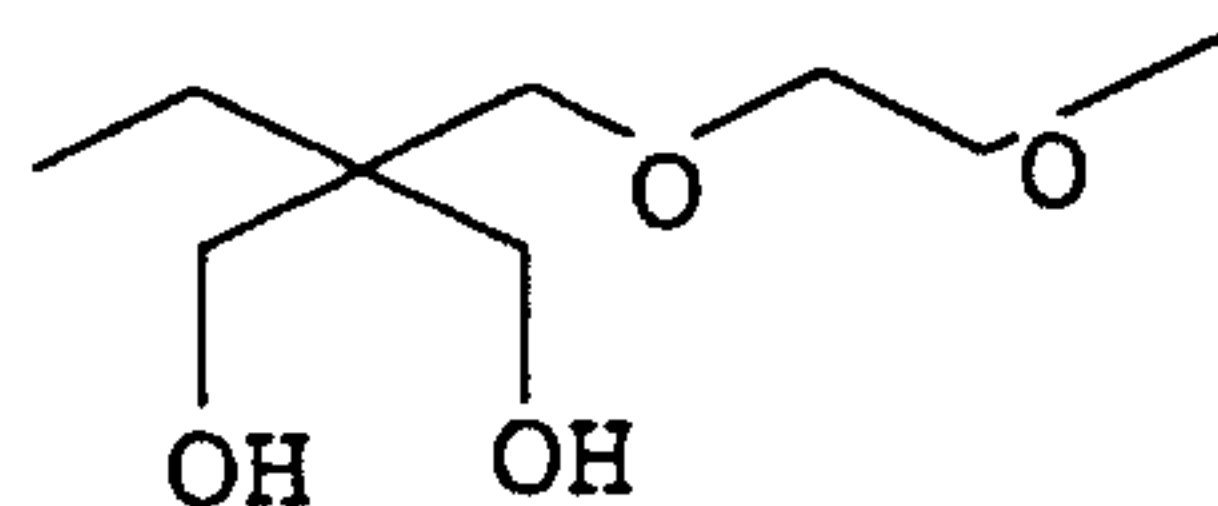
Examples of R^3 are hydrogen, methyl, ethyl, n-propyl, n-butyl,
45 2-methylpropyl, 2-methylbutyl, 2-ethyl-3-hydroxypropyl, 2-methyl-3-hydroxypropyl, 2,2-bis(hydroxymethyl)butyl, 2,2-bis(hydroxymethyl)propyl, 2,2-dimethyl-3-hydroxypropyl,

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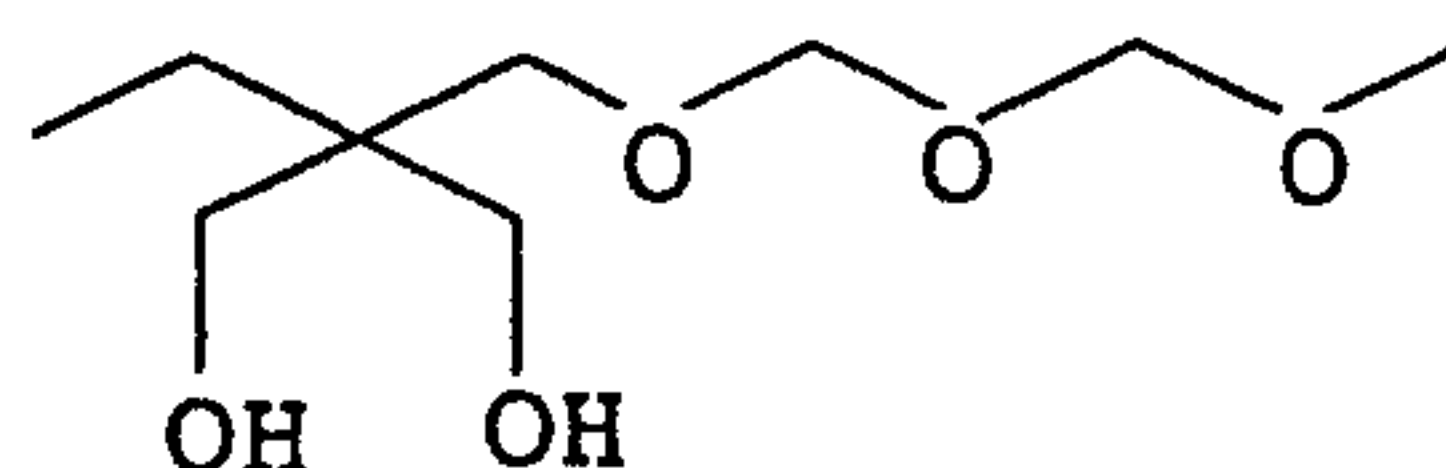
3-hydroxypropyl, 3-hydroxy-2-(hydroxymethyl)propyl or 3-hydroxy-2,2-bis(hydroxymethyl)propyl.

