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(54) Titre : SYSTÈME DE STABILISANT CONÇU POUR STABILISER DU PVC
(54) Title: STABILIZER SYSTEM FOR STABILIZING PVC

(57) **Abrégé/Abstract:**

Disclosed are stabilizer mixtures comprising at least a) one alkanolamine or one reaction product of a monofunctional or polyfunctional epoxide and ammonia or a monofunctional or polyfunctional dialkyl(aryl)amine or monoalkyl(aryl)amine, and b) one uracil or one initial product and an optional perchlorate salt.



Abstract

Disclosed are stabilizer mixtures comprising at least a) one alkanolamine or one reaction product of a monofunctional or polyfunctional epoxide and ammonia or a monofunctional or polyfunctional dialkyl(aryl)amine or monoalkyl(aryl)amine, and b) one uracil or one initial product and an optional perchlorate salt.

WO 2004/065470

PCT/EP2003/014691

Stabilizer system for stabilizing PVC

The invention relates to stabilizer mixtures, encompassing at least one alkanolamine, at least one
5 uracil, and, if appropriate, one perchlorate salt, the mixtures being suitable for stabilizing chlorine-containing polymers.

There are many additives which can stabilize PVC.
10 Compounds of the heavy metals lead, barium and cadmium are particularly well suited to this purpose, but are nowadays subject to criticism on environmental grounds or due to their heavy metal content (cf. "Plastics Additives Handbook", H. Zweifel, Carl Hanser Verlag,
15 5th edn., 2001, pp. 427-483 and "Kunststoff Handbuch PVC" [Plastics Handbook PVC], volume 2/1, W. Becker/D. Braun, Carl Hanser Verlag, 2nd edn., 1985, pages 531-538; and also Kirk-Othmer: "Encyclopedia of Chemical Technology", 4th ed., 1994, Vol. 12, Heat Stabilizers,
20 pp. 1071-1091).

Processors and consumers are increasingly refusing to use these stabilizers.

Attempts therefore continue to find effective stabilizers and stabilizer mixtures which are free from
25 lead, barium and cadmium. The intention here is also to provide a composition which has stabilizing action with respect to thermal and/or photochemical degradation and which, as a constituent of halogen-containing polymers, gives excellent initial color and also gives color
30 stability.

A mixing specification matched to the processing method can be provided here, appropriate for the prevailing requirements, which may be based on health and safety
35 at work, approval restrictions or process reliability. Surprisingly, this invention provides combinations of substances which are physiologically non-hazardous in plastics and which in some cases certainly do not provide satisfactory processing stability when used

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alone.

The applicant's specification WO 02/48249 A2 discloses compounds of the formula (I) in combination with at least one perchlorate salt. The comparative and inventive examples of this specification show that compounds of the general formula (I), used alone, do not contribute to acceptable initial color.

10 It has now been found that mixtures composed of a) at least one alkanolamine or one reaction product of a mono- or polyfunctional epoxide and of ammonia or of a mono- or polyfunctional dialkyl(aryl)- or monoalkyl(aryl)amine of the general formula (I), and of
15 b) at least one uracil of the general formula (II) or, respectively, of their precursors of the general formula (III), and, if appropriate, one perchlorate salt, in particular a perchlorate of an alkali metal or of an alkaline earth metal, are particularly suitable
20 for stabilizing chlorine-containing polymers, in particular PVC. The object set, to provide a stabilizer mixture complying with the requirements placed upon initial color, has been met via this novel combination. Further addition of a perchlorate salt, in particular a
25 perchlorate of an alkali metal or of an alkaline earth metal, can improve the stabilization of chlorine-containing polymers, in particular PVC.

The use of other classes of amines alone without perchlorate does not give satisfactory processing
30 stability, and in particular the initial color of the desired moldings does not differ substantially from that of an unstabilized specimen, the consequence therefore being that the requirements for good initial color and process reliability desired by processors are
35 not met.

The β -hydroxyalkanolamines used in combination with the uracils of structure (II) or with their precursors of structure (III) can assume the function of improving initial color. This permits production of moldings with

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service properties complying with expectations over a prolonged period.

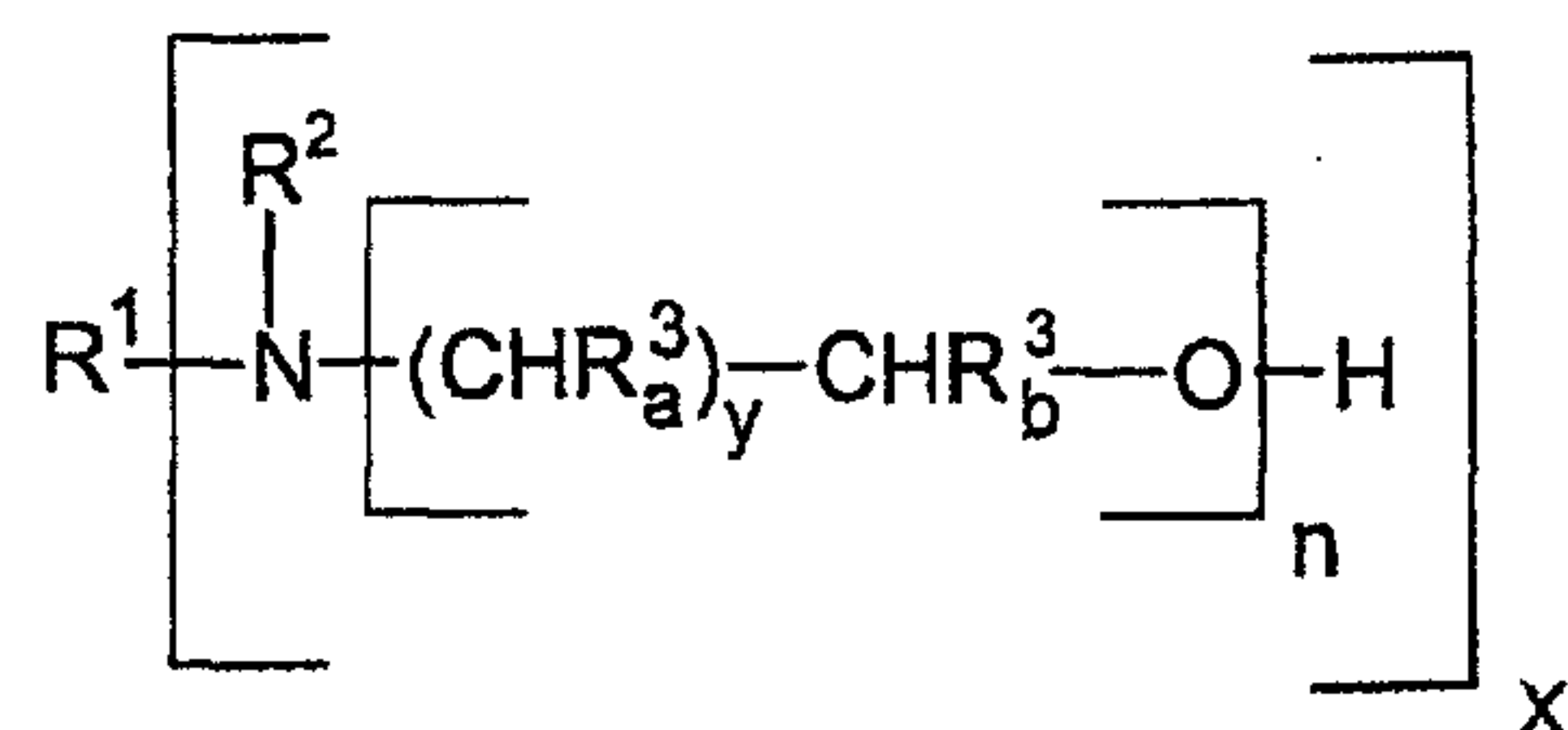
Surprisingly, synergistic action of the claimed combination, extending beyond the action of comparative
5 mixing specifications comprising the individual components, has also been found in systems with perchlorate.

The present invention therefore provides stabilizer
10 mixtures, encompassing at least

- a) one alkanolamine or/and one reaction product of a mono- or polyfunctional epoxide and of ammonia or of a mono- or polyfunctional
15 dialkyl(aryl)- or monoalkyl(aryl)amine of the formula (I) and
- b) one uracil of the formula (II) or its precursor of the formula (III), and, if
20 appropriate,
- c) one perchlorate salt.

For the alkanolamine of the formula (I) here

25



$x = 1, 2 \text{ or } 3;$

$y = 1, 2, 3, 4, 5 \text{ or } 6;$

30 $n = \text{from } 1 \text{ to } 10;$

R^1 and $\text{R}^2 =$ independently of one another H, $\text{C}_1\text{-C}_{22}\text{-alkyl}$,
 $[-(\text{CHR}_a^3)_y - \text{CHR}_b^3 - \text{O}-]_n - \text{H}$, $[-(\text{CHR}_a^3)_y - \text{CHR}_b^3 - \text{O}-]_n - \text{CO}-\text{R}^4$,
 $\text{C}_2\text{-C}_{20}\text{-alkenyl}$, $\text{C}_2\text{-C}_{18}\text{-acyl}$, $\text{C}_4\text{-C}_8\text{-cycloalkyl}$, where this
 may have OH substitution in the β -position, $\text{C}_6\text{-C}_{10}\text{-aryl}$,
 35 $\text{C}_7\text{-C}_{10}\text{-alkaryl}$ or $\text{C}_7\text{-C}_{10}\text{-aralkyl}$, or, if $x = 1$, R^1 and R^2

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may also, together with the N, form a closed ring having from 4 to 10 members, composed of carbon atoms and, where appropriate, of up to 2 heteroatoms, or if $x = 2$, R^1 may also be C_2 - C_{18} -alkylene which, at both

5 β -carbon atoms, may have OH substitution and/or have interruption by one or more O atoms and/or by one or more NR^2 groups, or be dihydroxy-substituted tetrahydrodicyclopentadienylene, dihydroxy-substituted ethylcyclohexanylene, dihydroxy-substituted

10 4,4'-(bisphenol A dipropyl ether)ylene, isophoronylene, dimethylcyclohexanylene, dicyclohexylmethanylene or 3,3'-dimethyldicyclohexylmethanylene, and if $x = 3$, R^1 may also be trihydroxy-substituted (tri-N-propyl isocyanurate)triyl;

15 R^3_a and R^3_b = independently of one another C_1 - C_{22} -alkyl, C_2 - C_6 -alkenyl, C_6 - C_{10} -aryl, H or CH_2 -X- R^5 , where X = O, S, -O-CO- or -CO-O-;

R^4 = C_1 - C_{18} -alkyl/alkenyl or phenyl; and

R^5 = H, C_1 - C_{22} -alkyl, C_2 - C_{22} -alkenyl or C_6 - C_{10} -aryl.

20

The invention also provides stabilizer mixtures where the alkanolamine is a reaction product of a mono- or polyfunctional epoxide and of ammonia or of a mono- or polyfunctional dialkyl(aryl)- or monoalkyl(aryl)amine.

25

Examples of the alkanolamines of the general formula (I) are compounds where R^1 and R^2 = methyl, ethyl, propyl, butyl, cyclohexyl, octyl, lauryl, tetradecyl, hexadecyl, stearyl, oleyl, allyl, phenyl or benzyl or

30 hydroxyalkyl and R^3 = H, methyl, ethyl, propyl or butyl. Preference is given to alkanolamines where R^1 = lauryl, tetradecyl, hexadecyl, stearyl, or oleyl, where R^2 = hydroxyalkyl. It is also possible to use ethoxylates and propoxylates of triethanol- and tri-

35 isopropanolamine, and also of fatty amines of vegetable or animal origin. Preference is given to trialkanolamines and monoalkyl/alkenyldialkanolamines where R^3 = H or methyl and $y = 1$, in particular fatty amines which have been reacted twice with ethylene

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oxide or with propylene oxide. Other compounds with very good suitability can be found in the following list.

- 5 Methyl- or dimethylamine reacted once or twice with ethylene oxide or with propylene oxide.

Propyl- or dipropylamine reacted once or twice with ethylene oxide or with propylene oxide.

10

Isopropyl- or diisopropylamine reacted once or twice with ethylene oxide or with propylene oxide.

- 15 Butyl- or dibutylamine reacted once or twice with ethylene oxide or with propylene oxide.

Isobutyl- or diisobutylamine reacted once or twice with ethylene oxide or with propylene oxide.

- 20 Pentyl- or dipentylamine reacted once or twice with ethylene oxide or with propylene oxide.

Isopentyl- or diisopentylamine reacted once or twice with ethylene oxide or with propylene oxide.

25

Hexyl- or dihexylamine reacted once or twice with ethylene oxide or with propylene oxide.

- 30 Isohexyl- or diisohexylamine reacted once or twice with ethylene oxide or with propylene oxide.

Heptyl- or diheptylamine reacted once or twice with ethylene oxide or with propylene oxide.

- 35 Isoheptyl- or diisoheptylamine reacted once or twice with ethylene oxide or with propylene oxide.

Octyl- or dioctylamine reacted once or twice with ethylene oxide or with propylene oxide.

Isooctyl- or diisooctylamine reacted once or twice with ethylene oxide or with propylene oxide.

- 5 Nonyl- or dinonylamine reacted once or twice with ethylene oxide or with propylene oxide.

Isononyl- or diisononylamine reacted once or twice with ethylene oxide or with propylene oxide.

10

Decyl- or didecylamine reacted once or twice with ethylene oxide or with propylene oxide.

- 15 Isodecyl- or diisodecylamine reacted once or twice with ethylene oxide or with propylene oxide.

Undecyl- or diundecylamine reacted once or twice with ethylene oxide or with propylene oxide.

- 20 Isoundecyl- or diisoundecylamine reacted once or twice with ethylene oxide or with propylene oxide.

Dodecyl- or didodecylamine reacted once or twice with ethylene oxide or with propylene oxide.

25

Isododecyl- or diisododecylamine reacted once or twice with ethylene oxide or with propylene oxide.

- 30 Tridecyl- or ditridecylamine reacted once or twice with ethylene oxide or with propylene oxide.

Isotridecyl- or diisotridecylamine reacted once or twice with ethylene oxide or with propylene oxide.

- 35 Tetradecyl- or ditetradecylamine reacted once or twice with ethylene oxide or with propylene oxide.

Hexadecyl- or dihexadecylamine reacted once or twice with ethylene oxide or with propylene oxide.

Octadecyl- or dioctadecylamine reacted once or twice with ethylene oxide or with propylene oxide.

- 5 Eicosyl- or dieicosylamine reacted once or twice with ethylene oxide or with propylene oxide.

Docosyl- or didocosylamine reacted once or twice with ethylene oxide or with propylene oxide.

10

N-Methylbutylamine reacted with ethylene oxide or with propylene oxide.

- 15 N-Ethylbutylamine reacted with ethylene oxide or with propylene oxide.

Allyl- or diallylamine reacted once or twice with ethylene oxide or with propylene oxide.

- 20 Crotyl- or dicrotylamine reacted once or twice with ethylene oxide or with propylene oxide.

Octadecenyl- or dioctadecenylamine reacted once or twice with ethylene oxide or with propylene oxide.

25

Benzyl- or dibenzylamine reacted once or twice with ethylene oxide or with propylene oxide.

- 30 Cyclohexyl- or dicyclohexylamine reacted once or twice with ethylene oxide or with propylene oxide.

N-Methylcyclohexylamine reacted with ethylene oxide or with propylene oxide.

- 35 N-Ethylcyclohexylamine reacted with ethylene oxide or with propylene oxide.

4-Vinyl-1-cyclohexene diepoxide reacted twice with diethanol- or diisopropanolamine.

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Dicyclopentadiene diepoxide reacted twice with diethanol- or diisopropanolamine.

Bisphenol A diglycidyl ether reacted twice with
5 diethanol- or diisopropanolamine.

Trisglycidyl isocyanurate reacted three times with diethanol- or diisopropanolamine.

10 Preference is given to trialkanolamines and monoalkyl/alkenyldialkanolamines where R^3_a and R^3_b = independently of one another H or methyl and $y = 1$.

The compounds of the general formula (I) where $y =$ from
15 1 to 6, i.e. having up to 6 methylene groups between the amino group and the hydroxy-substituted carbon atom, have been found to be suitable for use as a PVC stabilizer in combination with a perchlorate salt.

