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Stabiliser system for the stabilisation of halogenated polymers

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- Erklärungen gemäß Regel 4.17:**
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 - Erfindererklärung (Regel 4.17 Ziffer iv) nur für US
- Veröffentlicht:**
- mit internationalem Recherchenbericht
- Zur Erklärung der Zweibuchstaben-Codes und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

unterbrochen sein kann, oder für dihydroxy-substituiertes Tetrahydro-dicyclopentadienyl, dihydroxy-substituiertes Ethyl-cyclohexan-yl, dihydroxy-substituiertes 4,4'-(Bisphenol-A-dipropylether)yl, Isophoron-yl, Dimethylcyclohexan-yl, Dicyclohexylmethan-yl oder 3,3'-Dimethyldicyclohexyl-methan-yl stehen, und wenn $x = 3$, kann R^1 zusätzlich für trihydroxy-substituiertes (Tri-N-propylisocyanurat)triyl stehen; R^2, R^3 , = unabhängig voneinander C_1 - C_{22} -Alkyl-, C_2 - C_6 -Alkenyl-, C_6 - C_{10} -Aryl-, II oder CII_2 - $X-R^5$, wobei $X = O, S, -O-CO-$ oder $-CO-O-$; $R^4 = C_1$ - C_{18} -Alkyl/Alkenyl oder Phenyl; und $R^5 = II, C_1$ - C_{22} -Alkyl-, C_2 - C_{22} -Alkenyl oder C_6 - C_{10} -Aryl.

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Stabiliser system for the stabilisation of halogenated
polymers

The invention relates to stabilizer mixtures encompassing at least a sulphate ester salt and/or sulphonate salt and an
5 alkanolamine which are suitable for stabilizing halogen-containing polymers.

For example, PVC as halogen-containing polymer may be stabilized by a large number of additives. Compounds of lead, of barium, and of cadmium are particularly well suited
10 to this purpose, but are nowadays controversial for environmental reasons or because of their heavy metal content (cf. "Plastics Additives Handbook" H. Zweifel, Carl Hanser Verlag, 5th Edition 2001, pp. 427-483, and "Kunststoff Handbuch PVC" [Plastics Handbook PVC], Volume
15 2/1, W. Becker and D. Braun, Carl Hanser Verlag, 2nd Edition, 1985, pp. 531-538; and Kirk-Othmer: "Encyclopedia of Chemical Technology", 4th Edition, 1994, Vol. 12, Heat Stabilizers, pp. 1071-1091) .

There is therefore a continuing search for effective
20 stabilizers and stabilizer mixtures which are free from lead, barium and cadmium.

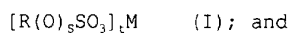
It has now been found that mixtures made from at least one alkanolamine of the general formula (II), and from at least one sulphate ester salt and/or sulphonate salt of the
25 formula (I), in particular alkali metal or alkaline earth metal salt, are particularly highly suitable for stabilizing chlorine-containing polymers, in particular PVC.

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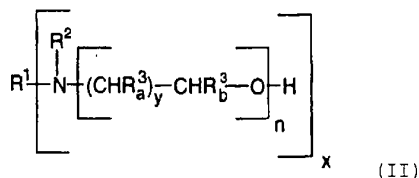
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In a first aspect, the present invention provides a stabilizing mixture for stabilizing chlorine-containing polymers against thermal-induced degradation, comprising

- a) at least one sulphate ester salt and/or sulphonate salt of the formula (I)