Typical formaldehyde-containing acetals, for example in the case of the synthesis of the trihydric alcohol trimethylolpropane (TMP) from formaldehyde and n butyraldehyde in the presence of catalytic amounts of trialkylamine, are the following TMP-formaldehyde-methanol acetals (IIIa) and (IIIb):

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(IIIa)

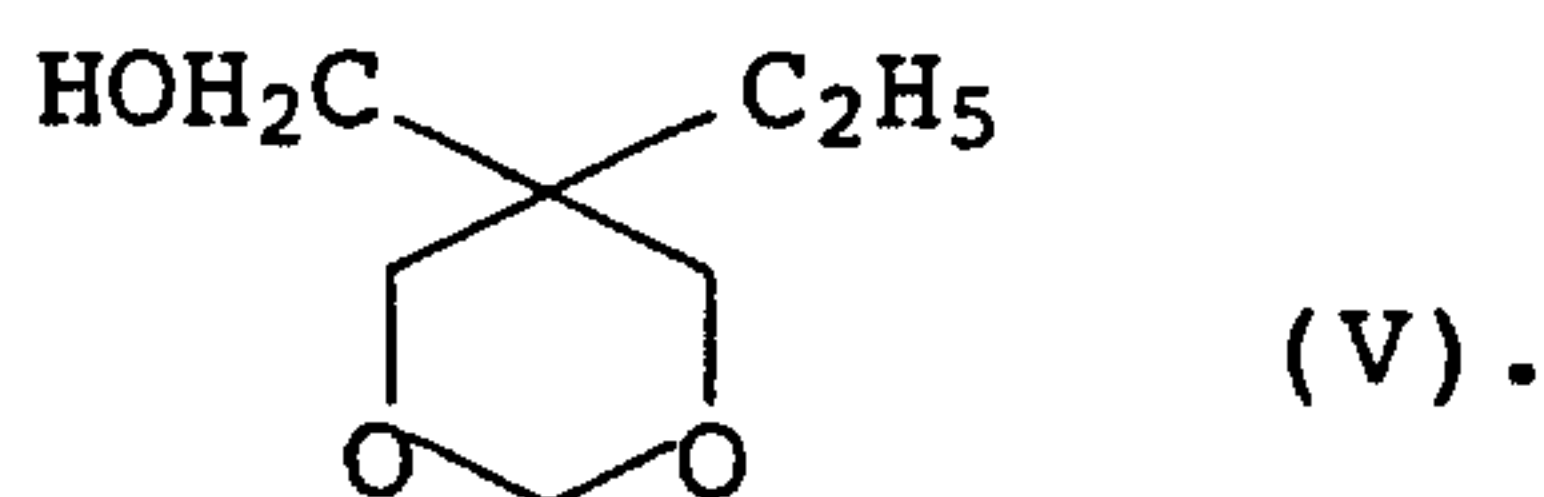


(IIIb)

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which can be present in the crude product of the hydrogenation process in a proportion of 0.05 to 10% by weight, and also the linear bis-TMP formal $[C_2H_5C(CH_2OH)_2CH_2O]CH_2$ (IV) and the cyclic TMP formal

20



(V).

25

The formation of these acetals containing units of the polyhydric alcohol, especially TMP units, is obviously unwanted because they markedly reduce the yield of desired product and moreover have an adverse effect on the use properties of the product alcohol. To avoid these disadvantages, it is desirable to remove the formaldehyde-containing acetals. Various methods of achieving this are disclosed in the literature.

US 6 096 905 discloses a process in which a composition containing the linear bis-TMP formal or the linear bistrimethylolethane formal is treated with a strongly acidic catalyst at 30 to 300°C for ½ to 8 hours.