20 According to the invention it is also possible to use compounds of the general formula (I) where $x = 2$, i.e. compounds which have two hydroxyalkylamino groups per molecule. Examples of these are N,N,N',N'-
tetrakis(2-hydroxyethyl)ethylenediamine, N,N,N',N'-
25 tetrakis(2-hydroxy-1-propyl)ethylenediamine, N,N,N',N'-tetrakis(2-hydroxyethyl)propylenediamine and N,N,N',N'-tetrakis(2-hydroxy-1-propyl)propylenediamine and
N,N,N',N'-tetrakis(2-hydroxyethyl)hexamethylenediamine, preference being given to four-fold reactions of
30 1,6-hexamethylene- or 1,8-octamethylenediamine or neopentanediamine with ethylene oxide or with propylene oxide, or analogous reactions of bisaminomethylcyclohexane or isophoronediamine or 4,4'-diaminodicyclohexylmethane or 3,3'-dimethyl-4,4'-diaminodicyclo-
35 hexylmethane.

According to the invention, it is also possible to use compounds of the general formula (I) where $x = 3$, i.e. those which have three hydroxyalkylamino groups per

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molecule. An example of these is a reaction product of trisglycidyl isocyanurate with mono- or diethanolamine or mono- or dipropanolamine.

- 5 The alkanolamines of the general formula (I) are chemicals which can be purchased or can be prepared by known methods via N-alkylation of an appropriate amine or ammonia (cf. Kirk-Othmer, Vol. 2, Alkanolamines).
- 10 Examples of the preferred alkanolamines of the general formula (I) are tris(2-hydroxyethyl)amine, tris(2-hydroxy-1-propyl)amine, bis(2-hydroxyethyl)-2-hydroxy-1-propylamine, N-n-butyl-N,N-bis(2-hydroxyethyl)amine, N,N-bis(n-butyl)-N-(2-hydroxyethyl)amine,
- 15 N-(3-n-butyloxy-2-hydroxy-1-propyl)-N,N-bis(2-hydroxyethyl)amine, N-(1,3-dihydroxy-2-hydroxymethyl-2-propyl)-N,N-bis(2-hydroxyethyl)amine, N,N-bis(2-hydroxyethyl)-N-palmitylamine, N,N-bis(2-hydroxyethyl)-N-oleylamine,
- 20 stearylamine, N,N-bis(2-hydroxyethyl)-N-stearylamine, N-(2-hydroxyethyl)morpholine and N-(2,3-dihydroxy-1-propyl)morpholine, bishydroxyethylpiperazine and bishydroxyisopropylpiperazine and reaction products of glycidyl ethers with mono- or dialkylamine or ammonia,
- 25 and also the alkanolamines derived therefrom, for example ethanolamine, diethanolamine, n-propanolamine, isopropanolamine, n-dipropanolamine, or isodipropanolamine.
- 30 Very particular preference is given to adducts of olefin oxides, such as octene oxide, decene oxide, dodecene oxide, tetradecene oxide, hexadecene oxide, octadecene oxide, eicosene oxide and docosene oxide, and also epoxystearyl alcohol with diethanol- or
- 35 diisopropanolamine. These compounds with an OH function in the β -position at both ends of a relatively long alkyl chain, for example N-(2-hydroxyhexadecyl)diethanolamine, N-(2-hydroxy-3-octyloxypropyl)diethanolamine, N-(2-hydroxy-3-decyloxypropyl)diethanolamine,

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N-(2-hydroxy-3-octyloxypropyl)diethanolamine and bis-N-(2-hydroxy-3-phenyloxypropyl)ethanolamine are a particularly suitable component in the stabilizer systems of the invention.

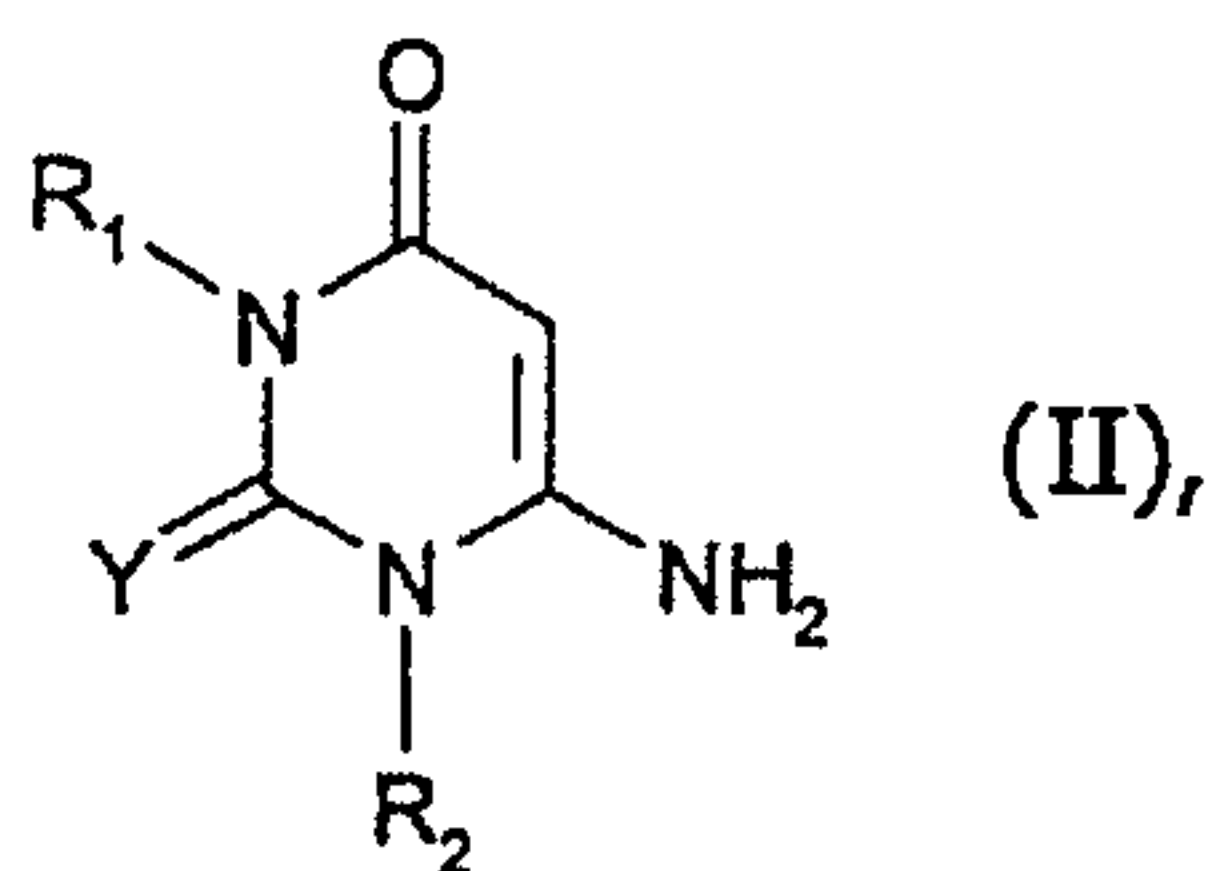
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This list is given only by way of example and does not claim to be comprehensive.

The amounts to be used of the compounds of the formula (I) to achieve stabilization in chlorine-containing polymer are advantageously from 0.01 to 10% by weight, preferably from 0.05 to 5% by weight, in particular from 0.1 to 3% by weight.

15 The inventive composition comprises, alongside at least one representative of the alkanolamines of the structure (I), at least one representative of the uracils of the general structure (II). According to the invention, the group of the uracils is defined as that
20 of the derivatives of structure (II) and also that of the cyanoacetylureas of the structure (III), which are precursors of the uracils.

Compounds of the formula (II) have previously been
25 described in DE-A-1 694 873, EP-A-0 065 934, EP-A-0 041 479, and EP-A-0 768 336, and can be prepared by known methods in a process involving one or more steps.



30 where

R1 and R2, independently of one another, are C1-C24-alkyl, which may have interruption by -CO₂- and/or by 1 or more oxygen atoms, and/or may have substitution by one or more OH groups, examples here being
35 -CH₂-O-CH₂-CH₂-O-CH₃, -CH₂-O-CH₂-CH₂-CH₂-O-CH₃,

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-CH₂-O-CH₂-CH₂-CH₂-CH₂-O-CH₃, -CH₂-CH₂-O-CH₂-CH₂-O-CH₂-CH₃,
 -CH₂-CH₂-O-CH₂-CH₂-O-CH₂-CH₂-O-CH₂-CH₃, etc. or are
 C3-C24-alkenyl, branched or unbranched, or are C5-C8-
 cycloalkyl, unsubstituted or substituted with from 1 to
 5 3 C1-C4-alkyl, C1-C4-alkoxy, or C5-C8-cycloalkyl
 groups, or with hydroxy groups, or with Cl atoms, or
 are C7-C9-phenylalkyl, unsubstituted or substituted on
 the phenyl ring with from 1 to 3 C1-C4-alkyl, C1-C4-
 alkoxy, or C5-C8-cycloalkyl groups, or with hydroxy
 10 groups, or with Cl atoms, and R1 or R2 may also be
 hydrogen, and Y is S or O. For compounds of the formula
 (II) here:

examples of C1-C4-alkyl are methyl, ethyl, n-propyl,
 isopropyl, n-butyl, isobutyl, sec-butyl or tert-butyl.
 15 Preference is given to C1-C4-alkyl, if appropriate with
 interruption by -CO₂-.

Examples of C1-C24-alkyl other than the radicals just
 mentioned are pentyl, hexyl, heptyl, octyl, 2-
 ethylhexyl, isooctyl, decyl, nonyl, undecyl, dodecyl,
 20 tetradecyl, hexadecyl, octadecyl, eicosyl, docosyl or
 tetracosyl.

Examples of the alkenyl radicals are vinyl, allyl,
 methallyl, 1-butenyl or 1-hexenyl, 1-octenyl,
 25 2-octenyl, decenyl, undecenyl, tetradecenyl, hexa-
 decenyl, octadecenyl and eicosenyl, preferably allyl.
 The alkyl or alkenyl radicals may be branched or
 unbranched radicals.

30 Examples of C1-C4-alkoxy are methoxy, ethoxy, propoxy,
 isopropoxy, butoxy or isobutoxy.

Examples of C5-C8-cycloalkyl are cyclopentyl, cyclo-
 hexyl, cycloheptyl or cyclooctyl.

Examples of C7-C9-phenylalkyl are benzyl, 1- or
 35 2-phenylethyl, 3-phenylpropyl, α,α -dimethylbenzyl or
 2-phenylisopropyl, preferably benzyl.

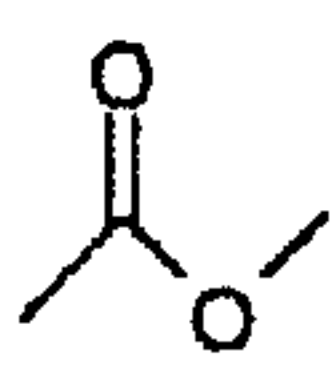
If the cycloalkyl groups or the phenyl group of the
 phenylalkyl radicals have substitution, preference is

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then given to two or one substituent(s), particular preference among the substituents being given to chlorine, hydroxy, methyl or methoxy.

Examples of C3-C6-alkenyl are vinyl, allyl, methallyl,
 5 1-butenyl or 1-hexenyl, preferably allyl.

If the alkyl radicals have interruption, they necessarily include at least 2 carbon atoms. -CO₂- here

means a  group.

10

Examples of C1-C22-alkyl radicals with interruption by -CO₂- are branched or straight-chain radicals, e.g. methoxycarbonylmethyl, methoxycarbonylethyl, methoxycarbonylpropyl, methoxycarbonylbutyl, methoxycarbonyl-
 15 hexyl, methoxycarbonyloctyl, ethoxycarbonylmethyl, ethoxycarbonylethyl, ethoxycarbonylpropyl, ethoxycarbonylbutyl, ethoxycarbonylhexyl, ethoxycarbonyloctyl, n-propoxycarbonylmethyl, n-propoxycarbonylethyl, n-propoxycarbonylbutyl, n-propoxycarbonylhexyl,
 20 n-propoxycarbonyloctyl, isopropoxycarbonylmethyl, isopropoxycarbonylethyl, isopropoxycarbonylbutyl, isopropoxycarbonylhexyl, isopropoxycarbonyloctyl, n-butoxycarbonylmethyl, n-butoxycarbonylethyl, n-butoxycarbonylbutyl, n-butoxycarbonylhexyl or tert-butoxycarbonylmethyl. This list makes no claim to be
 25 comprehensive, but gives the structural principle, which is readily comprehensible to the person skilled in the art.

30 By way of example, methoxycarbonylethyl is preferred.

Preference is given here to compounds of the formula (II), where

R1 and R2, independently of one another, are C1-C18-
 35 alkyl and hydrogen.

It is particularly preferable either that

R1 and R2 are identical and are methyl, ethyl, propyl,

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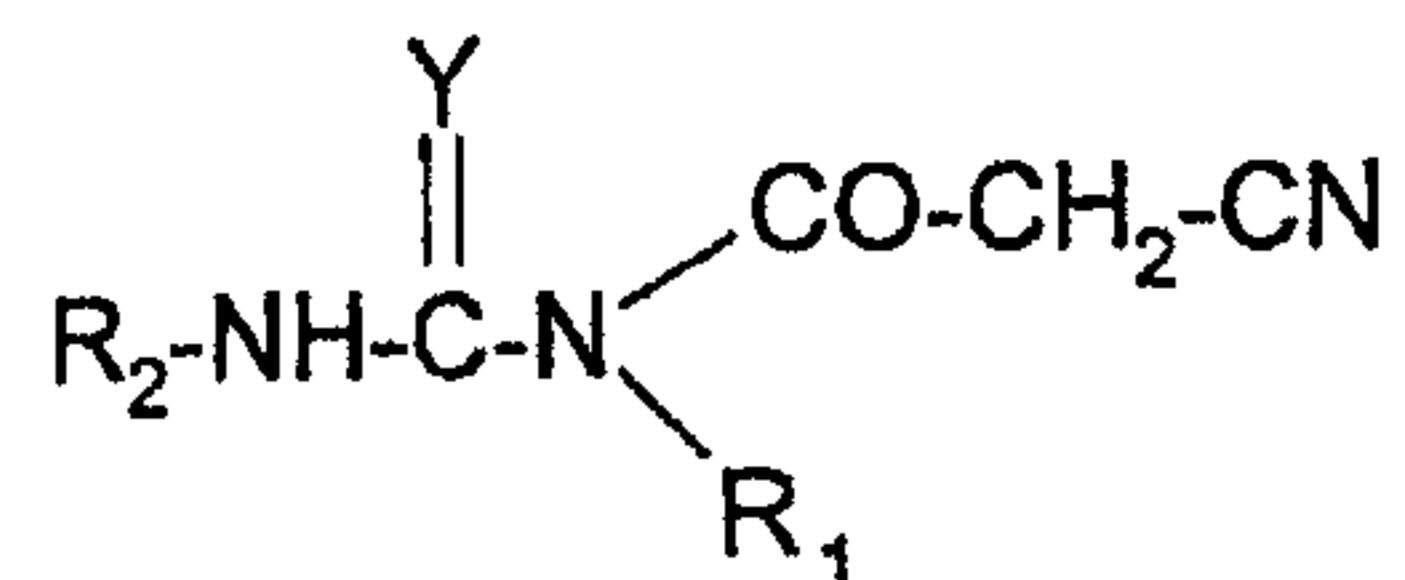
butyl, allyl or octyl, or that they are different and are ethyl and allyl.

If only one of the two substituents R1 or R2 is
5 hydrogen, the carbon chain of the remaining radical is larger than C2, and the above then applies correspondingly to the possible further substitution pattern. R1 or R2 can therefore be C3-C24-alkyl, which may have interruption by -CO₂- and/or by 1 or more
10 oxygen atoms, and/or may have substitution by one or more OH groups, or can be C3-C24-alkenyl, branched or unbranched, or can be C5-C8-cycloalkyl, unsubstituted or substituted with from 1 to 3 C1-C4-alkyl, C1-C4-alkoxy, or C5-C8-cycloalkyl groups, or with hydroxy
15 groups, or with Cl atoms, or can be C7-C9-phenylalkyl, unsubstituted or substituted on the phenyl ring with from 1 to 3 C1-C4-alkyl, C1-C4-alkoxy, or C5-C8-cycloalkyl groups, or with hydroxy groups, or with Cl atoms. Preference is given to the monosubstituted, in
20 the 1- or 3-position of the formula (II), alkyl, alkenyl or alkoxyalkyl derivatives where R1 or R2 is propyl or butyl or cyclohexyl or is C3-C6-alkyl interrupted by an oxygen atom. Examples of particularly preferred compounds are: 1-propyl-2-aminouracil,
25 1-propyl-4-aminouracil, 1-allyl-2-aminouracil, 1-allyl-4-aminouracil, 1-methoxyethyl-2-aminouracil, 1-methoxyethyl-4-aminouracil.