- b) at least one alkanolamine of the formula (II)



wherein M is an alkali metal cation, alkaline earth metal cation, lanthanoid (cerium) cation or aluminium cation, t is the valency of the metal cation; s = 0 or 1 and R is C₁-C₂₂ alkyl, phenyl, C₇-C₁₀ phenylalkyl, or C₇-C₂₄ alkylphenyl and

x = 1, 2 or 3,

y = 1, 2, 3, 4, 5 or 6,

n = 1 - 10

R¹ and R² are independently H, C₁-C₂₂ alkyl, $[-(CHR_a^3)_y-CHR_b^3-O-]_n-H$, $[-(CHR_a^3)_y-CHR_b^3-O-]_n-CO-R^4$, C₂-C₂₀ alkenyl, C₂-C₁₈ acyl, C₄-C₈ cycloalkyl, which may be OH-substituted in the β position, C₆-C₁₀ aryl, C₇-C₁₀ alkaryl or C₇-C₁₀ aralkyl, or when x = 1, R¹ and R² together with the N atom to which they are bonded are joined together to form a closed 4-10 membered heterocyclic ring of carbon atoms optionally containing up

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to 2 heteroatoms, or when $x = 2$, R^1 may be a C_2-C_{18} alkyene which may be OH-substituted at both β -carbon atoms and/or may be interrupted by one or more O-atoms and/or one or more NR^2 groups, or a dihydroxy-substituted

- 5 tetrahydrodicyclopentadienylene, dihydroxy-substituted ethylcyclohexanylene, dihydroxysubstituted 4,4'-(bisphenol A dipropyl ether)ylene, isophoronylene, dimethylcyclohexanylene, dicyclohexylmethanylene, or 3,3'-
10 trihydroxysubstituted (tri-N-propyl isocyanurate) triyl;

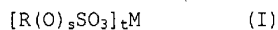
R^3_a and R^3_b independently are a C_1-C_{22} alkyl, C_2-C_6 alkenyl, C_6-C_{10} aryl, H or CH_2-X-R^5 , where X = O, S, -O-CO- or -CO-O-;

R^4 is a C_1-C_{18} alkyl/alkenyl or phenyl, and

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

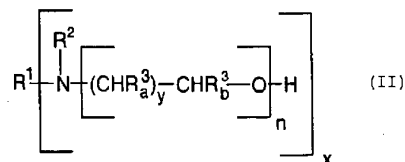
Disclosed herein are stabilizer mixtures comprising at least

- a) one sulphate ester salt and/or sulphonate salt of the formula (I)



b) and one alkanolamine of the formula (II)

5



where: M = alkali metal cation, alkaline earth metal cation, lanthanoid (cerium) cation or aluminium cation, t = valency of the metal cation, namely 1, 2 or 3;

10 s = 0 or 1 and R = C₁-C₂₂-alkyl, phenyl, C₇-C₁₀-phenylalkyl, C₇-C₂₄-alkylphenyl

and

x = 1, 2 or 3,

y = 1, 2, 3, 4, 5 or 6,

15 n = 1 - 10

R¹, R² = independently H, C₁-C₂₂-alkyl, $[-(\text{CHR}^3_a)_y - \text{CHR}^3_b - \text{O}]_n - \text{H}$, $[-(\text{CHR}^3_a)_y - \text{CHR}^3_b - \text{O}]_n - \text{CO} - \text{R}^4$, C₂-C₂₀-alkenyl, C₂-C₁₈-acyl, C₄-C₈-cycloalkyl, which may be OH-substituted in the β position, C₆-C₁₀-aryl, C₇-C₁₀-

20 alkaryl or C₇-C₁₀-aralkyl, or when x = 1, R¹ and R² may additionally combine with the N to form a closed 4-10-membered ring of carbon atoms and optionally up to 2 heteroatoms, or when x = 2, R¹ may additionally

be C₂-C₁₈-alkylene which may be OH-substituted at both β-carbon atoms and/or may be interrupted by one or more O-atoms and/or one or more NR² groups, or

25 dihydroxy-substituted tetrahydrodicyclopentadienylene, dihydroxy-substituted ethylcyclohexanylene, dihydroxy-substituted 4,4'-(bisphenol A dipropyl ether)ylene, isophoronylene, dimethylcyclohexanylene, dicyclohexylmethanylene, or

30 3,3'-dimethyldicyclohexylmethanylene, and if x = 3, R¹ may also be trihydroxy-substituted (tri-N-propyl

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isocyanurate)triyl;

R^3_a, 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-;

5 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.