GB-A 1 290 036 describes a process in which a crude TMP solution obtained by the inorganic Cannizzaro process is treated with a cation exchanger.

A disadvantage of both the processes known from the state of the art is that the acidic medium can lead to secondary reactions that can have a negative effect on the properties, such as the color number, of the desired polyhydric alcohol.

5

The object of the present invention is therefore to provide a process which makes it possible to obtain polyhydric alcohols, especially TMP, with a low content of formaldehyde-containing acetals. The novel process should also make it possible to work
5 up crude solutions of the polyhydric alcohols which have a product content of 60 to 95% by weight and a water content of less than 5% by weight.

The object is achieved by a process for the removal of
10 formaldehyde-containing acetals from polyhydric alcohols. In said process, after it has been prepared, the polyhydric alcohol is separated from low boilers by distillation, then subjected to tempering and then purified, preferably by distillation.

15 It has been found according to the invention that, in the case of trimethylolpropane, not only TMP but also the cyclic TMP formal, the high-boiling linear bis-TMP formal and methanol are formed from the TMP-formaldehyde-methanol acetals of general formulae IIA and IIB, which are among the medium boilers, by the tempering
20 step according to the invention. Said tempering step thus produces a mixture comprising low-boiling components (cyclic TMP formal, methanol) and high boilers, which can be separated from the product alcohol considerably more easily by distillation.

25 It has further been found that it is advantageous to treat crude solutions of the polyhydric alcohols that have product contents of 60 to 95% by weight, preferably of 75 to 85% by weight, and water contents of less than 5% by weight, by the process according to the invention. The abovementioned crude solutions
30 can be obtained by a procedure in which, after the synthesis of the polyhydric alcohol, only the low boilers, such as water, methanol and the free amine used as catalyst, are separated off.

Early removal of the formaldehyde-containing acetals
35 substantially facilitates the subsequent work-up. Polyhydric alcohols with contents of bound formaldehyde (FA number) of less than 1000 ppm by weight, preferably of less than 500 ppm by weight, become accessible.

40 It is of course also possible to use polyhydric alcohol with product contents of >95% by weight which has already been distilled. If TMP is used in the tempering step according to the invention, it is also possible to use TMP solutions with a content of >98%. Particularly low color numbers can be achieved
45 by using polyhydric alcohol which has already been distilled.

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The process according to the invention can be used for the removal of formaldehyde-containing acetals from polyhydric alcohols, especially TMP, of any origin. It is possible to use batches originating from the organic or inorganic Cannizzaro process. The best results have been obtained when the alcohols used in the tempering step according to the invention, for the purpose of decomposing the acetals, originate from the hydrogenation process. In every case it is important here that the alcohol has first been separated from low boilers and has a purity within the abovementioned range.

In particular, the tempering step according to the invention is applicable to any polyhydric alcohols that can be prepared by the condensation of formaldehyde with higher aldehydes in the presence of catalytic amounts of trialkylamine, followed by hydrogenation. Suitable higher aldehydes are practically any alkanals having an acidic hydrogen atom in the α -position to the carbonyl group. Starting materials which can be used are aliphatic aldehydes having 2 to 24 C atoms that can be linear or branched or can contain alicyclic groups. Other suitable starting materials are araliphatic aldehydes, provided that they contain a methylene group in the α -position to the carbonyl group. The starting materials used are generally aralkylaldehydes having 8 to 24 C atoms, preferably 8 to 12 C atoms, for example phenylacetaldehyde. It is preferable α -aliphatic aldehydes having 2 to 12 C atoms, for example 3-ethyl-, 3-n-propyl-, 3-isopropyl-, 3-n-butyl-, 3-isobutyl-, 3-sec-butyl- and 3-tert-butyl-butanal, as well as the corresponding n-pentanals, n-hexanals and n-heptanals; 4-ethyl-, 4-n-propyl-, 4-isopropyl-, 4-n-butyl-, 4-isobutyl-, 4-sec-butyl- and 4-tert-butyl-pentanals, -n-hexanals and -n-heptanals; 5-ethyl-, 5-n-propyl-, 5 isopropyl-, 5-n-butyl-, 5-isobutyl-, 5-sec-butyl- and 5-tert-butyl-n-hexanals and n-heptanals; 3-methylhexanal and 3-methylheptanal; 4-methylpentanal, 4-methylheptanal, 5-methylhexanal and 5-methylheptanal; 3,3,5-trimethyl-n-pentyl-, 3,3-diethylpentyl-, 4,4-diethylpentyl-, 3,3-dimethyl-n-butyl-, 3,3-dimethyl-n-pentyl-, 5,5-dimethylheptyl-, 3,3-dimethylheptyl-, 3,3,4-trimethylpentyl-, 3,4-dimethylheptyl-, 3,5-dimethylheptyl-, 4,4-dimethylheptyl-, 3,3-diethylhexyl-, 4,4-dimethylhexyl-, 4,5-dimethylhexyl-, 3,4-dimethylhexyl-, 3,5-dimethylhexyl-, 3,3-dimethylhexyl-, 3,4-diethylhexyl-, 3-methyl-4-ethylpentyl-, 3-methyl-4-ethylhexyl-, 3,3,4-trimethylpentyl-, 3,4,4-trimethylpentyl-, 3,3,4-trimethylhexyl-, 3,4,4-trimethylhexyl- and 3,3,4,4-tetramethylpentyl-aldehyde; C₂- to C₁₂-n-alkanals are particularly preferred.