According to the invention, it is also possible to use
30 the cyanoacetylureas (III), which are the synthetic precursors of the uracils, in combination with the structures of the formula (I). These are known to the person skilled in the art and are described in US Patent 2,598,936, and in the applicant's specification
35 US 6211270, and in J. Org. Chem. 16, 1897-1890 (1951), and can be prepared by known methods. The starting ureas are commercially available or can be prepared by known processes.

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Cyanoacetylureas of the formula (III)



where

- 5 Y is oxygen or sulfur, and
 R1 is C1-C24-alkyl, which may have interruption by
 -CO₂- and/or by oxygen atoms, and/or may have
 substitution by from 1 to 3 OH groups, or is C3-C24-
 alkenyl, C7-C10-phenylalkyl, C5-C8-cycloalkyl, C7-C10-
 10 alkylphenyl, phenyl or naphthyl, where in each case the
 aromatic radical may have substitution by -OH, C1-C12-
 alkyl and/or OC1-C4-alkyl, and R2 is as defined for R1,
 or, if R1 is hydrogen then R2 can also be C3-C24-alkyl,
 which may have interruption by -CO₂- and/or by oxygen
 15 atoms and/or may have substitution by from 1 to 3 OH
 groups, or can be C3-C24-alkenyl, C7-C10-phenylalkyl,
 C5-C8-cycloalkyl, C7-C10-alkylphenyl, phenyl or
 naphthyl, where in each case the aromatic radical may
 have substitution by -OH, by C1-C12-alkyl and/or by
 20 OC1-C4-alkyl, have particularly good suitability in the
 combination described according to the invention for
 stabilizing chlorine-containing polymers, e.g. PVC.

For compounds of the formula (III):

- 25 Examples of C1-C4-alkyl are methyl, ethyl, n-propyl,
 isopropyl, n-butyl, isobutyl, sec-butyl or tert-butyl.
 Examples of C1-C24-alkyl, other than the radicals just
 mentioned, are pentyl, hexyl, heptyl, octyl, 2-ethyl-
 hexyl, isooctyl, decyl, nonyl, undecyl or dodecyl, and
 30 also tetradecyl, hexadecyl, octadecyl, eicosyl, docosyl
 or tetracosyl. Preference is given to C1-C8-alkyl, if
 appropriate having interruption by -CO₂-. Examples of
 C5-C8-cycloalkyl are cyclopentyl, cyclohexyl, cyclo-
 heptyl or cyclooctyl, preferably cyclohexyl.

35

Examples of C7-C10-alkylphenyl are tolyl or mesityl, in

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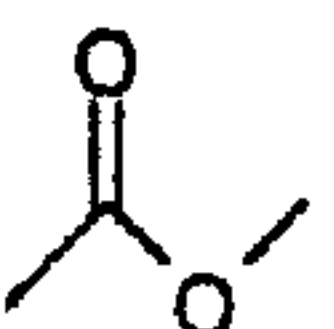
particular tolyl. Examples of C7-C10-phenylalkyl are benzyl, 1- or 2-phenylethyl, 3-phenylpropyl, α,α -dimethylbenzyl or 2-phenylisopropyl, preferably benzyl and 2-phenethyl, in particular benzyl.

5

If the aromatic radical has substitution, it preferably has three, two or in particular one substituent, and the substituents are in particular hydroxy, methyl, ethyl, methoxy or ethoxy.

10 Examples of C3-C8-alkenyl are allyl, methallyl, 1-butenyl, 1-hexenyl, 1-octenyl or 2-octenyl, preferably allyl.

If the alkyl radicals have interruption, they
15 necessarily include at least 2 carbon atoms.

-CO₂- here is a  group.

Examples of alkyl radicals with interruption by -CO₂- can be found in the text associated with formula (II).

20 Preference is given here to compounds of the formula (III) where

Y is oxygen, and also to those where the radicals R1 and R2 are identical. Other advantageous compounds are those where Y is sulfur.

25 Further preference is given to compounds of the formula (III) where R1 and R2 are C1-C8-alkyl, C3-C5-alkenyl, benzyl or 2-phenethyl.

Particular preference is given to compounds of the formula (III) where R1 and R2 are C1-C4-alkyl, allyl or
30 benzyl.

Examples which may be mentioned are N,N'-dimethyl-N-cyanoacetylurea, N,N'-diethyl-N-cyanoacetylurea, N,N'-dioctyl-N-cyanoacetylurea, etc. This list is given
35 only by way of example and does not make any claim to be comprehensive.

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Other preferred compounds here are those of the formula (III)

where

Y is oxygen, and also those where the radicals R1 and
5 R2 differ from one another. In particular for R1 = H.
R2 is then C3-C12-alkyl which may have interruption by
-CO₂- and/or by oxygen atoms, and/or may have
substitution by from 1 to 3 OH groups, or is then
10 C3-C12-alkenyl, C7-C10-phenylalkyl, C5-C8-cycloalkyl,
C7-C10-alkylphenyl, phenyl or naphthyl, where in each
case the aromatic radical may have substitution by -OH,
by C1-C12-alkyl and/or by OC1-C4-alkyl. Other
advantageous compounds are those where Y is sulfur.
Particular preference is given to compounds of the
15 formula (III) where R1 = H and
R2 = C3-C8-alkyl, methoxyethyl, allyl or benzyl.

It should expressly be mentioned here that the reaction
of the cyanoacetylureas of the general formula (III) to
20 give the corresponding uracils of the general formula
(II) can take place even before preparation of the
stabilizer has ended. This is known to the person
skilled in the art from the literature and derives from
the synthetic principle of preparation of uracils from
25 cyanoacetylureas. By way of example, N,N'-dibutyl-N-
cyanoacetylurea (formula (III): R1 = R2 = butyl) will
react to give the analogous 1,3-dibutyl-4-aminouracil.
Particularly if the matrix here comprises basic
compounds. This precondition is moreover met merely by
30 the other possible components of the matrix, e.g.
commercially available calcium stearate or zeolite. In
this context, the matrix in the selected inventive
examples comprises the alkanolamine alone, or one or
more compounds from the group of the plastics additives
35 and plastics stabilizers and of the halogen-containing
organic plastics. If the matrix comprises liquid
constituents, this reaction is accelerated in
accordance with the kinetics of chemical reactions.

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Representatives of the general formula (I) which are liquid at room temperature or at processing temperature are particularly suitable for this purpose.

5 This reaction of the cyanoacetylurea to give the uracil is in particular also promoted by temperature increases brought about via mixing or processing, or brought about via the preparation of the stabilizer, and these may be spray processes or melting processes. It is not
10 necessary for the reaction here to proceed to completion. The two species may be present alongside one another in various ratios. However, certain conditions can give practically quantitative conversion. There are no restrictions per se on the
15 selection of the basic compounds for the reaction of the cyanoacetylurea intermediate to give the uracil. Suitable compounds are any of those whose aqueous or alcoholic extract reacts as a base, or which in any other way induce the reaction, examples being:

20 alkali metal hydroxides, alkaline earth metal hydroxides, zeolites, Alcamizer products or amines. The reaction may take place before the end of the process to prepare the stabilizer, or during the process of
25 mixing the stabilizer components alone, or in the presence of the entire formulation, either in the mixer or in the subsequent course of processing.

The amount of the compounds of the formula (III) to be
30 used to achieve stabilization in the chlorine-containing polymer is advantageously from 0.01 to 10% by weight, preferably from 0.05 to 5% by weight, in particular from 0.1 to 3% by weight.

35 The invention also provides combinations of the stabilizer mixtures encompassing at least alkanolamine or a reaction product of a mono- or polyfunctional epoxide and of ammonia or of a mono- or polyfunctional dialkyl(aryl)- or monoalkyl(aryl)amine of the formula

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(I) and uracils of the formula (II) or their precursors of the formula (III) encompassing at least one halogen-containing oxyacid, e.g. a perchlorate salt.

5 The perchlorate salts are known to the person skilled in the art, examples are those of the formula $M(\text{ClO}_4)_n$, where M is Li, Na, K, Mg, Ca, Sr, Ba, Zn, Al, La, Ce, or a hydrotalcite layer-lattice cation, or an organic onium salt cation. The index n is 1, 2 or 3, as
10 appropriate for the valency of M, or if a hydrotalcite layer-lattice cation is present $0 < n \leq 1$.

These perchlorate salts may be used in various familiar supply forms; e.g. in the form of a salt or solution in
15 water or in an organic solvent, as they stand, or absorbed onto a carrier material such as PVC, Ca silicate, zeolites or hydrotalcites. Examples are perchlorate salts dissolved or complexed using alcohols (polyols, cyclodextrins) or using ether alcohols or
20 ester alcohols or crown ethers or plasticizers. Partial esters of the polyols are to be regarded as ester alcohols here. In the case of polyhydric alcohols or polyols it is also possible to use their dimers, trimers, oligomers and polymers, examples being di-,
25 tri-, tetra- and polyglycols, and also di-, tri- and tetrapentaerythritol or polyvinyl alcohol in various degrees of polymerization. Other solvents which may be used are phosphate esters, and also cyclic and acyclic carbonic esters. Other embodiments are described in EP
30 0 394 547, EP 0 457 471 and WO 94/24200. Depending on the carrier material used or process for application to the carrier, the structure of the perchlorate salts may be either amorphous or else semicrystalline or crystalline. The person skilled in the art is also
35 aware of mixtures of the various states of aggregation.

It is preferable to use sodium/potassium perchlorate salts.

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Examples of the amount of the perchlorates that can be used are from 0.001 to 5 parts by weight, advantageously from 0.01 to 3 parts by weight, particularly preferably from 0.01 to 2 parts by weight, 5 based on 100 parts by weight of PVC.

The use of ethanolammonium perchlorate salts for inhibiting discoloration of chlorine-containing resin is disclosed in JP-A 61-9451. These are perchlorate 10 salts with ammonium-salt structure, which can be obtained via addition of primary, secondary or tertiary ethanolamines to a perchloric acid solution. Ammonium perchlorate salts are generally compounds sensitive to heat and shock and therefore create a certain risk of 15 explosion, making them unsuitable for industrial applications.

The invention also provides combinations of the stabilizer mixtures composed of at least one alkanol- 20 amine or of a reaction product of a mono- or polyfunctional epoxide and of ammonia or of a mono- or polyfunctional dialkyl(aryl)- or monoalkyl(aryl)amine of the formula (I) and of uracils of the formula (II) or of their precursors of the formula (III) with at 25 least one other conventional additive or conventional stabilizer.

The invention also provides combinations of the stabilizer mixtures composed of at least one alkanol- 30 amine or one reaction product of a mono- or polyfunctional epoxide and of ammonia or of a mono- or polyfunctional dialkyl(aryl)- or monoalkyl(aryl)amine of the formula (I) and of uracils of the formula (II) or of their precursors of the formula (III) with at 35 least one perchlorate salt and with at least one other conventional additive or conventional stabilizer.

The inventive compositions may therefore also have been treated with other conventional additives, such as

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polyols and disaccharide alcohols, hydroxycarboxylic acids or their salts, glycidyl compounds, hydrotalcites, zeolites (aluminosilicates of alkali metals or alkaline earth metals), compounds from the group of the calcium aluminum hydroxides or their hydrates, compounds from the group of the calcium aluminum hydroxohydrogenphosphites or their hydrates, compounds from the group of the aluminum hydroxides or their hydrates, compounds from the group of the calcium aluminum hydroxo(hydrogen)carbonates or their hydrates, compounds from the group of the lithium layer-lattice compounds or their hydrates, fillers, metal soaps, alkali metal compounds and alkaline earth metal compounds, fillers/pigments, lubricants, plasticizers, phosphites, pigments, epoxidized fatty acid esters and other epoxy compounds, flame retardants, antioxidants, UV absorbers, gelling agents, compatibilizers, antistatic agents, antifogging agents, light stabilizers, optical brighteners and blowing agents. Particular preference is given to epoxidized soy oils, alkaline earth metal soaps or aluminum soaps and phosphites.

Examples of these additional components are listed and explained at a later stage below (cf. "Handbook of PVC Formulating" by E.J. Wickson, John Wiley & Sons, New York 1993).

Stabilization of chlorine-containing polymers, in particular PVC, by means of hydrocalumites, catoites and calcium aluminum hydroxohydrogenphosphites is disclosed in WO 92/13914, WO 93/25613, DE 3 941 902 and DE 4 106 411. The compounds from the group of the calcium aluminum hydroxides or their hydrates are generally described in "Ullmann's Encyclopedia of Industrial Chemistry" (5th edition, 1986): Vol. A5 - Cement and Concrete (pp. 505 et seq.); Kirk-Othmer "Encyclopedia of Chemical Technology" (4th edition, 1993): Vol. 5 - Cement (pp. 572 et seq.); P. Barnes

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"Structure and Performance of Cements" (Appl. Sci. Publ. N. Y., 1983); F.M. Lea "The Chemistry of Cement and Concrete" (E. Arnold Publ. London, 1971); H.F.W. Taylor "Cement Chemistry" (Acad. Press, London, 1992) - chapter 6: Hydrated aluminate phases (pp. 167 et seq.).

The stabilizing action of lithium layer-lattice compounds on the PVC is described by way of example in EP-A-0 761 756 and in DE-A-4 425 275. All of these compounds may have been surface-modified, if desired.

Polyols and disaccharide alcohols

Examples of compounds of this type which may be used are: pentaerythritol, dipentaerythritol, tripentaerythritol, trimethylolethane, bistrimethylolpropane, inositol (cyclitols), polyvinyl alcohol, bistrimethylolpropane, sorbitol (hexitols), maltitol, isomaltitol, cellobiitol, lactitol, Lycasin, mannitol, lactose, leucrose, tris(hydroxyethyl) isocyanurate, tris(hydroxypropyl) isocyanurate, Palatinitol, tetramethylolcyclohexanol, tetramethylolcyclopentanol, tetramethylolcyclopyranol, xylitol, arabinitol (pentitols), tetritols, glycerol, diglycerol, polyglycerol, thiodiglycerol or 1- α -D-glycopyranosyl-D-mannitol dihydrate. Among these, preference is given to the disaccharide alcohols. It is also possible to use polyol syrups, such as sorbitol syrup, mannitol syrup and maltitol syrup.

Examples of the amount which may be used of the polyols are from 0.01 to 20 parts by weight, advantageously from 0.1 to 20 parts by weight and in particular from 0.1 to 10 parts by weight, based on 100 parts by weight of PVC.

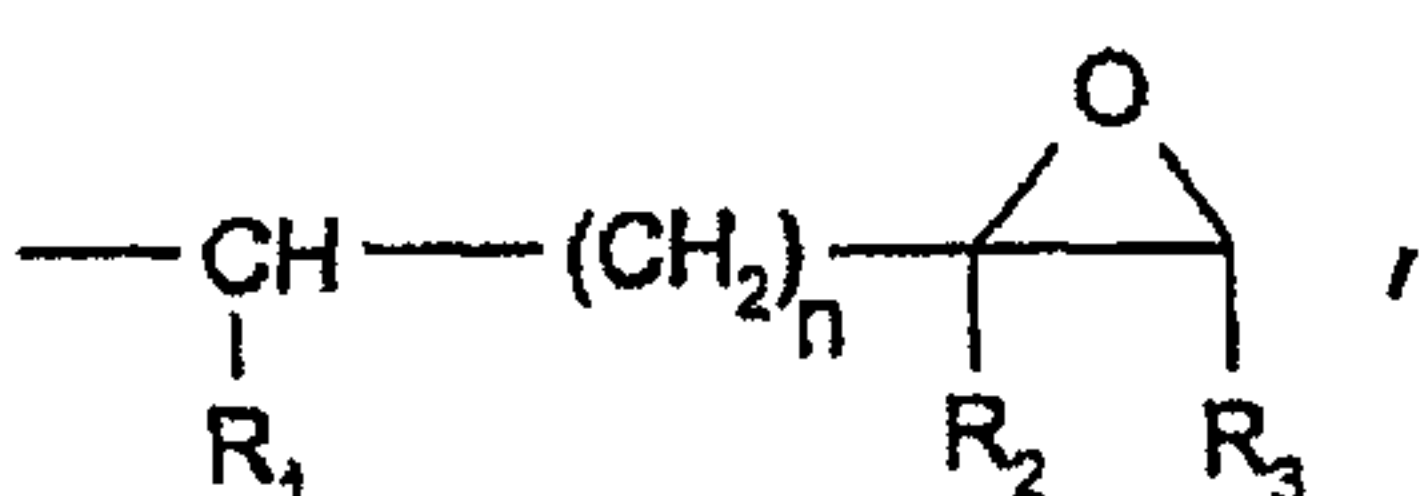
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Hydroxycarboxylic acids

Use may be made of salts or mixtures of salts of hydroxycarboxylic acids having fewer than 4 hydroxy groups and fewer than 10 carbon atoms. Among these are compounds listed in detail in the patent application WO 02/06389. Compounds having one or two hydroxy groups have proven particularly effective. Other substitution patterns may be present, examples being aldehyde, keto, acyl, amino, aminoalkyl, aminoaryl and/or halide substituents. If the compound bears two or more acid functions, at least one of these is in salt form. The salts are preferably those selected from the group Li, K, Na, Ca, Mg, Ba, Sr, Al, Fe, La, Ce, Mn or zinc. Preference, depending on the application, is particularly given to the salts of lactic acid, e.g. sodium lactate, or salts of citric acid.