Also disclosed herein are stabilizer mixtures comprising at least

- 10 a) one sulphate ester salt and/or sulphonate salt of the formula (I)
- b) one reaction product made from a mono- or polyfunctional epoxide and from ammonia or from a mono- or polyfunctional dialkyl(aryl)- or monoalkyl (aryl) amine.

15 In a second aspect, the present invention provides a composition comprising a chlorine-containing polymer and a stabilizer mixture according to the first aspect.

In a third aspect, the present invention provides a process for stabilizing chlorine-containing polymers against
20 thermal-induced degradation by adding the stabilizer mixture according to the first aspect to a chlorine-containing polymer.

In a fourth aspect, the present invention provides a consumer article comprising a polyvinyl chloride stabilized
25 against thermal-induced degradation by the stabilizer mixture according to the first aspect.

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Examples of the alkanolamines of the general formula (II) are compounds where R^1 and R^2 = methyl, ethyl, propyl, butyl, cyclohexyl, octyl, lauryl, tetradecyl, hexadecyl, stearyl, oleyl, allyl, phenyl or benzyl, hydroxyalkyl and R^3 = H, methyl, ethyl, propyl or butyl. Preference is given to alkanolamines where R^1 = lauryl, tetradecyl, hexadecyl, stearyl, oleyl, where R^2 = hydroxyalkyl. It is also possible to use ethoxylates and propoxylates of triethanol- and triisopropanolamine, or else to use fatty amines of plant or animal origin. Preference is given to trialkanolamines and mono-alkyl/alkenyl-dialkanolamines where R^3 = H or methyl and $y = 1$, in particular fatty amines that have been reacted twice with ethylene or with propylene oxide. Other compounds which are very highly suitable may be taken from the following list.

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;

Nonyl- or dinonylamine reacted once or twice with ethylene oxide or with propylene oxide;

- 5 Isononyl- or diisononylamine reacted once or twice with ethylene oxide or with propylene oxide;

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

10

Isodecyl- or diisodecylamine reacted once or twice with ethylene oxide or with propylene oxide;

- 15 Undecyl- or diundecylamine reacted once or twice with ethylene oxide or with propylene oxide;

Isoundecyl- or diisoundecylamine reacted once or twice with ethylene oxide or with propylene oxide;

- 20 Dodecyl- or didodecylamine reacted once or twice with ethylene oxide or with propylene oxide;

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

25

Tridecyl- or ditridecylamine reacted once or twice with ethylene oxide or with propylene oxide;

- 30 Isotridecyl- or diisotridecylamine reacted once or twice with ethylene oxide or with propylene oxide;

Tetradecyl- or ditetradecylamine reacted once or twice with ethylene oxide or with propylene oxide;

- 35 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;

Eicosyl- or dieicosylamine reacted once or twice with ethylene oxide or with propylene oxide;

5

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

10 Octadecenyl- or dioctadecenylamine reacted once or twice with ethylene oxide or with propylene oxide;

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

15 Cyclohexyl- or dicyclohexylamine reacted once or twice with ethylene oxide or with propylene oxide;

N-methylcyclohexylamine reacted with ethylene oxide or with propylene oxide;

20

N-ethylcyclohexylamine reacted with ethylene oxide or with propylene oxide;

25 4-Vinyl-1-cyclohexene diepoxide reacted twice with diethanol- or diisopropanolamine;

Dicyclopentadiene diepoxide reacted twice with diethanol- or diisopropanolamine;

30 Bisphenol A diglycidyl ether reacted twice with diethanol- or diisopropanolamine;

Trisglycidyl isocyanurate reacted three times with diethanol- or diisopropanolamine.