Particularly preferred polyhydric alcohols within the framework of the present invention are trimethylolethane, trimethylolpropane, trimethylolbutane, dimethylolpropane, 1,1-, 1,2-, 1,3- and 1,4-cyclohexanedimethanol, 2-ethyl-1,3-propanediol, 2-methyl-1,3-propanediol, glycerol, neopentyl glycol, pentaerythritol and dipentaerythritol. The very particularly preferred alcohol is trimethylolpropane.

10 If the process according to the invention is used to remove formaldehyde-containing acetals from crude solutions of polyhydric alcohols, especially TMP, with product contents of 60 to 95% by weight, the crude product obtained by the hydrogenation process (the hydrogenation discharge) is subjected to a dehydration prior to the tempering step, in which water and other low boilers, such as methanol and trialkylamine or trialkylammonium formate, are separated off by distillation.

20 If the process according to the invention is used to remove formaldehyde-containing acetal from TMP of high purity (product content > 98% by weight) prepared by the hydrogenation process, said high-purity TMP can be prepared by the process described in German laid-open patent application DE-A1-199 63 435 entitled "Verfahren zur Reinigung von durch Hydrierung hergestelltem Trimethylolpropan durch kontinuierliche Destillation" (Application: BASF AG). Here the crude product obtained after hydrogenation is first subjected to a dehydration, in which water and other low boilers, such as methanol, trialkylamine or trialkylammonium formate, are separated off by distillation. This distillation can be carried out at pressures of < 400 mbar, preferably of 20 to 200 mbar, at bottom temperatures of <200 C and for short residence times so that the trialkylammonium formate formed reacts to only a small extent with TMP to give TMP formates and trialkylamine. The distillation can also be carried out at pressures of >200 mbar, preferably of >400 mbar, at bottom temperatures of >140°C and for long residence times so that at least the bulk of the TMP reacts with trialkylammonium formate to give TMP formates and trialkylamine.

30

The high boilers are then separated off in the next step. This is done by distilling from the bottom product, at 210 to 250°C, those components which are volatile at these temperatures. The high boilers thus remain in the bottom product. The resulting low-boiling TMP-rich fraction is then worked up by distillation (first purification by distillation), unwanted low boilers being separated off. The pure product obtained can be subjected to a second purification by distillation to give a particularly clean product.

10 It is possible to use either TMP originating from the first purification by distillation or TMP taken from the second purification by distillation.

Polyhydric alcohols with low contents of formaldehyde-containing acetals can be prepared by the tempering step according to the invention, which is generally followed by a distillation or is carried out simultaneously therewith. In particular, it is possible to obtain TMP with contents of bound formaldehyde of less than 1000 ppm by weight and color numbers of up to ≤ 30 APHA.