Glycidyl compounds

20

They contain the glycidyl group $\text{---CH---(CH}_2\text{)}_n\text{---}$  ,

bonded directly to carbon, to oxygen atoms, to nitrogen atoms or to sulfur atoms, where either R_1 and R_3 are both hydrogen, R_2 is hydrogen or methyl and $n = 0$ or R_1 and R_3 together are $\text{---CH}_2\text{---CH}_2\text{---}$ or $\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---}$, R_2 is then hydrogen and $n = 0$ or 1.

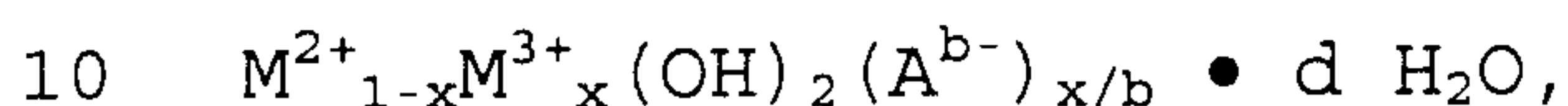
It is preferable to use glycidyl compounds having two functional groups. However, it is also possible in principle to use glycidyl compounds having one, three or more functional groups.

Diglycidyl compounds having aromatic groups are mainly used. The amount preferably used of the terminal epoxy compounds is at least 0.1 part, for example from 0.1 to 50 parts by weight, advantageously from 1 to 30 parts by weight and in particular from 1 to 25 parts by weight, based on 100 parts by weight of PVC.

Hydrotalcites

The chemical composition of these compounds is known to the person skilled in the art, e.g. from the patents
 5 DE 3 843 581, US 4,000,100, EP 0 062 813 and WO 93/20135.

Compounds from the hydrotalcite series may be described by the following general formula



where

M^{2+} = one or more of the metals selected from the group consisting of Mg, Ca, Sr, Zn and Sn

M^{3+} = Al or B,

15 A^n is an anion of valency n,

b is a number from 1 to 2,

$0 < x \leq 0.5,$

m is a number from 0 to 20.

Preference is given to compounds with

20 $A^n = OH^-, ClO_4^-, HCO_3^-, CH_3COO^-, C_6H_5COO^-, CO_3^{2-},$
 $(CHOHCOO)_2^{2-}, (CH_2COO)_2^{2-}, CH_3CHOHCOO^-, HPO_3^-$ or $HPO_4^{2-}.$

Examples of hydrotalcites are

$Al_2O_3 \cdot 6MgO \cdot CO_2 \cdot 12H_2O$ (i), $Mg_{4.5}Al_2(OH)_{13} \cdot CO_3 \cdot 3.5H_2O$ (ii),
 25 $4MgO \cdot Al_2O_3 \cdot CO_2 \cdot 9H_2O$ (iii), $4MgO \cdot Al_2O_3 \cdot CO_2 \cdot 6H_2O,$
 $ZnO \cdot 3MgO \cdot Al_2O_3 \cdot CO_2 \cdot 8-9H_2O$ and $ZnO \cdot 3MgO \cdot Al_2O_3 \cdot CO_2 \cdot 5-6H_2O.$
 Types i, ii and iii are very particularly preferred.

30 Zeolites (aluminosilicates of alkali metals and/or of alkaline earth metals)

These may be described by the following general formula $M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot wH_2O$, where n is the charge on the cation M;

35 M is an element of the first or second main group, such as Li, Na, K, Mg, Ca, Sr or Ba;

y : x is a number from 0.8 to 15, preferably from 0.8 to 1.2; and

w is a number from 0 to 300, preferably from 0.5 to 30.

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Examples of zeolites are sodium aluminosilicates of the formulae

Na₁₂Al₁₂Si₁₂O₄₈ . 27 H₂O [zeolite A], Na₆Al₆Si₆O₂₄ . 2 NaX .
 7.5 H₂O, X = OH, halogen, ClO₄ [sodalite]; Na₆Al₆Si₃₀O₇₂ .
 5 24 H₂O; Na₈Al₈Si₄₀O₉₆ . 24 H₂O; Na₁₆Al₁₆Si₂₄O₈₀ . 16 H₂O;
 Na₁₆Al₁₆Si₃₂O₉₆ . 16 H₂O; Na₅₆Al₅₆Si₁₃₆O₃₈₄ . 250 H₂O [zeolite
 Y], Na₈₆Al₈₆Si₁₀₆O₃₈₄ . 264 H₂O [zeolite X];

or the zeolites which can be prepared by partial or
 complete exchange of the Na atoms by Li atoms, K atoms,
 10 Mg atoms, Ca atoms, Sr atoms or Zn atoms, for example
 (Na,K)₁₀Al₁₀Si₂₂O₆₄ . 20 H₂O ; Ca_{4.5}Na₃[(AlO₂)₁₂(SiO₂)₁₂] .
 30 H₂O; K₉Na₃[(AlO₂)₁₂(SiO₂)₁₂] . 27 H₂O.

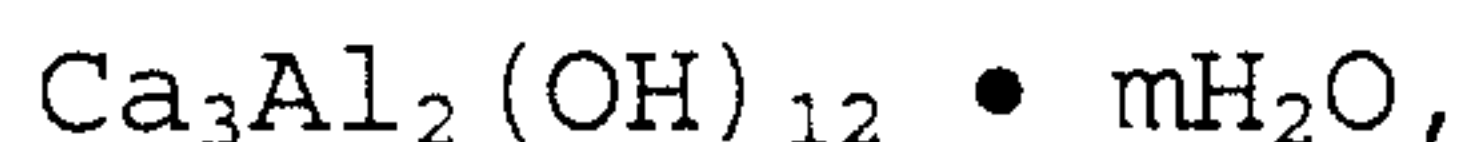
Very particular preference is given to Na zeolite A and
 Na zeolite P.

15 The hydrotalcites and/or zeolites may be used in
 amounts of, for example, 0.1 to 20 parts by weight,
 expediently 0.1 to 10 parts by weight and in particular
 0.1 to 5 parts by weight, based on 100 parts by weight
 of halogen-containing polymer.

20

Katoites

Compounds suitable for the inventive stabilizer
 combinations from the group of the katoites can be
 25 described by the general formula



where

$$m = 0-10.$$

30

The compounds mentioned may, if appropriate, have been
 surface-modified. They have a very particular crystal
 lattice, (known as hydrogarnet structure), which
 distinguishes them from other calcium aluminum hydroxy
 35 compounds.

This crystal lattice, together with lattice
 separations, is described in the article by
 C. Cohen-Addad and P. Ducros in Acta Cryst. (1967), 23,
 pages 220 to 225. By way of example, these materials

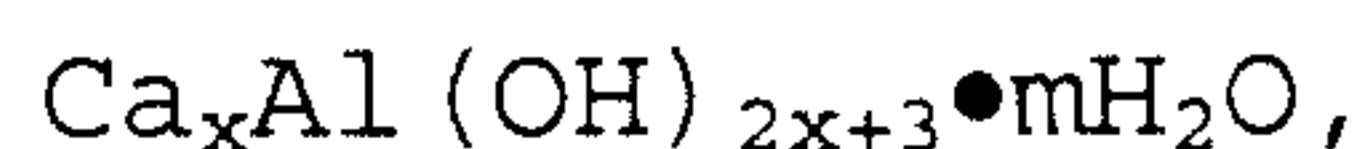
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may be prepared by a method based on German patent specification DE 2 424 763.

Hydrocalumites

5

Compounds suitable for the inventive stabilizer combinations and derived from the group of the hydrocalumites are described by the general formula:



10 where

$x = 1$ to 4 and

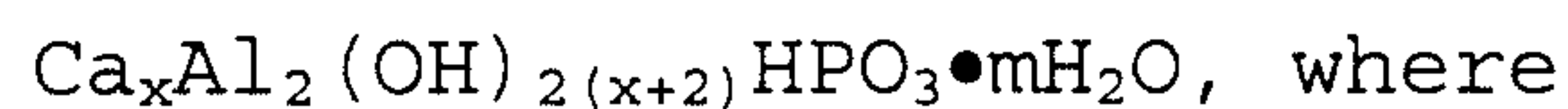
$m =$ from 0 to 8.

Preferred compounds are those where, in the above
15 general formula,

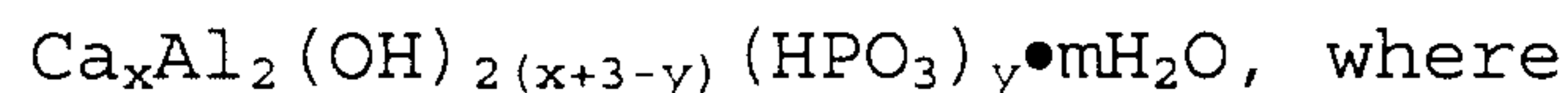
$x = 2$ or 3.

Calcium aluminum hydroxy(hydrogen)phosphites

20 Suitable compounds from the group of the basic CHAPs, calcium aluminum hydroxyhydrogenphosphites, have the general formula



$x =$ from 2 to 8 and

25 $m =$ from 0 to 12, or

$x =$ from 2 to 12,

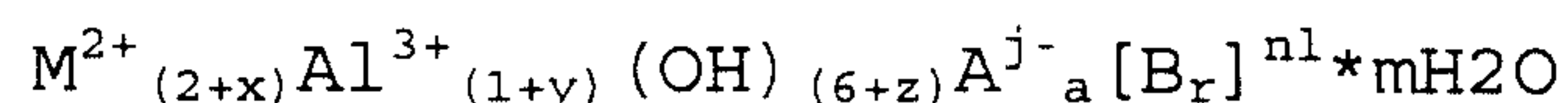
$$\frac{2x+5}{2} > y > 0 \text{ and}$$

$m =$ from 0 to 12,

30 with the exception $y = 1$, if $x =$ from 2 to 8.

Other examples of the hydrocalumites which via variation of the metal cation M and of the acid anions A or B of the general formula below

35



and are described in detail in patent specification WO

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02/098964, pages 18-20. In one preferred embodiment, M is calcium, which may be present in a mixture with magnesium or zinc or magnesium and zinc. For the purposes of the preferred embodiment, the composition is selected to be free from the heavy metal zinc. If a surface treatment is desired, the product may be modified accordingly using the methods and reagents known to the person skilled in the art.

10 Lithium layer-lattice compounds

Lithium aluminum layer-lattice compounds have the general formula A



15 where

MII is Mg, Ca or Zn and

An⁻ is a selected anion of valency n or a mixture of anions

and the indices are in the range

20 $0 < a < (b-2)/2,$

$1 < b < 6$ and

$m = \text{from } 0 \text{ to } 30$

with the proviso that $b-2a > 2$ or

the general formula B

25 $[\text{Al}_2(\text{Li}_{(1-x)} \cdot \text{MII}_x)(\text{OH})_6]n(\text{An}^-)_{1+x} \cdot m\text{H}_2\text{O}$

where

MII, A, m and n are as defined above and

x complies with the condition $0.01 \leq x < 1$.

30 The preparation of the layer-lattice compounds mentioned is characterized by reacting lithium hydroxide, lithium oxide and/or its compounds capable of conversion to hydroxide, metal(II) hydroxides, metal(II) oxides and/or their compounds derived from
35 the metals mentioned and capable of conversion to hydroxides, and aluminum hydroxides and/or their compounds capable of conversion to hydroxides, and also acids and/or their salts or mixtures thereof with one another in an aqueous medium, at a pH of from 8 to 10

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and at temperatures of from 20 to 250°C, and isolating the resultant solid product of the reaction. The reaction time is preferably 0.5 to 40 hours, in particular from 3 to 15 hours.

5

The product directly produced from the reaction described above can be isolated from the aqueous reaction medium by known processes, preferably via filtration. The product isolated from the reaction is also worked up in a manner known per se, for example via washing of the filter cake with water and drying of the washed residue at temperatures of, for example, from 60 to 150°C, preferably at from 90 to 120°C. For the reaction with aluminum it is possible to use either fine-particle, activated metal(III) hydroxide in combination with sodium hydroxide or to use an NaAlO₂. Lithium, or one of the metal(II) compounds mentioned, may be used in the form of fine-particle lithium oxide or fine-particle lithium hydroxide, or a mixture thereof, or in the form of fine-particle metal(II) oxide or fine-particle metal(II) hydroxide or a mixture thereof. The corresponding acid anions may be used at various concentrations, e.g. directly in the form of acid or else in the form of salt.

25

The reaction temperatures are preferably from about 20 to 250°C, more particularly from about 60 to 180°C. Catalysts or accelerators are not required. The water of crystallization of the substances may be removed entirely or partially by heating.

30

In their use as stabilizers, the dried layer-lattice compounds do not evolve water or any other gas at the usual processing temperatures of from 160 to 220°C for PVC, and therefore no blistering defects occur in the moldings.

35

The anion An in the above general formula can be sulfate, sulfite, sulfide, thiosulfate, peroxide,

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peroxosulfate, peroxodisulfate, hydrogenphosphate, hydrogenphosphite, carbonate, halides, nitrate, nitrite, hydrogensulfate, hydrogencarbonate, hydrogen-sulfite, hydrogensulfide, dihydrogenphosphate, dihydrogenphosphite, monocarboxylic anions, such as acetate and benzoate, amide, azide, hydroxide, hydroxylamine, hydroazide, acetylacetonate, phenolate, pseudohalides, halites, halates, perhalates, periodate, permanganate, dianions of dicarboxylic acids, e.g. phthalate, oxalate, maleate or fumarate, bisphenolates, phosphate, pyrophosphate, phosphite, pyrophosphite, trianions of tricarboxylic acids, e.g. citrate, trisphenolates, and many others, or else a mixture thereof. Among these, preference is given to hydroxide, carbonate, phosphite and maleate.

To improve the dispersibility of the substances in halogen-containing thermoplastic polymer compositions, these may be surface-treated with a higher fatty acid, e.g. stearic acid, with an anionic surfactant, with a silane coupling agent, with a titanate coupling agent, or with a glycerol ester of a fatty acid.

The calcium aluminum hydroxides, calcium aluminum hydroxohydrogenphosphites, aluminum hydroxides, calcium aluminum hydroxo(hydrogen)carbonates and lithium layer-lattice compounds described above may be not only crystalline but also semicrystalline and/or amorphous.

30 Fillers

Fillers such as calcium carbonate, dolomite, wollastonite, magnesium oxide, magnesium hydroxide, silicates, china clay, talc, glass fibers, glass beads, wood flour, mica, metal oxides or metal hydroxides, carbon black, graphite, rock flour, heavy spar, glass fibers, talc, kaolin and chalk are used. Preference is given to chalk (HANDBOOK OF PVC FORMULATING E. J. Wickson, John Wiley & Sons, Inc., 1993, pp. 393-449)

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and reinforcing agents (TASCHENBUCH der Kunststoff-additive [Plastics Additives Handbook], R. Gächter & H. Müller, Carl Hanser, 1990, pp. 549-615).

The fillers may be used in amounts of preferably at least one part by weight, for example 5 to 200 parts by weight, expediently 10 to 150 parts by weight and in particular from 15 to 100 parts by weight, based on 100 parts by weight of PVC.

10 Metal soaps

Metal soaps are primarily metal carboxylates, preferably of relatively long-chain carboxylic acids. Well-known examples of these are stearates and laurates, and also oleates and salts of relatively short-chain aliphatic or aromatic alkanecarboxylic acids, such as acetic acid, propionic acid, butyric acid, valeric acid, hexanoic acid, sorbic acid; oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, fumaric acid, citric acid, benzoic acid, salicylic acid, phthalic acids, hemimellitic acid, trimellitic acid, pyromellitic acid.

Metals which should be mentioned are: Li, Na, K, Mg, Ca, Sr, Ba, Zn, Al, La, Ce and rare earth metals. Use is frequently made of so-called synergistic mixtures, such as barium/zinc stabilizers, magnesium/zinc stabilizers, calcium/zinc stabilizers or calcium/magnesium/zinc stabilizers. The metal soaps may be used either alone or in mixtures. An overview of common metal soaps is found in Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A16 (1985), pp. 361 et seq. Besides the compounds mentioned, use may also be made of organoaluminum compounds, and of compounds analogous to the abovementioned compounds, in particular aluminum tristearate, aluminum distearate, and aluminum monostearate, and also aluminum acetate and basic derivatives derived therefrom.

- 30 -

US 4,060,512 and US 3,243,394 give further explanations concerning the aluminum compounds which can be used and those which are preferred.

5 Besides the abovementioned compounds, use may also be made of organic rare earth compounds, in particular compounds analogous to the abovementioned compounds. The term rare earth compound means particularly compounds of the elements cerium, praseodymium,
10 neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, lanthanum and yttrium, particular preference being given to mixtures with cerium. Other preferred rare earth compounds are found in EP-A-0 108 023.
15 Examples of the amount of the metal soaps or their mixtures which may be used are from 0.001 to 10 parts by weight, advantageously from 0.01 to 8 parts by weight, particularly preferably from 0.05 to 5 parts by weight, based on 100 parts by weight of PVC.

20

Compounds of alkali metals and of alkaline earth metals

For the purposes of the present invention, these are mainly the carboxylates of the acids described above,
25 but also corresponding oxides or, respectively, hydroxides or carbonates. Mixtures of these with organic acids are also possible. Examples are LiOH, NaOH, KOH, CaO, Ca(OH)₂, MgO, Mg(OH)₂, Sr(OH)₂, Al(OH)₃, CaCO₃ and MgCO₃ (and also basic carbonates, such as
30 magnesia alba and huntite), and also fatty-acid salts of Na and of K. In the case of alkaline earth metal carboxylates and Zn carboxylates it is also possible to use adducts of these with MO or M(OH)₂ (M = Ca, Mg, Sr or Zn), so-called "overbased" compounds. In addition to
35 the stabilizers according to the invention it is preferable to use alkali metal carboxylates, alkaline earth metal carboxylates and/or aluminum carboxylates.

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Lubricants

Examples of possible lubricants are: montan wax, fatty acid esters, (ox.) polyethylene waxes, polypropylene waxes, (ox.) paraffin waxes, amide waxes, chloroparaffins, glycerol esters and alkaline earth metal soaps, and fatty ketones, and also the lubricants, or combinations of the lubricants, listed in EP 0 259 783, based on complex esters. Other lubricants which may be used are mentioned in "Plastics Additives Handbook", Carl Hanser Verlag, 5th edition, 2001, pages 511-552.

Plasticizers

15

Examples of organic plasticizers are those from the following groups:

A) Phthalates: such as preferably di-2-ethylhexyl, diisononyl and diisodecyl phthalate, also known by the common abbreviations DOP (dioctyl phthalate, di-2-ethylhexylphthalate), DINP (diisononyl phthalate), DIDP (diisodecyl phthalate).

B) Esters of aliphatic dicarboxylic acids, in particular esters of adipic, azelaic, and sebacic acid: preferably di-2-ethylhexyl adipate and diisooctyl adipate.

C) Trimellitic esters, such as tri-2-ethylhexyl trimellitate, triisodecyl trimellitate (mixture), triisotridecyl trimellitate, triisooctyl trimellitate (mixture), and also tri-C₆-C₈-alkyl, tri-C₆-C₁₀-alkyl, tri-C₇-C₉-alkyl and tri-C₉-C₁₁-alkyl trimellitate. Common abbreviations are TOTM (trioctyl trimellitate, tri-2-ethylhexyl trimellitate), TIDTM (triisodecyl trimellitate) and TITDTM (triisotridecyl trimellitate).

D) Epoxy plasticizers: by way of example here, mention may be made of epoxidized unsaturated fatty acids, e.g. epoxidized soybean oil, epoxidized linseed oil, epoxidized sunflower oil, epoxidized rapeseed oil,

epoxidized tallow oil, epoxidized olive oil. Other epoxidized fatty acid esters which may be mentioned are the variants based on the monoesters of fatty acids and on monohydric alcohols, disclosed in WO 02/060884 A1.

5 Other variants of epoxidized fatty acid esters are produced via transesterification of, for example, triacetin, described in DE-A-30 04 660. Among these are the epoxidized glyceride acetates, obtainable by transesterifying epoxidized fatty acid esters with

10 triacetin. The molar ratio here can be selected so that, if desired, the appropriate diglyceride monoacetates are quantitatively predominant. Detailed examples and processes are disclosed in patent specification WO 02/060884 A1. The preparation of other

15 derivatives, such as the monoglyceride diacetates, is also disclosed in US-A2-895 966. All of the mixtures as described actually mostly comprise complex mixtures derived from the transesterification reactions.

E) Polymeric plasticizers: the commonest starting

20 materials for preparing polyester plasticizers are: dicarboxylic acids, such as adipic, phthalic, azelaic or sebacic acid; diols, such as 1,2-propanediol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol and diethylene glycol.

25 F) Phosphoric esters: a definition of these esters is given in the abovementioned "Taschenbuch der Kunststoffadditive" ["Plastics Additives Handbook"], Chapter 5.9.5, pp. 408-412. Examples of these phosphoric esters are tributyl phosphate, tri-2-ethyl-

30 butyl phosphate, tri-2-ethylhexyl phosphate, tri-chloroethyl phosphate, 2-ethylhexyl diphenyl phosphate, cresyl diphenyl phosphate, triphenyl phosphate, tricresyl phosphate and trixylenyl phosphate. Preference is given to tris(2-ethylhexyl) phosphate and

35 Reofos® 50 and 95 (Ciba Spezialitätenchemie).

G) Chlorinated hydrocarbons (paraffins)

H) Hydrocarbons

I) Monoesters, e.g. butyl oleate, phenoxyethyl oleate, tetrahydrofurfuryl oleate and alkylsulfonates.

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J) Glycol esters, e.g. diglycol benzoates.

K) Representatives of citric acid plasticizers

Among these are the citric esters of the general
 5 formula B, derived from 2-hydroxy-1,2,3-propanetri-
 carboxylic acid as described in WO 02/094927



10 where

each R is a straight-chain or branched alkyl radical
 having from 4 to 18 carbon atoms and $R_1 = H$, or $R_1 =$
 R_2CO . If R_1 is not H, R_2 is a straight-chain or
 branched alkyl radical having from 1 to 10 carbon
 15 atoms. Preferred alcohol components R used in the
 citric ester are C6-C14 alkanols, which may be branched
 or unbranched, and the alkanol radicals here may be
 identical or different.

Compounds which may be listed as non-restricting
 20 examples are triethyl citrate (Citrofol A I), tributyl
 citrate (Citrofol B I), triethyl acetylcitrate
 (Citrofol A II), tributyl acetylcitrate (Citrofol B
 II), tri-n-hexyl acetylcitrate, tri-n-hexyl n-butyryl-
 citrate, tri-n-(hexyl/octyl/decyl) acetylcitrate and
 25 tri-n-(octyl/decyl) acetylcitrate.

L) Perhydrophthalic, perhydroisophthalic and perhydro-
 terephthalic esters, and also perhydrogenated glycol
 benzoate and perhydrogenated diglycol benzoate esters.
 Preference is given to perhydrogenated diisononyl
 30 phthalate ([®]Hexamoll DINCH - BASF) as described in
 DE 19.756.913, DE 19.927.977, DE 19.927.978 and DE
 19.927.979.

A definition of these plasticizers and examples of the
 35 same are given in "Kunststoffadditive" ["Plastics
 Additives"], R. Gächter/H. Müller, Carl Hanser Verlag,
 3rd Ed., 1989, Chapter 5.9.6, pp. 412 - 415, and in
 "PVC Technology", W. V. Titow, 4th Ed., Elsevier Publ.,
 1984, pp. 165-170. It is also possible to use mixtures

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of different plasticizers.

Examples of the amount which may be used of the plasticizers are 5 to 20 parts by weight, expediently
5 10 to 20 parts by weight, based on 100 parts by weight of PVC. Rigid or semirigid PVC preferably comprises up to 10%, particularly preferably up to 5%, of plasticizer, or no plasticizer.

10 Pigments

Suitable substances are known to the person skilled in the art. Examples of inorganic pigments are TiO_2 , pigments based on zirconium oxide, BaSO_4 , zinc oxide
15 (zinc white) and lithopones (zinc sulfide/barium sulfate), carbon black, carbon black-titanium dioxide mixtures, iron oxide pigments, Sb_2O_3 , $(\text{Ti}, \text{Ba}, \text{Sb})\text{O}_2$, Cr_2O_3 , spinels, such as cobalt blue and cobalt green, $\text{Cd}(\text{S}, \text{Se})$, ultramarine blue. Examples of organic
20 pigments are azo pigments, phthalocyanine pigments, quinacridone pigments, perylene pigments, diketo-pyrrolopyrrole pigments and anthraquinone pigments. TiO_2 in micronized form is also preferred. A definition and further descriptions are found in the "Handbook of
25 PVC Formulating", E.J. Wickson, John Wiley & Sons, New York, 1993.

Phosphites

30 Organic phosphites are known costabilizers for chlorine-containing polymers. Examples are trioctyl, tridecyl, tridodecyl, tritridecyl, tripentadecyl, trioleyl, tristearyl, triphenyl, tricresyl, trisnonylphenol, tris-2,4-tert-butylphenyl or tricyclohexyl
35 phosphite.

Other suitable phosphites are various mixtures of aryl dialkyl or alkyl diaryl phosphites, e.g. phenyl dioctyl, phenyl didecyl, phenyl didodecyl, phenyl

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ditridecyl, phenyl ditetradecyl, phenyl dipentadecyl, octyl diphenyl, decyl diphenyl, undecyl diphenyl, dodecyl diphenyl, tridecyl diphenyl, tetradecyl diphenyl, pentadecyl diphenyl, oleyl diphenyl, stearyl diphenyl and dodecyl bis-2,4-di-tert-butylphenyl phosphite.

It is also advantageous to use phosphites of various di- or polyols: examples are tetraphenyl dipropylene glycol diphosphite, polydipropylene glycol phenyl phosphite, tetramethylolcyclohexanol decyl diphosphite, tetramethylolcyclohexanol butoxyethoxyethyl diphosphite, tetramethylolcyclohexanol nonylphenyl diphosphite, bisnonylphenyl ditrimethylolpropane diphosphite, bis-2-butoxyethyl ditrimethylolpropane diphosphite, trishydroxyethyl isocyanurate hexadecyl triphosphite, didecyl pentaerythrityl diphosphite, distearyl pentaerythrityl diphosphite, bis-2,4-di-tert-butylphenyl pentaerythrityl diphosphite, and also mixtures of these phosphites and aryl/alkyl phosphite mixtures of empirical composition $(H_{19}C_9C_6H_4)O_{1.5}P(OC_{12,13}H_{25,27})_{1.5}$ or $[C_8H_{17}-C_6H_4-O-]_2P[i-C_8H_{17}O]$, $(H_{19}C_9C_6H_4)O_{1.5}P(OC_{9,11}H_{19,23})_{1.5}$.

An example of the amount which may be used of the organic phosphites is from 0.01 to 10 parts by weight, advantageously from 0.05 to 5 parts by weight, and in particular from 0.1 to 3 parts by weight, based on 100 parts by weight of PVC.

30

Epoxidized fatty acid esters and other epoxy compounds

The inventive stabilizer combination may also preferably comprise at least one epoxidized fatty acid ester. Esters of fatty acids from natural sources (fatty acid glycerides) may especially be used here, examples being soy oil or rapeseed oil. However, it is also possible to use synthetic products, such as epoxidized butyl oleate. It is also possible to use

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epoxidized polybutadiene and polyisoprene, if appropriate also in partially hydroxylated form, or glycidyl acrylate and glycidyl methacrylate in the form of homo- or copolymer. These epoxy compounds may also
5 have been applied to an alumino salt compound; in this connection see also DE-A-4 031 818.

Antioxidants

10 Alkylated monophenols, e.g. 2,6-di-tert-butyl-4-methylphenol, alkylthiomethylphenols, e.g. 2,4-dioctylthiomethyl-6-tert-butylphenol, alkylated hydroquinones, e.g. 2,6-di-tert-butyl-4-methoxyphenol, hydroxylated
15 thiodiphenyl ethers, e.g. 2,2'-thiobis(6-tert-butyl-4-methylphenol), alkylidenebisphenols, e.g. 2,2'-methylenebis(6-tert-butyl-4-methylphenol), benzyl compounds, e.g. 3,5,3',5'-tetra-tert-butyl-4,4'-di-hydroxydibenzyl ether, hydroxybenzylated malonates, e.g. dioctadecyl 2,2-bis(3,5-di-tert-butyl-2-hydroxy-
20 benzyl)malonate, hydroxybenzylaromatics, e.g. 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, triazine compounds, e.g. 2,4-bis(octyl-mercapto-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, phosphonates and phosphonites, e.g. dimethyl
25 2,5-di-tert-butyl-4-hydroxybenzylphosphonate, acylaminophenols, e.g. 4-hydroxylauranilide, esters of beta-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid, of beta-(5-tert-butyl-4-hydroxy-3-methylphenyl)-propionic acid, of beta-(3,5-dicyclohexyl-4-hydroxy-
30 phenyl)propionic acid, esters of 3,5-di-tert-butyl-4-hydroxyphenylacetic acid with mono- or polyhydric alcohols, amides of beta-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid, e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine, vitamin
35 E (tocopherol), and derivatives.

An example of the amount which may be used of the antioxidants is from 0.01 to 10 parts by weight, advantageously from 0.1 to 10 parts by weight, and in particular from 0.1 to 5 parts by weight, based on 100

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parts by weight of PVC.

UV absorbers and light stabilizers

5 Examples of these are: 2-(2'-hydroxyphenyl)benzo-
triazoles, such as 2-(2'-hydroxy-5'-methylphenyl)-
benzotriazole, 2-hydroxybenzophenones, esters of
unsubstituted or substituted benzoic acids, such as
4-tert-butylphenyl salicylate, phenyl salicylate,
10 acrylates, nickel compounds, oxalamides, such as
4,4'-dioctyloxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-
butyloxanilide, 2-(2-hydroxyphenyl)-1,3,5-triazines,
such as 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-
triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-
15 dimethylphenyl)-1,3,5-triazine, sterically hindered
amines, such as bis(2,2,6,6-tetramethylpiperidin-4-yl)
sebacate, bis(2,2,6,6-tetramethylpiperidin-4-yl)
succinate.

20 Blowing agents

Examples of blowing agents are organic azo compounds
and organic hydrazo compounds, tetrazoles, oxazines,
isatoic anhydride, and also soda and sodium
bicarbonate. Preference is given to azodicarbonamide
25 and sodium bicarbonate and also mixtures of these.

Definitions and examples of impact modifiers and
processing aids, gelling agents, antistats, biocides,
metal deactivators, optical brighteners, flame
30 retardants, antifogging agents, and compatibilizers,
are described in "Kunststoffadditive" ["Plastics
Additives"], R. Gächter/H. Müller, Carl Hanser Verlag,
3rd edn., 1989, "Plastics Additives Handbook"
H. Zweifel, Carl Hanser Verlag, 5th edn., 2001 and in
35 "Handbook of Polyvinyl Chloride Formulating"
E.J. Wilson, J. Wiley & Sons, 1993, and also in
"Plastics Additives" G. Pritchard, Chapman & Hall,
London, 1st edition, 1998.

Impact modifiers are also described in detail in

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"Impact Modifiers for PVC", J.T. Lutz/
D.L. Dunkelberger, John Wiley & Sons, 1992.

5 The invention further provides compositions which
comprise a chlorine-containing polymer and comprise an
inventive stabilizer mixture.

10 The amount used of the compounds of the general
formulae (I) in these compositions, in order to achieve
stabilization in the chlorine-containing polymer, is
advantageously from 0.01 to 10 parts by weight,
preferably from 0.05 to 5 parts by weight, in
particular from 0.1 to 2 parts by weight, based on 100
parts by weight of PVC.

15 The amount used of the compounds of the general
formulae (II) in these compositions, in order to
achieve stabilization in the chlorine-containing
polymer, is advantageously from 0.01 to 10 parts by
20 weight, preferably from 0.05 to 5 parts by weight, in
particular from 0.1 to 2 parts by weight, based on 100
parts by weight of PVC.

25 The amount used of the compounds of the general
formulae (III) in these compositions, in order to
achieve stabilization in the chlorine-containing
polymer, is advantageously from 0.01 to 10 parts by
weight, preferably from 0.05 to 5 parts by weight, in
particular from 0.1 to 2 parts by weight, based on 100
30 parts by weight of PVC.