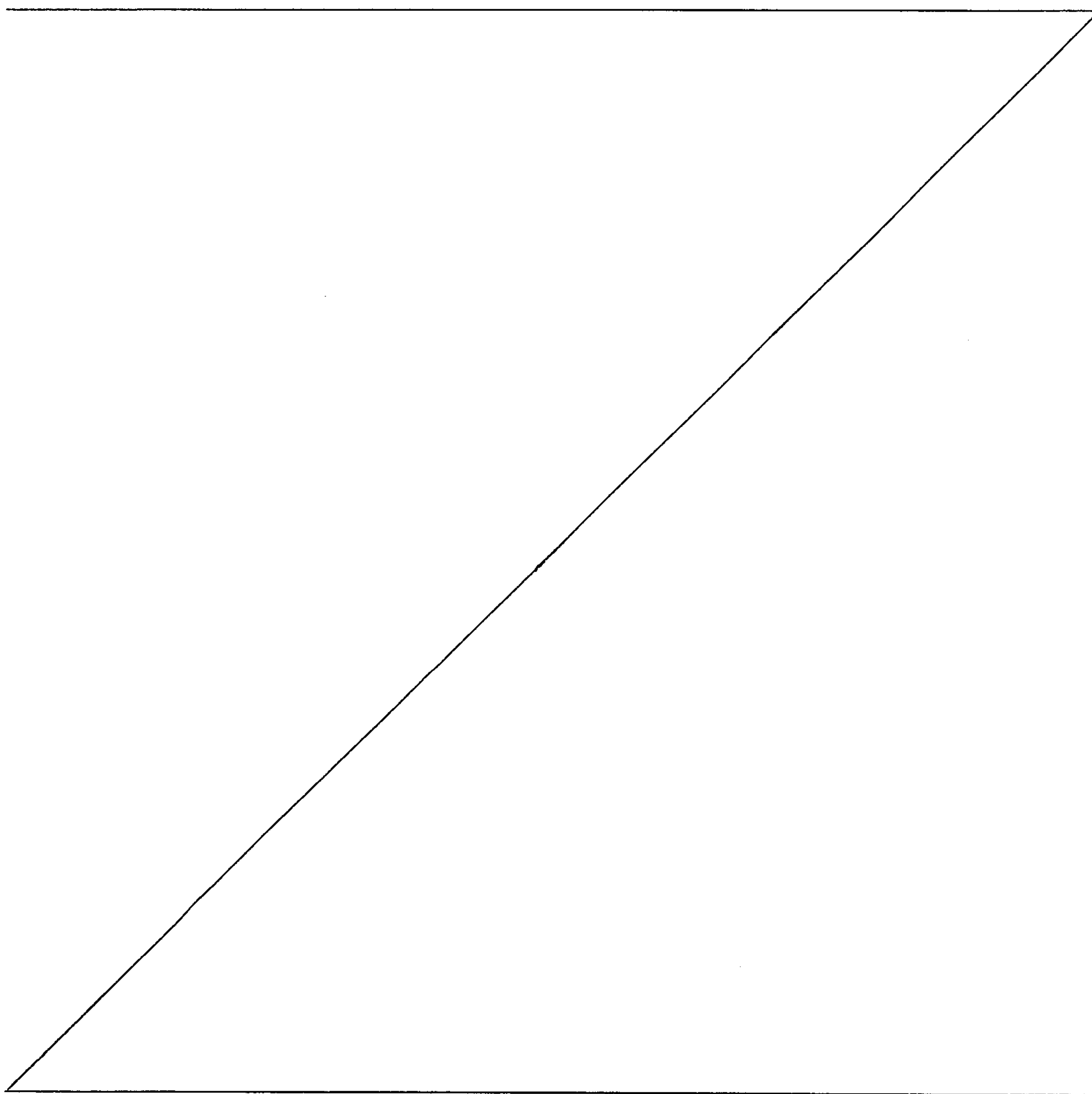
20 TMP which has been worked up according to the above mentioned German laid-open patent application DE-A1 199 63 435 and subjected to the first purification by distillation generally has color numbers of 40 to 150 APHA. These color numbers have been improved to values of ≤ 20 APHA by the tempering according to the present invention.

30 For the desired contents of formaldehyde-containing acetals to be achieved in the tempering step according to the invention, it is necessary to observe specific reaction conditions that can vary as a function of, for instance, the type of polyhydric alcohol used, the purities of the products used, the apparatuses used and other additives which may be present. Those skilled in the art can determine these reaction conditions by experiment. In general the tempering step according to the invention is carried out at temperatures of 100 to 300°C, preferably of 160 to 240°C, for residence times of 5 min to 24 h, preferably of 15 min to 4 h, and at pressures of 100 mbar to 200 bar, preferably of 1 to 10 bar. If the polyhydric alcohol to be purified is TMP, the

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tempering step according to the invention is carried out at temperatures of 100 to 300°C, preferably of 160 to 240°C, for residence times of 5 min to 24 h, preferably of 15 min to 4 h, and at the pressures mentioned above.

The tempering step according to the invention can be carried out, continuously or batchwise, using the conventional apparatuses known to those skilled in the art. In the batch procedure, the process according to the invention is preferably carried out in a stirred container; in the continuous procedure, it is preferably



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carried out in a tube reactor, it being possible in this case to use a sump or trickle procedure.

The very particularly preferred embodiment of the tempering according to the invention is the continuous sump procedure in a tube reactor.

In all these procedural variants, the reaction container can be provided with the conventional fixed packing materials known to those skilled in the art, for example Raschig or Pall rings, or packings such as sheet metal packings, in order to improve the mixing of the components. Supports and/or catalysts in the conventional forms, for example rods or tablets, can also be present in order to accelerate the reactions taking place in the tempering step according to the invention. Examples of suitable supports/catalysts include TiO_2 , Al_2O_3 , SiO_2 , supported H_3PO_4 and zeolites.

The tempering step according to the invention transforms the medium-boiling acetals IIA and IIB into low-boiling and high-boiling components.

The product alcohol can easily be separated by distillation from the low-boiling and high-boiling components formed. The tempering step according to the invention is therefore generally followed by a distillation. Because the high-boiling compounds formed from the acetal components Ia and Ib in the tempering step according to the invention generally differ markedly from the product alcohols in terms of their boiling behavior, they can be separated off by means of simple distillative measures or methods having only a small separation effect. Separation units with only one distillation stage, for example falling film evaporators or thin film evaporators, often suffice for this purpose. If appropriate, especially when the distillation also serves to purify the product alcohol further, more expensive separation processes or separation apparatuses - generally columns with several separation stages, for example packed columns or bubble-cap columns - will be used.

The conventional conditions in respect of pressure and temperature, known to those skilled in the art, will be observed in the distillation, said conditions naturally also depending on the product alcohol used.

In one embodiment of the present invention, the tempering step can also be combined with the distillation. In this case the tempering takes place at the bottom of the distillation column,

10

where the polyhydric product alcohol is separated from the high-boiling components formed in the tempering and, if appropriate, from other impurities. If the tempering step and the distillation are combined into one stage, it is important to
5 observe the abovementioned reaction conditions in respect of pressure, temperature and, in particular, residence time in order to achieve an adequate decomposition of the components responsible for the color number. When the tempering step and distillation step are combined into a single process step, it is
10 preferable to add acid.

In this case too, of course, apparatuses with a low or high separation efficiency are used according to requirements.

15 As already mentioned, when TMP is the product alcohol used in the process according to the present invention, a suitable TMP is one which has been purified by the process disclosed in the German patent application of file number 199 63 435.1. It is possible here to use a TMP originating either from the first purification
20 by distillation or from the second purification by distillation. If this process is used, it is particularly preferable, in one variant of the invention, to carry out the tempering step after the first purification by distillation, in the conventional apparatuses. This is followed by the second purification by
25 distillation, to which is carried out, for instance, in a column, a falling film evaporator or a thin film evaporator. In another variant, the TMP obtaining after the first purification by distillation is preferably improved in terms of the color number in a tempering step which is carried out with the addition of a
30 suitable acid and which has been combined with the second purification by distillation into a single process step. If an acid is added, it is preferable to use phosphoric acid.

Examples

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The process according to the invention will now be illustrated with the aid of the Examples which follow.

Example 1: Preparation of TMP

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An apparatus consisting of two heatable stirred tanks with an overall capacity of 72 l, interconnected by overflow tubes, was fed continuously with fresh aqueous formaldehyde solution (4300 g/l) in the form of a 40% aqueous solution, with n
45 butyraldehyde (1800 g/h) and with fresh trimethylamine as

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catalyst (130 g/h) in the form of a 45% aqueous solution, the reactors being kept at a temperature of 40°C.