An example of the amount which may be used of the
perchlorate salt is from 0.001 to 5 parts by weight,
advantageously from 0.01 to 3 parts by weight,
35 particularly preferably from 0.01 to 2 parts by weight,
based on 100 parts by weight of PVC.

Examples of the chlorine-containing polymers to be
stabilized are:

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polymers of vinyl chloride, of vinylidene chloride, vinyl resins whose structure contains vinyl chloride units, such as copolymers of vinyl chloride and vinyl esters of aliphatic acids, in particular vinyl acetate, 5 copolymers of vinyl chloride with esters of acrylic or methacrylic acid and with acrylonitrile, copolymers of vinyl chloride with diene compounds and with unsaturated dicarboxylic acids or anhydrides of these, such as copolymers of vinyl chloride with diethyl 10 maleate, diethyl fumarate or maleic anhydride, postchlorinated polymers and copolymers of vinyl chloride, copolymers of vinyl chloride and vinylidene chloride with unsaturated aldehydes, ketones and others, such as acrolein, crotonaldehyde, vinyl methyl 15 ketone, vinyl methyl ether, vinyl isobutyl ether and the like; polymers of vinylidene chloride and copolymers of the same with vinyl chloride and with other polymerizable compounds; polymers of vinyl chloroacetate and of dichlorodivinyl ether; chlorinated 20 polymers of vinyl acetate, chlorinated polymeric esters of acrylic acid and of alpha-substituted acrylic acid; polymers of chlorinated styrenes, such as dichlorostyrene; chlorinated rubbers; chlorinated polymers of ethylene; polymers and postchlorinated 25 polymers of chlorobutadiene and copolymers of these with vinyl chloride, chlorinated natural or synthetic rubbers, and also mixtures of the polymers mentioned with themselves or with other polymerizable compounds. For the purposes of this invention, PVC includes 30 copolymers with polymerizable compounds, such as acrylonitrile, vinyl acetate or ABS, where these may be suspension polymers, bulk polymers or else emulsion polymers. Preference is given to a PVC homopolymer, also in combination with polyacrylates.

35

Other possible polymers are graft polymers of PVC with EVA, ABS or MBS. Other preferred substrates are mixtures of the abovementioned homo- and copolymers, in particular vinyl chloride homopolymers, with other

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thermoplastic or/and elastomeric polymers, in particular blends with ABS, MBS, NBR, SAN, EVA, CPE, MBAS, PMA, PMMA, EPDM or with polylactones, in particular from the group consisting of ABS, NBR, NAR, 5 SAN and EVA. The abbreviations used for the copolymers are familiar to the skilled worker and have the following meanings: ABS: acrylonitrile-butadiene-styrene; SAN: styrene-acrylonitrile; NBR: acrylonitrile-butadiene; NAR: acrylonitrile-acrylate; 10 EVA: ethylene-vinyl acetate. Other possible polymers are in particular styrene-acrylonitrile copolymers based on acrylate (ASA). A preferred component in this context is a polymer composition which comprises, as components (i) and (ii), a mixture of 25-75% by weight 15 of PVC and 75-25% by weight of the copolymers mentioned. Components of particular importance are compositions made from (i) 100 parts by weight of PVC and (ii) 0-300 parts by weight of ABS and/or SAN-modified ABS and 0-80 parts by weight of the copolymers 20 NBR, NAR and/or EVA, but in particular EVA. For the purposes of the present invention it is also possible to stabilize in particular recycled materials of chlorine-containing polymers, specifically the polymers described in more detail above, which have been 25 degraded by processing, use or storage. Recycled material from PVC is particularly preferred.

The compounds which may be used concomitantly according to the invention, and also the chlorine-containing 30 polymers, are well known to the skilled worker and are described in detail in "Kunststoffadditive" ["Plastics Additives"], R. Gächter/H. Müller, Carl Hanser Verlag, 3rd edn., 1989; in DE 197 41 778 and in EP-A 99 105 418.0 of 03.17.1999.

35

The inventive stabilizer system for chlorine-containing polymer compositions is represented by non-plasticized or plasticizer-free, or substantially plasticizer-free

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compositions.

The inventive compositions are particularly suitable in the form of unplasticized formulations for hollow
5 articles (bottles), packaging foils (thermoforming foils), blown foils, crash-pad foils (automobiles), pipes, foams, heavy profiles (window frames), thin-wall profiles, construction profiles, external cladding, fittings, office foils, and apparatus casings
10 (computers, household devices). Preferred other compositions in the form of plasticized formulations are suitable for wire sheathing, cable insulation, decorative foils, roof sheeting, foams, agricultural sheeting, hoses, sealing profiles, office foils, and
15 sheeting for air-supported structures.

Examples of use of the inventive compositions in the form of plastisols are synthetic leather, flooring, textile coatings, wallcoverings, metal coatings (coil
20 coatings), and underbody protection for motor vehicles. Examples of sintered-PVC uses of the inventive compositions are slush, metal coatings and coil coatings, and Luvitherm foils in the EPVC sector.

25 The stabilizers may advantageously be incorporated by the following methods: in the form of an emulsion or dispersion (an example of a possible form being that of a paste-like mixture, and an advantage of the inventive combination in that supply form being the stability of
30 the paste); in the form of a dry mixture during the mixing of added components or polymer mixtures; via direct addition to the processing apparatus (e.g. calender, mixer, kneader, extruder, or the like), or in the form of a solution or melt or flakes or
35 granules/pellets in dust-free form in the form of a one-pack system.

The inventive stabilized PVC likewise provided by the invention can be prepared in a manner known per se, and

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to this end the inventive stabilizer mixture and, if appropriate, other additives are mixed with the PVC, using apparatus known per se, such as the above-mentioned processing apparatus. The stabilizers here
5 can be added individually or in a mixture, or else in the form of what are known as masterbatches.

The PVC stabilized by the present invention may be converted to the desired form by known methods.
10 Examples of these processes are milling, calendering, extrusion, injection molding, or spinning, or else extrusion blow molding. The stabilized PVC can also be processed to give foams.

By way of example, a PVC stabilized according to the invention is particularly suitable for hollow articles (bottles), packaging foils (thermoforming foils), blown foils, pipes, foams, heavy profiles (window frames), thin-wall profiles, construction profiles, external
15 cladding, fittings, office foils, and apparatus casings (computers, household devices).

The inventive PVC is particularly suitable for semi-rigid and plasticized formulations, in particular in
25 the form of plasticized formulations for wire sheathing, or cable insulation, which is particularly preferred. In the form of semirigid formulations, the inventive PVC is particularly suitable for decorative foils, foams, agricultural sheeting, hoses, sealing
30 profiles, and office foils.

Examples of use of the inventive PVC in the form of plastisol are synthetic leather, flooring, textile coatings, wall, coverings, metal coatings coil coatings
35 and underbody protection for motor vehicles.

Examples of sintered-PVC uses of the PVC stabilized according to the invention are slush coatings and coil coatings for plastisol formulations, for semirigid

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formulations, and for plasticized formulations. For further details in this connection, see "Kunststoffhandbuch PVC" [Plastics handbook PVC], vol. 2/2, W. Becker/H. Braun, 2nd edn., 1985, Carl Hanser Verlag, pages 1236-1277.

The examples below illustrate the invention but do not restrict the same. As in the rest of the description, data relating to parts and percentages are based on weight.

Examples

The composition of test formulations as in the tables is given below. The data are in parts by weight, based on 100 parts of PVC resin.

A laboratory extruder was used to extrude strips in accordance with the formulations, starting from the respective dry mixtures. To produce the strips, the PVC powder mixtures and the additives mentioned were prepared by the conventional hot/cold mixing technique and homogenized and plastified in a twin-screw extruder.

The extrusion parameters are as follows: Weber CE-3, conical twin screw: screw rotation rate 13 rpm, temperature control in individual zones: barrel section in zone 1: 170°C, zone 2 at 165°C, zone 3 at 170°C, and zone 4 at 180°C. The die temperature was adjusted to 190°C. Die geometry: 50 × 2 mm.

Initial color was determined as yellowness index (YI) to ASTM D1925-70. The results are given in the tables below. Low YI values mean good stabilization.

Long-term stability was further determined via determination of thermal stability to DIN VDE 0472. Here, the test piece was heated to 200°C in a glass

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tube in an oil bath, the bottom of which had been sealed by fusion (AR glass from Peco-Laborbedarf GmbH, Darmstadt), and the time at which visible red coloration of the universal pH indicator paper was observed (corresponding to pH of 3) was determined.

The stability of the PVC was further determined via the dehydrochlorination test (DHC test), carried out by a method based on DIN 53381, sheet 3. Here, the time required for the dehydrochlorination curve to rise to a conductivity of 200 $\mu\text{S}/\text{cm}$ was measured at 180°C.

Example 1

	A 1	A 2	A 3	A 4	A 5	A 6	A 7
PVC (Shin Etsu 6704)	100	100	100	100	100	100	100
Compound 1	---	---	---	---	---	---	0.1
Zeolite A	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Calcium stearate	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Marklube TM 367	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Licowax TM PE 520	0.6	0.6	0.6	0.6	0.6	0.6	0.6
AC 629 A	0.1	0.1	0.1	0.1	0.1	0.1	0.1
1,3-Dimethyl-4-aminouracil	---	0.1	0.2	---	---	0.1	0.1
TEA	---	---	---	0.1	0.2	0.1	0.1
Test results							
Color measurement							
Yellowness Index extruded strip/ initial color	red-violet	31	26	73	73	27	23

15

PVC Shin Etsu 6704, K value 67 (ex Shin Etsu)

Compound 1 = mixture composed of 9% NaClO_4 , 45% CaCO_3 , 40% CaSiO_3 , 6% H_2O

Marklube 367 = paraffin wax (ex Crompton)

20 Licowax PE 520 = polyethylene wax (ex Clariant)

AC 629 A = oxidized polyethylene wax (ex Honeywell)

TEA = triethanolamine in the form of commercially

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available product

1,3-dimethyl-4-aminouracil in the form of commercially available product

5 From the table it can be seen that the inventive composition A6 has surprising stabilizer action when compared with the comparative mixtures. This clearly meets an objective of this invention, improvement of initial color. For assessment of processing properties, 10 the initial color of the test specimen is especially important for providing sufficient processing stability. Even small differences in the YI value here are relevant. The particular effect of a combination of compounds of the structure (I) with compounds of the 15 structure (II) is seen to be significant here. The compound of the formula (I), used alone, does not have a satisfactory effect on the initial color of the PVC, as shown by the comparative examples A 4 and A 5. Synergistic action is only released in combination with 20 a compound of formula (II), as shown in example A6. It can also be seen that the stabilization of the polymer via use of alkanolamines in combination with uracils can be still further raised via addition of perchlorates, as stated in inventive example A7.

25

Example 2

	A 4	A 5	B 1	B 2	B 3
PVC (Shin Etsu 6704)	100	100	100	100	100
Compound 1	---	---	---	---	---
Zeolite A	1.0	1.0	1.0	1.0	1.0
Calcium stearate	0.4	0.4	0.4	0.4	0.4
Marklube 367	0.6	0.6	0.6	0.6	0.6
Licowax PE 520	0.6	0.6	0.6	0.6	0.6
AC 629 A	0.1	0.1	0.1	0.1	0.1
N,N'-Dimethyl-N-cyanoacetylurea	---	---	0.1	0.2	0.1
TEA	0.1	0.2	---	---	0.1

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Test results					
Color measurement					
Yellowness Index extruded strip/ initial color	73	73	36	30	28

PVC Shin Etsu 6704, K value 67 (ex Shin Etsu)

Compound 1 = mixture composed of 9% NaClO_4 , 45% CaCO_3 ,
40% CaSiO_3 , 6% H_2O

5 Marklube 367 = paraffin wax (ex Crompton)

Licowax PE 520 = polyethylene wax (ex Clariant)

AC 629 A = oxidized polyethylene wax (ex Honeywell)

TEA = triethanolamine in the form of commercially
available product

10

From the table it can be seen that the inventive
composition B3 has improved stabilizer action when
compared with the comparative mixtures. This clearly
meets an objective of this invention, improvement of
15 initial color. For assessment of processing properties,
the range of initial color of the test specimen is
especially important. The particular effect of a
combination of compounds of the structure (I) with
compounds of the structure (III) is seen to be
20 significant here.

Example 3/1

The following formulations were roll-milled at 180°C
25 for 5 minutes on mixing rolls. The milled sheet formed
was used to produce a pressed sheet at 180°C in a
preheated multi-daylight sheet press. Pressed sheet
thickness: 1 mm, press time: 1 minute. Yellowness index
was determined to ASTM D1925-70. Low YI values mean
30 good stabilization and, respectively, initial color.
High percentages mean good transparency.

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	C 1	C 2	C 3	C 4	C 5	C 6	C 7
Evipol TM SH 5730	100	100	100	100	100	100	100
Paraloid TM BTA III/N2	5	5	5	5	5	5	5
Paraloid TM K 120N	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Paraloid TM K 175	0.5	0.5	0.5	0.5	0.5	0.5	0.5
E wax	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Loxiol TM G 16	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Epox. soybean oil	3.0	3.0	3.0	3.0	3.0	3.0	3.0
NaP/H ₂ O	0.6	0.6	0.6	0.6	0.6	0.6	0.6
TEA	0.2	0.4	---	---	0.2	0.2	0.2
1,3-Dioctyl-4-amino-uracil	---	---	0.1	0.3	0.1	0.2	0.2
Mark TM CH 300							0.5
Color measurement on 1 mm pressed sheets							
Yellowness Index YI	43.8	36.1	83.1	54.4	24.4	18.4	14.8
Transparency	90.5	91.1	78.0	89.9	92.3	93.1	92.9

EvipolTM SH 5730 PVC, K value 57 (ex EVC)

ParaloidTM K 175/K 120N = acrylate processing aid (ex Rohm & Haas)

5 ParaloidTM BTA III/N2 = methacrylate-butadiene-styrene modifier (ex Rohm & Haas)

E wax = ester wax/montan wax (ex Clariant)

LoxiolTM G 16 = fatty acid partial ester (ex Henkel)

10 NaP/H₂O = 30% strength sodium perchlorate solution in water

MarkTM CH 300 = mixed aryl/alkyl phosphite (ex Crompton)

TEA = triethanolamine in the form of commercially available product

15 From the table it can be seen that the inventive composition C 5 provides an improvement in stabilizer action when compared with the comparative mixtures. It can also be seen that stabilization of the polymer via use of alkanolamines in combination with uracils can be
20 still further raised via addition of phosphites, as

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stated in inventive example C 7.

Example 3/2

- 5 The formulations were roll-milled at 180°C for 5 minutes on mixing rolls. The milled sheet formed was used to produce a pressed sheet at 180°C in a preheated multi-daylight sheet press. Pressed sheet thickness: 1 mm, press time: 1 minute. Yellowness index was
 10 determined to ASTM D1925-70. Low YI values mean good stabilization and, respectively, initial color. High percentages mean good transparency.

	C 1	C 2	C 8	C 9	C 10	C 11	C 12
Evipol SH 5730 PVC	100	100	100	100	100	100	100
Paraloid BTA III/N2	5	5	5	5	5	5	5
Paraloid K 120N	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Paraloid K 175	0.5	0.5	0.5	0.5	0.5	0.5	0.5
E wax	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Loxiol G 16	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Epox. soybean oil	3.0	3.0	3.0	3.0	3.0	3.0	3.0
NaP/H ₂ O	0.6	0.6	0.6	0.6	0.6	0.6	0.6
TEA	0.2	0.4	---	---	0.2	0.2	0.2
1,3-Dimethyl-4-amino-uracil	---	---	0.1	0.3	0.1	0.2	0.2
Phosphite Mark CH 300							0.5
Color measurement on 1 mm pressed sheets							
Yellowness Index YI	43.8	36.1	55.7	24.1	16.3	14.2	11.6
Transparency	90.5	91.1	88.8	91.1	92.8	92.5	92.6

- 15 Evipol SH 5730 PVC, K value 57 (ex EVC)
 Paraloid K175/K 120N = acrylate processing aid (ex Rohm & Haas)
 Paraloid BTA III/N2 = methacrylate-butadiene-styrene modifier (ex Rohm & Haas)
 20 E wax = ester wax/montan wax (ex Clariant)

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Loxiol G 16 = fatty acid partial ester of glycerol (ex Henkel)

NaP/H₂O = 30% strength sodium perchlorate solution in water

5 Phosphite Mark CH 300 = mixed aryl/alkyl phosphite (ex Crompton)

TEA = triethanolamine in the form of commercially available product

10 From the table it can be seen that the inventive compositions C 10 and C 11 provide an improvement in stabilizer action when compared with the comparative mixtures. It can also be seen that stabilization of the polymer via use of alkanolamines in combination with
15 uracils can be still further raised via addition of phosphites, as stated in inventive example C 12.