The discharge was led directly into the upper part of a falling
5 film evaporator with attached column (11 bar superheated steam), where it was separated by distillation under normal pressure into a low-boiling top product, essentially containing n-butyraldehyde, ethylacrolein, formaldehyde, water and trimethylamine, and a high-boiling bottom product.

10

The top product was continuously condensed and recycled into the reactors described above.

The high-boiling bottom product from the evaporator (approx.
15 33.5 kg/h) was treated continuously with fresh trimethylamine catalyst (50 g/h in the form of a 45% aqueous solution) and led into a heatable tube reactor with an empty volume of 12 l, provided with packing materials, the reactor being kept at a temperature of 40°C.

20

The discharge from the secondary reactor was introduced continuously into the upper part of another distillation device for separation of the formaldehyde (11 bar superheated steam), where it was separated by distillation into a low-boiling top
25 product, essentially containing ethylacrolein, formaldehyde, water and trimethylamine, and a high-boiling bottom product. The low-boiling top product (27 kg/h) was continuously condensed and recycled into the first stirred tank, while the high-boiling bottom product was collected.

30

In addition to water, the resulting bottom product contained essentially dimethylolbutyraldehyde, formaldehyde and traces of monomethylolbutyraldehyde. It was then subjected to a continuous hydrogenation. This was done by hydrogenating the reaction
35 solution at 90 bar and 115°C in a primary reactor by the circulation/trickle procedure and in a downstream secondary reactor by the circulation procedure. The catalyst was prepared analogously to D of DE 198 09 418. It contained 24% of CuO, 20% of Cu and 46% of TiO₂. The apparatus used consisted of a heated
40 primary reactor 10 m in length (internal diameter: 27 mm) and a heated secondary reactor 5.3 m in length (internal diameter: 25 mm). The circulation throughput was 25 l/h of liquid and the reactor feed was adjusted to 4 kg/h. 4 kg/h of hydrogenation discharge were accordingly obtained.

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The mixture obtained after the hydrogenation was then separated from water and trimethylamine according to the German patent application entitled "Verfahren zur Reinigung von durch Hydrierung hergestelltem Trimethylpropan durch kontinuierliche Destillation" (Applicant: BASF AG). The crude mixture was first fed into the middle of the low-boiler column and the dehydration was carried out at 400 mbar and 180°C. The chosen reflux ratio was 0.3. A bottom discharge was obtained (1.1 kg/h) which had the composition shown in Table 1 below, determined by gas chromatography. The gas chromatographic determination of the compositions indicated in this patent application was performed using a DB5 column from J & W Scientific with a length of 30 m, a diameter of 0.32 mm and a 1 µm coating. The detector was an FID.

15 Comparative Example C2

TMP prepared according to Example 1 was used in Example 2. The bottom discharge from Example 1 was led at a flow rate of 1.15 l/h - corresponding to a residence time of 2.3 h - through a 2.6 l container kept at room temperature, and the resulting discharge was then worked up as described in DE 199 63 435. This was done by first separating the high-boiling fraction from the crude solution at 20 mbar by means of a high-boiler separator consisting of a stripping column with falling film evaporator. The crude TMP freed of high boilers was condensed at the top of the column. The temperature at the bottom of the column was adjusted to 223°C.

The crude TMP freed of high boilers was purified by distillation in a column provided with a stripping section and an enriching section. Components boiling between water and TMP were drawn off via the top and residual high boilers were recycled into the high-boiler separator via the bottom. The purification by distillation was carried out at a pressure of 20 mbar and with a reflux ratio of 25. The purified TMP, having the composition described in Example 1, was obtained in gaseous form at the lateral vapor take-off directly above the evaporator, and condensed.

40 Example 3 and 4

Examples 3 and 4 are carried out in the same way as Example 2 except that the 2.8 l container, in the form of a bulb or a pipe coil, was kept at a temperature of 180°C to 200°C. After tempering, distillation was carried out as described in Example 2 and the composition was determined by gas chromatography.

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The content of bound formaldehyde is calculated as the sum of the molecular weight fraction of formaldehyde equivalents in the particular formaldehyde acetal, multiplied by its fraction in the reaction mixture, found by analysis. The formaldehyde content, also called the FA number, was determined from the formaldehyde-containing acetals as a fraction in percent by weight according to the following formula:

Content (formaldehyde) =

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$$C_{(\text{TMP-FA-Me})} \cdot \frac{M_{\text{FA}}}{M_{\text{TMP-FA-Me}}} + C_{(\text{TMP-diFA-Me})} \cdot \frac{M_{\text{FA}}}{M_{\text{TMP-diFA-Me}}} +$$

$$15 \quad C_{(\text{cyclTMP-formal})} \cdot \frac{M_{\text{FA}}}{M_{\text{cyclTMP-formal}}} + C_{(\text{TMP-FA-TMP})} \cdot \frac{M_{\text{FA}}}{M_{\text{TMP-FA-TMP}}}$$

where

20 TMP-FA-Me

denotes TMP-formaldehyde-methanol acetal
(IIIa)

FA

denotes formaldehyde

Me

denotes methanol

TMP-diFA-Me

denotes TMP-diformaldehyde-methanol acetal
(IIIb)

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cycl.TMP formal

denotes cyclic TMP formal (V)

C

denotes concentration

M

denotes molecular weight

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Table 1:

5	No.		TMP [% by weight]	(IIIa) [% by weight]	(IIIb) [% by weight]	(V) [% by weight]	(IV) [% by weight]	FA number [ppm]
	1	Dehy- dration only	84.0	1.39	0.38	2.04	0.5	n.d.
10	2	After distil- lation without temper- ing	98.9	0.1	0.31	0.05	0.1	1273
15	3	Temper- ing at 180°C + distil- lation	99.0	0.1	0.19	0.05	0.05	873
20	4	Temper- ing at 200°C + distil- lation	99.2	0.02	0.09	0.02	0.05	388

25 IIIa TMP-diformaldehyde-methanol acetal
IIIb TMP-formaldehyde-methanol acetal
IV linear bis-TMP formal
V cyclic TMP formal
n.d. not determined

30 The result summarized in Table 1 shows that the process according to the invention affords TMP with formaldehyde contents below 1000 ppm by weight, preferably below 500 ppm by weight.

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WHAT IS CLAIMED IS:

1. A process for the removal of formaldehyde-containing acetals from polyhydric alcohols, wherein, after it has been prepared, the polyhydric alcohol is separated from low boilers by distillation, then subjected to a tempering and then purified again.
2. A process as claimed in claim 1, wherein the purification made after the tempering is carried out by distillation.
3. A process as claimed in claim 1 or 2, wherein the polyhydric alcohol used in the tempering has been prepared by the hydrogenation process.
- 10 4. A process as claimed in any one of claims 1 to 3, wherein the polyhydric alcohol used has a purity ranging from 60 to 95% by weight.
5. A process as claimed in any one of claims 1 to 3, wherein the polyhydric alcohol has a purity higher than 95% by weight.
6. A process as claimed in any one of claims 1 to 5, wherein the tempering step is carried out at temperatures of 100 to 300°C for residence times of 5 min to 24 h, and at pressures of 100 mbar to 200 bar.
7. A process as claimed in claim 6, wherein the tempering step is carried out at temperatures of 160 to 240°C.
8. A process as claimed in claim 6 or 7, wherein the tempering step is carried out
20 residence times of 15 min to 4 h.
9. A process as claimed in any one of claims 6 to 8, wherein the tempering step is carried out at pressures of 1 to 10 bar.

10. A process as claimed in any one of claims 6 to 9, wherein the polyhydric alcohol is trimethylolpropane.

11. A process as claimed in claim 10, wherein the trimethylolpropane has a purity higher than 98% by weight.

12. A process as claimed in any one of claims 1 to 11, wherein the tempering step and the subsequent purification by distillation are combined into a single process step.

13. A process as claimed in any one of claims 1 to 12, wherein the tempering is carried out batchwise.

10 14. A process as claimed in claim 13, wherein the tempering is carried out in a stirred tank.

15. A process as claimed in any one of claims 1 to 12, wherein the tempering is carried out continuously.

16. A process as claimed in claim 15, wherein the tempering is carried out in a tube reactor by a trickle procedure.

17. A process as claimed in claim 15, wherein the tempering is carried out in a tube reactor by a sump procedure.