Example 4

20 The following formulations were roll-milled at 180°C for 5 minutes on mixing rolls. The milled sheet formed was used to produce a pressed sheet at 180°C in a preheated multi-daylight sheet press. Pressed sheet thickness: 1 mm, press time: 1 minute. Yellowness index
25 was determined to ASTM D1925-70. Low YI values mean good stabilization and, respectively, initial color. High percentages mean good transparency. The Congo Red value was determined at 200°C to DIN 473/811/3/2. High
30 minute values mean good thermal stability of the test specimen. The time taken to reach conductivity of 200 μ S/cm was measured. The higher the value from this dehydrochlorination test (DHC), the better the stabilization.

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	D 1	D 2	D 3	D 4	D 5	D 6	D 7	D 8
PVC (Evipol SH 7020)	100	100	100	100	100	100	100	100
DEHP	20	20	20	20	20	20	20	20
Epox. soybean oil	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
NaP/BDG	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
AC 629 A	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
TEA	0.2	0.4	---	---	0.2	---	---	---
Diethanolsoyamine	---	---	---	---	---	0.2	0.4	0.2
1,3-Dibutyl-4-aminouracil	---	---	0.2	0.3	0.1	---	---	0.1
Color measurement on 1 mm pressed sheets								
Yellowness Index YI	17.4	14.7	15.8	12.2	9.7	15.7	13.9	9.1
Transparency	96.7	95.9	97.3	97.4	97.3	97.6	97.6	98.1
Congo Red	17	28	10	10	21	10	22	17
DHC [200□S/cm]	117	152	88	93	128	89	129	115

Evipol 7020 PVC, K value 70 (ex EVC)

DEHP = di-2-ethylhexyl phthalate in the form of commercially available product

5 NaP/BDG = 30% strength sodium perchlorate solution in butyl diglycol

TEA = triethanolamine in the form of commercially available product

10 Diethanolsoyamine = bis(2-hydroxyethyl)soyamine in the form of commercially available product

1,3-Dibutyl-4-aminouracil

AC 629 A = oxidized polyethylene wax (ex Honeywell)

15 From the table it can be seen that the inventive compositions D5 and D8 have improved stabilizer action when compared with the comparative mixtures.

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Example 5

The formulations were roll-milled at 180°C for 5 minutes on mixing rolls. The milled sheet formed was used to produce a pressed sheet at 180°C in a preheated multi-daylight sheet press. Pressed sheet thickness: 1 mm, press time: 1 minute. Yellowness index was determined to ASTM D1925-70. Low YI values mean good stabilization and, respectively, initial color. High percentages mean good transparency.

	E 1	E 2	E 3	E 4	E 5	E 6	E 7	E 8	E 9	E 10	E 11
Evipol SH 7020 PVC	100	100	100	100	100	100	100	100	100	100	100
DEHP	47	47	47	47	47	47	47	47	47	47	47
Epox. soybean oil	3	3	3	3	3	3	3	3	3	3	3
Loxiol G 71 S	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Calcium stearate	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
NaP/BDG	---	---	---	---	---	---	---	---	0.5	0.5	0.5
1,3-Dioctyl- 4-amino- uracil	---		0.2	0.2		0.2		0.2	0.2	0.2	0.2
TEA	---	0.2		0.2					0.2		
Diethanol- soyamine					0.2	0.2				0.2	
TIPA							0.2	0.2			0.2
Color measurement on 1 mm pressed sheets											
Yellowness Index YI	66.3	56.1	24.3	13.9	87.2	18.2	72.5	17.0	10.2	9.6	9.6
b value	21.9	23.4	14.2	10.7	23.9	10.7	30.4	10.1	5.7	5.6	5.8
Transparency	74.7	85.2	97.5	97.8	66.4	97.8	84.6	97.9	96.5	96.8	97.6

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- Evipol SH 7020 PVC, K value 70 (ex EVC)
- DEHP = di-2-ethylhexyl phthalate in the form of commercially available product
- NaP/BDG = 30% strength sodium perchlorate solution in
- 5 butyl diglycol
- Loxiol G 71 S = multicomponent ester lubricant (ex Henkel)
- TEA = triethanolamine in the form of commercially available product
- 10 Diethanolsoyamine = ES-2 in the form of commercially available product
- TIPA = triisopropanolamine in the form of commercially available product
- 15 From the table it can be seen that the inventive compositions E4, E6, and E8 provide an improvement in stabilizer action when compared with the comparative mixtures. It can also be seen that stabilization of the polymer can be still further raised via addition of
- 20 perchlorate, as stated in inventive examples E9, E10, and E11.

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CLAIMS:

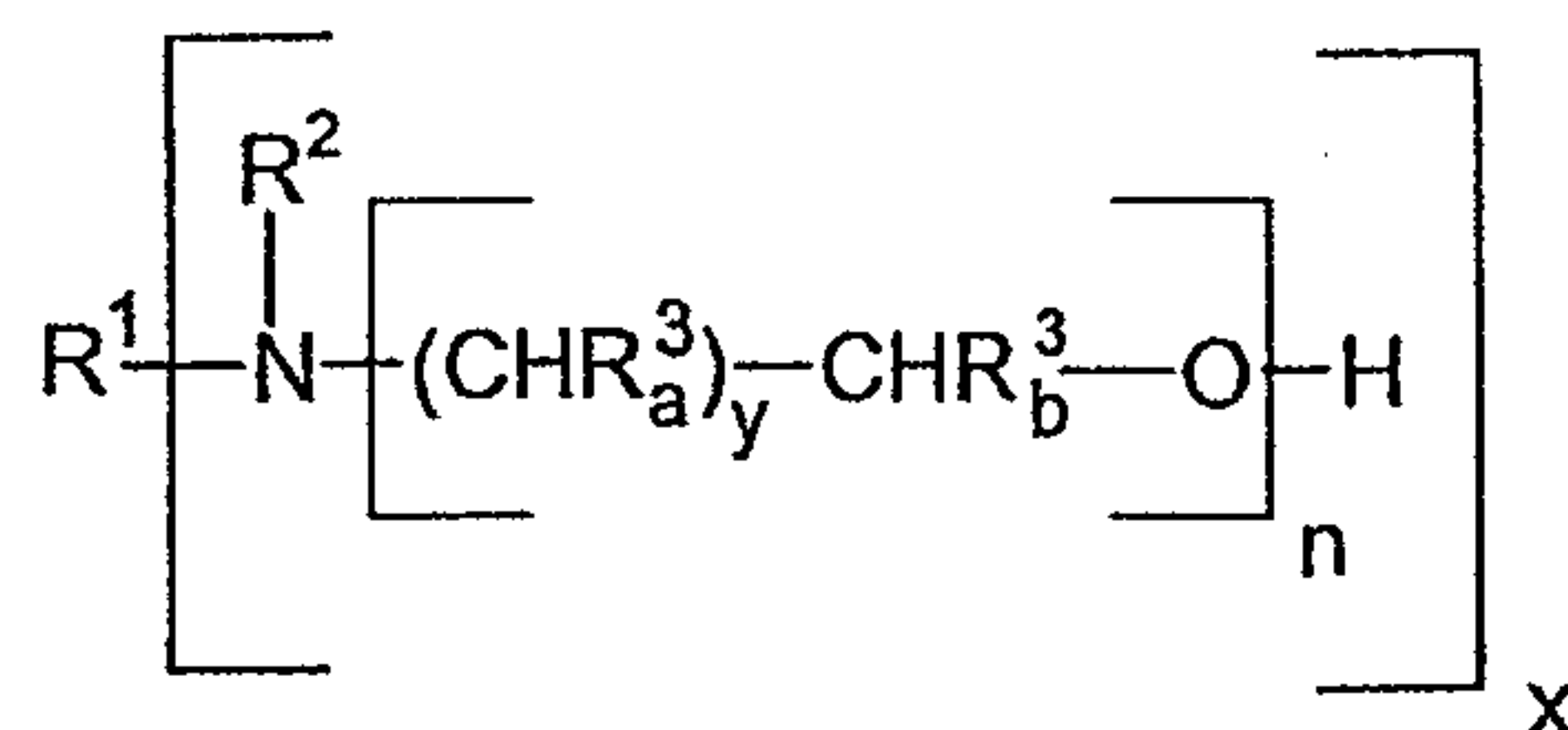
1. A stabilizer mixture for stabilizing chlorine-containing polymers, comprising at least

5

- a) one alkanolamine of the formula (I)
b) one uracil of the formula (II)

where, for the alkanolamine of the formula (I)

10



$x = 1, 2 \text{ or } 3;$

$y = 1, 2, 3, 4, 5 \text{ or } 6;$

15

$n = \text{from } 1 \text{ to } 10;$

R^1 and $\text{R}^2 =$ independently of one another H, $\text{C}_1\text{-C}_{22}$ -alkyl, $[-(\text{CHR}_a^3)_y - \text{CHR}_b^3 - \text{O}-]_n\text{-H}$, $[-(\text{CHR}_a^3)_y - \text{CHR}_b^3 - \text{O}-]_n\text{-CO-R}^4$, $\text{C}_2\text{-C}_{20}$ -alkenyl, $\text{C}_2\text{-C}_{18}$ -acyl, $\text{C}_4\text{-C}_8$ -cyclo-

20

alkyl, where this may have OH substitution in the β -position, $\text{C}_6\text{-C}_{10}$ -aryl, $\text{C}_7\text{-C}_{10}$ -alkaryl or $\text{C}_7\text{-C}_{10}$ -aralkyl, or, if $x = 1$, R^1 and R^2 may also, together with the N, form a closed ring having from 4 to 10 members, composed of carbon atoms and, where appropriate, of up to 2 heteroatoms, or if $x = 2$,

25

R^1 may also be $\text{C}_2\text{-C}_{18}$ -alkylene which, at both β -carbon atoms, may have OH substitution and/or have interruption by one or more O atoms and/or by one or more NR^2 groups, or be dihydroxy-substituted tetrahydrodicyclopentadienylene,

30

dihydroxy-substituted ethylcyclohexanylene, dihydroxy-substituted 4,4'-(bisphenol A dipropyl ether)ylene, isophoronylene, dimethylcyclohexanylene, dicyclohexylmethanylene or 3,3'-dimethyldicyclohexylmethanylene, and if $x = 3$, R^1

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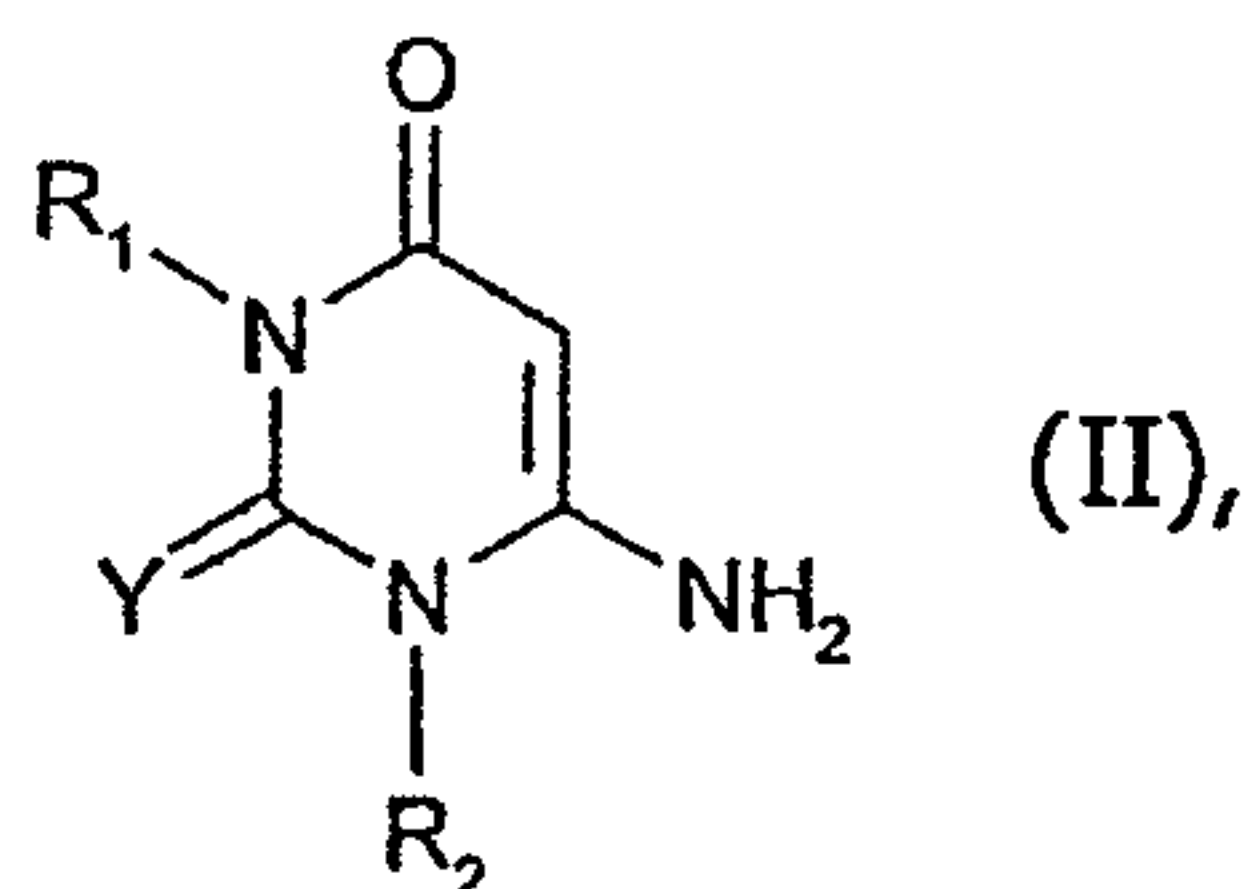
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may also be trihydroxy-substituted (tri-N-propyl isocyanurate)triyl;

R^3_a and R^3_b = independently of one another C_1 - C_{22} -alkyl, C_2 - C_6 -alkenyl, C_6 - C_{10} -aryl, H or CH_2 -X- R^5 ,
 5 where X = O, S, -O-CO- or -CO-O-;

R^4 = C_1 - C_{18} -alkyl/alkenyl or phenyl; and

R^5 = H, C_1 - C_{22} -alkyl, C_2 - C_{22} -alkenyl or C_6 - C_{10} -aryl;
 and for the uracil of the formula (II)



10

R_1 and R_2 , independently of one another, are C_1 - C_{24} -alkyl, which may have interruption by $-CO_2$ - and/or by 1 or more oxygen atoms, and/or may have
 15 substitution by one or more OH groups, or are C_3 - C_{24} -alkenyl, branched or unbranched, or are C_5 - C_8 -cycloalkyl, unsubstituted or substituted with from 1 to 3 C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy, or
 20 C_5 - C_8 -cycloalkyl groups, or with hydroxy groups, or with Cl atoms, or are C_7 - C_9 -phenylalkyl, unsubstituted or substituted on the phenyl ring with from 1 to 3 C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy, or
 25 C_5 - C_8 -cycloalkyl groups, or with hydroxy groups, or with Cl atoms, and R_1 or R_2 may also be hydrogen, and Y is S or O.

2. A stabilizer mixture for stabilizing chlorine-containing polymers, comprising at least

30 a) one reaction product of a mono- or polyfunctional epoxide and of ammonia or of a mono- or polyfunctional dialkyl(aryl)- or monoalkyl(aryl)amine of the formula (I) as claimed in claim 1 and

35 b) one uracil of the formula (II) as claimed in claim 1.

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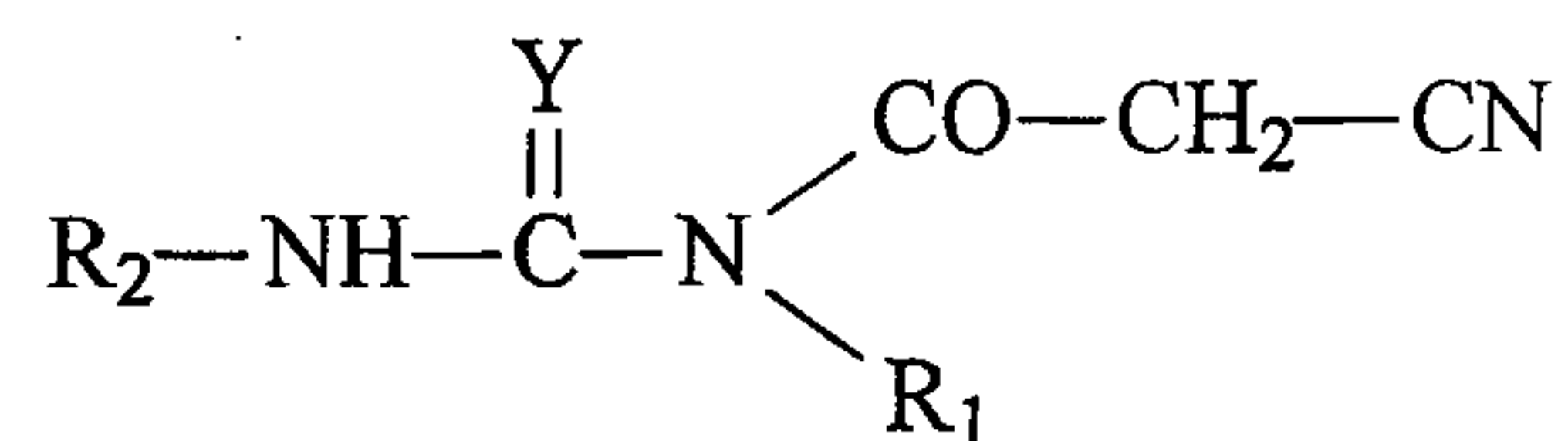
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3. A stabilizer mixture for stabilizing chlorine-containing polymers, comprising at least

a) one alkanolamine of the formula (I) as claimed in claim 1

b) one cyanoacetylurea of the formula (III)

5 formula (III)



where

Y is oxygen or sulfur, and

10 R₂ is C₁-C₂₄-alkyl, which may have interruption by —CO₂— and/or by oxygen atoms, and/or may have substitution by from 1 to 3 OH groups, or is C₃-C₂₄-alkenyl, C₇-C₁₀-phenylalkyl, C₅-C₈-cycloalkyl, C₇-C₁₀-alkylphenyl, phenyl or naphthyl, where in each case the aromatic radical may have substitution by —OH, C₁-C₁₂-alkyl and/or OC₁-C₄-alkyl, and R₁ is as defined for R₂, or R₁ is hydrogen.

15 4. A stabilizer mixture for stabilizing chlorine-containing polymers, comprising at least

a) one reaction product of a mono- or polyfunctional epoxide and of ammonia or of a mono- or polyfunctional dialkyl(aryl)- or monoalkyl(aryl)amine of the formula (I) as defined in claim 1, and

20 b) a cyanoacetylurea of the formula (III) as claimed in claim 3.

5. The stabilizer mixture as claimed in claim 2 and 4, where the polyfunctional epoxide is dicyclopentadiene diepoxide, vinylcyclohexene diepoxide, bisphenol A diglycidyl ether, or tris-glycidyl isocyanurate, and the dialkylamine is diethanolamine or diisopropanolamine, and the monoalkylamine is
25 monoethanolamine or monoisopropanolamine.

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6. The stabilizer mixture as claimed in any one of claims 1 to 5, where, in the compound with the general formula (I),

R_a^3 and R_b^3 , independently of one another, are H or CH_3 and $y = 1$.

7. The stabilizer mixture as claimed in any one of claims 1 to 6, where,
5 in the compound with the general formula (I),

$R^1 = R^2 = CH_2-CHR_b^3-OH$.

8. The stabilizer mixture as claimed in any one of claims 1 to 7, where the compounds of the general formula (I) are tris(2-hydroxy-1-propyl)amine, tris(2-hydroxyethyl)amine, bis(2-hydroxyethyl)-2-hydroxy-1-propyl)amine, or
10 alkyl/alkenyl-bis-(2-hydroxyethyl)amine, alkyl/alkenyl(2-hydroxy-1-propyl)amine, N-(2-hydroxyhexadecyl)diethanol-amine, N-(2-hydroxy-3-octyloxypropyl)diethanol-amine, N-(2-hydroxy-3-decyloxypropyl)diethanol-amine, or a mixture thereof.

9. The stabilizer mixture for stabilizing chlorine-containing polymers, as claimed in any one of claims 1 to 8, also comprising at least one perchlorate salt.

15 10. The stabilizer mixture as claimed in claim 9, where the perchlorate salt is a compound of the formula $M(ClO_4)_n$, where M is Li, Na, K, Mg, Ca, Sr, Ba, Zn, Al, La, Ce, or a hydrotalcite layer-lattice cation, or an organic onium cation; n is 1, 2 or 3, as appropriate for the valency of M, or if a hydrotalcite layer-lattice cation is present $0 < n \leq 1$.

20 11. The stabilizer mixture as claimed in claim 10, wherein $M = Na$ or K , and $n = 1$.

12. The stabilizer mixture as claimed in any one of claims 9 to 11, which further comprises possible reaction products of a phosphite with the perchlorate salt.

25 13. The stabilizer mixture as claimed in any one of claims 1 to 12, where a phosphite is also present, and/or possible reaction products of phosphite with the component of formula (I).

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14. The stabilizer mixture as claimed in claim 12 or 13, where the phosphite is distearyl pentaerythrityl diphosphite, triphenyl phosphite, trisnonylphenyl phosphite, phenyl didecyl phosphite, poly(dipropylene glycol) phenyl phosphite, tetraphenyl dipropylene glycol diphosphite, tetraisodecyl dipropylene glycol diphosphite, trisdipropylene glycol phosphite, decyl diphenyl phosphite, trioctyl phosphite, trilauryl phosphite or nonylphenyl_{1.5} C₁₂/C₁₃-alkyl_{1.5} phosphite.
15. The stabilizer mixture as claimed in any one of claims 1 to 14, also comprising an anhydrous hydrotalcite or a zeolite.
- 10 16. The stabilizer mixture as claimed in any one of claims 1 to 15, which also, if appropriate, comprises metal soaps, and/or, if appropriate, comprises another substance from the group of the polyols and disaccharide alcohols, salts of the hydroxycarboxylic acids, glycidyl compounds, hydrotalcites, aluminosilicates of alkali metals or of alkaline earth metals, hydroxides/oxides of alkali metals or of
15 alkaline earth metals, or the corresponding (hydrogen)carbonates or carboxylates, and fillers/pigments, plasticizers, antioxidants, light stabilizers, optical brighteners, lubricants and epoxidized fatty acid esters.
17. A composition comprising a chlorine-containing polymer and the stabilizer mixture as claimed in any one of claims 1 to 16.
- 20 18. A composition comprising a chlorine-containing polymer and the stabilizer mixture as claimed in claim 1, which comprises, based on 100 parts by weight of chlorine-containing polymer, from 0.01 to 10 parts by weight of the compound of the general formula (I) and from 0.01 to 10 parts by weight of the compound of the general formula (II).
- 25 19. A composition comprising a chlorine-containing polymer and the stabilizer mixture as claimed in claim 2, which comprises, based on 100 parts by weight of chlorine-containing polymer, from 0.01 to 10 parts by weight of the compound of the general formula (I) and from 0.01 to 10 parts by weight of the compound of the general formula (II).

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20. The composition as claimed in claim 19, where the polyfunctional epoxide is dicyclopentadiene diepoxide, vinylcyclohexene diepoxide, bisphenol A diglycidyl ether, or tris-glycidyl isocyanurate, and the dialkylamine is diethanolamine or diisopropanolamine, and the monoalkylamine is
5 monoethanolamine or monoisopropanolamine.

21. The composition as claimed in any one of claims 18 to 20, where, in the compound with the general formula (I),

R^3_a and R^3_b , independently of one another, are H or CH_3 and $y = 1$.

22. The composition as claimed in any one of claims 18 to 21, where, in
10 the compound with the general formula (I),

$R^1 = R^2 = CH_2-CH(R^3_b)-OH$.

23. The composition as claimed in any one of claims 18 to 22, where the compounds of the general formula (I) are tris(2-hydroxy-1-propyl)amine, tris(2-hydroxyethyl)amine, bis(2-hydroxyethyl)-2-hydroxy-1-propylamine, or
15 alkyl/alkenyl-bis-(2-hydroxyethyl)amine, alkyl/alkenyl(2-hydroxy-1-propyl)amine, N-(2-hydroxyhexadecyl)diethanol-amine, N-(2-hydroxy-3-octyloxypropyl)diethanol-amine, N-(2-hydroxy-3-decyloxypropyl)diethanol-amine, or a mixture thereof.

24. The composition for stabilizing chlorine-containing polymers, as claimed in any one of claims 18 to 23, also comprising at least one perchlorate
20 salt.

25. The composition as claimed in claim 24, where the perchlorate salt is a compound of the formula $M(ClO_4)_n$, where M is Li, Na, K, Mg, Ca, Sr, Ba, Zn, Al, La, Ce, or a hydrotalcite layer-lattice cation, or an organic onium cation; n is 1, 2 or 3, as appropriate for the valency of M, or if a hydrotalcite layer-lattice cation is
25 present $0 < n \leq 1$.

26. The composition as claimed in claim 25, wherein $M = Na$ or K , and $n = 1$.

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27. The composition as claimed in any one of claims 24 to 26, which further comprises possible reaction products of a phosphite with the perchlorate salt.

28. The composition as claimed in any one of claims 18 to 27, where a phosphite is also present, and/or possible reaction products of phosphite with the component of formula (I).

29. The composition as claimed in claim 27 or 28, where the phosphite is distearyl pentaerythrityl diphosphite, triphenyl phosphite, trisnonylphenyl phosphite, phenyl didecyl phosphite, poly(dipropylene glycol) phenyl phosphite, tetraphenyl dipropylene glycol diphosphite, tetraisodecyl dipropylene glycol diphosphite, trisdipropylene glycol phosphite, decyl diphenyl phosphite, trioctyl phosphite, trilauryl phosphite or nonylphenyl_{1.5} C₁₂/C₁₃-alkyl_{1.5} phosphite.

30. The composition as claimed in any one of claims 18 to 29, also comprising an anhydrous hydrotalcite or a zeolite.

31. The composition as claimed in any one of claims 18 to 30, which also, if appropriate, comprises metal soaps, and/or, if appropriate, comprises another substance from the group of the polyols and disaccharide alcohols, salts of the hydroxycarboxylic acids, glycidyl compounds, hydrotalcites, aluminosilicates of alkali metals or of alkaline earth metals, hydroxides/oxides of alkali metals or of alkaline earth metals, or the corresponding (hydrogen)carbonates or carboxylates, and fillers/pigments, plasticizers, antioxidants, light stabilizers, optical brighteners, lubricants and epoxidized fatty acid esters.

32. A composition comprising a chlorine-containing polymer and the stabilizer mixture as claimed in claim 3, which comprises, based on 100 parts by weight of chlorine-containing polymer, from 0.01 to 10 parts by weight of the compound of the general formula (I) and from 0.01 to 10 parts by weight of the compound of the general formula (III).

33. A composition comprising a chlorine-containing polymer and the stabilizer mixture as claimed in claim 4, which comprises, based on 100 parts by weight of chlorine-containing polymer, from 0.01 to 10 parts by weight of the

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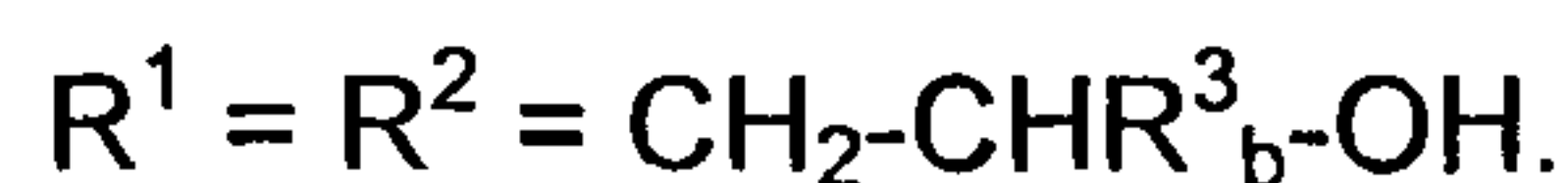
compound of the general formula (I) and from 0.01 to 10 parts by weight of the compound of the general formula (III).

34. The composition as claimed in claim 33, where the polyfunctional epoxide is dicyclopentadiene diepoxide, vinylcyclohexene diepoxide, bisphenol A diglycidyl ether, or tris-glycidyl isocyanurate, and the dialkylamine is diethanolamine or diisopropanolamine, and the monoalkylamine is monoethanolamine or monoisopropanolamine.

35. The composition as claimed in any one of claims 32 to 34, where, in the compound with the general formula (I),

10 R^3_a and R^3_b , independently of one another, are H or CH_3 and $y = 1$.

36. The composition as claimed in any one of claims 32 to 35, where, in the compound with the general formula (I),



37. The composition as claimed in any one of claims 32 to 36, where the compounds of the general formula (I) are tris(2-hydroxy-1-propyl)amine, tris(2-hydroxyethyl)amine, bis(2-hydroxyethyl)-2-hydroxy-1-propylamine, or alkyl/alkenyl-bis-(2-hydroxyethyl)amine, alkyl/alkenyl(2-hydroxy-1-propyl)amine, N-(2-hydroxyhexadecyl)diethanol-amine, N-(2-hydroxy-3-octyloxypropyl)diethanol-amine, N-(2-hydroxy-3-decyloxypropyl)diethanol-amine, or a mixture thereof.

20 38. The composition for stabilizing chlorine-containing polymers, as claimed in any one of claims 32 to 37, also comprising at least one perchlorate salt.

39. The composition as claimed in claim 38, where the perchlorate salt is a compound of the formula $M(ClO_4)_n$, where M is Li, Na, K, Mg, Ca, Sr, Ba, Zn, Al, La, Ce, or a hydrotalcite layer-lattice cation, or an organic onium cation; n is 1, 2 or 3, as appropriate for the valency of M, or if a hydrotalcite layer-lattice cation is present $0 < n \leq 1$.

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40. The composition as claimed in claim 39, wherein $M = \text{Na}$ or K , and $n = 1$.

41. The composition as claimed in any one of claims 38 to 40, which further comprises possible reaction products of a phosphite with the perchlorate
5 salt.

42. The composition as claimed in any one of claims 32 to 41, where a phosphite is also present, and/or possible reaction products of phosphite with the component of formula (I).

43. The composition as claimed in claim 41 or 42, where the phosphite
10 is distearyl pentaerythrityl diphosphite, triphenyl phosphite, trisnonylphenyl phosphite, phenyl didecyl phosphite, poly(dipropylene glycol) phenyl phosphite, tetraphenyl dipropylene glycol diphosphite, tetraisodecyl dipropylene glycol diphosphite, trisdipropylene glycol phosphite, decyl diphenyl phosphite, trioctyl phosphite, trilauryl phosphite or nonylphenyl_{1.5} C₁₂/C₁₃-alkyl_{1.5} phosphite.

15 44. The composition as claimed in any one of claims 32 to 43, also comprising an anhydrous hydrotalcite or a zeolite.

45. The composition as claimed in any one of claims 32 to 44, which also, if appropriate, comprises metal soaps, and/or, if appropriate, comprises another substance from the group of the polyols and disaccharide alcohols, salts
20 of the hydroxycarboxylic acids, glycidyl compounds, hydrotalcites, aluminosilicates of alkali metals or of alkaline earth metals, hydroxides/oxides of alkali metals or of alkaline earth metals, or the corresponding (hydrogen)carbonates or carboxylates, and fillers/pigments, plasticizers, antioxidants, light stabilizers, optical brighteners, lubricants and epoxidized fatty acid esters.

25 46. The composition as claimed in claim 18, 19, 32 or 33, which also comprises, based on 100 parts by weight of chlorine-containing polymer, from 0.001 to 5 parts by weight of a perchlorate salt.

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47. The composition as claimed in claim 18, 19, 32, 33 or 46, which also comprises, based on 100 parts by weight of chlorine-containing polymer, from 0.05 to 5 parts by weight of a phosphite.

48. A process for stabilizing chlorine-containing polymers via addition of
5 the stabilizer mixture as claimed in any one of claims 1 to 16 to a chlorine-containing polymer.

49. The process for stabilizing chlorine-containing polymers as claimed in claim 48, wherein the chlorine-containing polymer is plasticized PVC.

50. The process for stabilizing chlorine-containing polymers as claimed
10 in claim 48, wherein the plasticized PVC serves for production of floorcoverings, motor vehicle components, plasticized foils, hoses, injection moldings, or wire sheathing.

51. The process for stabilizing chlorine-containing polymers as claimed in claim 48, wherein the chlorine-containing polymer is unplasticized PVC.

15 52. The process for stabilizing chlorine-containing polymers as claimed in claim 48, wherein the chlorine-containing polymer serves for production of foils, or of PVC pipes, or of profiles.

53. A consumer item, comprising PVC, which has been stabilized via the stabilizer mixture as claimed in any one of claims 1 to 16.