35

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

It has been determined that compounds of the general formula (I) where $y = 1-6$, i.e. having up to 6 methylene groups between the amino group and the hydroxyl-substituted carbon atom, are useful as PVC stabilizer in combination with a sulphate ester salt and/or sulphonate salt.

According to the invention it is also possible to use compounds of the general formula (II) where $x = 3$, i.e. those which have three hydroxyalkylamino groups per molecule. An example here is the product of a reaction of trisglycidyl isocyanurate with mono- or diethanolamine or mono- or dipropanolamine.

The alkanolamines of the general formula (II) are commercially available chemicals or may be prepared by known methods, by N-alkylating a corresponding amine or ammonia (cf. Alkanolamines in Kirk-Othmer Encyclopedia of Chemical Technology, 4th Edition, J. Wiley & Sons N.Y., 1992, Vol. 2, pages 1-34).

Examples of the preferred alkanolamines of the general formula (II) 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, N-(3-n-butyl-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, N,N-bis(2-hydroxyethyl)-N-soyaamine, N,N-bis(2-hydroxyethyl)-N-stearylamine, N-(2-hydroxyethyl)-morpholine or N-(2,3-dihydroxy-1-propyl)morpholine, bishydroxyethylpiperazine or bishydroxyisopropylpiperazine and products of the reaction of glycidyl ethers with mono- or dialkylamine or ammonia, and also the alkanolamines derived from these, such as ethanol-

amine, diethanolamine, n-propanolamine, isopropanol-
amine, n-dipropanolamine or isodipropanolamine.

Very particular preference is given to addition
5 products 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
diisopropanolamine. These compounds having a β -
10 positioned OH function at both ends of a relatively
long alkyl chain, e.g. N-(2-hydroxyhexadecyl)diethanol-
amine, N-(2-hydroxy-3-octyloxypropyl)diethanolamine, N-
(2-hydroxy-3-decyloxypropyl)diethanolamine, N-
15 (2-hydroxy-3-octyloxypropyl)diethanolamine and bis-N-
(2-hydroxy-3-phenyloxypropyl)ethanolamine are
particularly suitable as a component in the stabilizer
systems of the invention.

The list merely gives examples and is not intended to
20 be comprehensive.

The sulphate ester salts and/or sulphonate salts are
known to the person skilled in the art (cf. Sulfonation
and Sulfation, Sulfonic Acids Sulfuric and Sulfurous
25 esters and surfactants in Kirk-Othmer Encyclopedia of
Chemical Technology, 4th Edition, J. Wiley & Sons N.Y.,
1992 Vol. 23, pp. 146-193, 194-217, 409-428 and
478-541). Examples are those of the formula
[R(O)_sSO₃]_tM, where M is Li, Na, K, Mg, Ca, Sr, Ba, Zn,
30 Al, La or Ce.

Use may be made of these sulphate ester salts and/or
sulphonate salts in their various commonly encountered
forms, e.g. as salt or as solution in water or in an
35 organic solvent or absorbed on a support, such as PVC,
Ca silicate, zeolites or hydrotalcites. Other examples
of such formulations are sulphate ester salts and/or
sulphonate salts complexed or dissolved using alcohols

(polyols, cyclodextrins) or using ether alcohols or ester alcohols or crown ether.

The sulphate ester salts and/or sulphonate salts preferably used are those of sodium and/or of potassium. Preference is given to salts of the monomethyl, -ethyl, -propyl, -butyl, -hexyl, -octyl, -isooctyl, -decyl, -lauryl, -hexadecyl and -octadecyl ester of sulphuric acid and/or to salts of methane-, ethane-, benzene-, toluene- and C₈-C₁₄-alkylbenzene-sulphonic acid.

The invention also provides combinations of the stabilizer mixtures according to the invention with at least one other conventional additive or stabilizer. The invention therefore includes combinations of the stabilizer mixtures encompassing at least one sulphate ester salt and/or sulphonate salt of the general formula (I) and at least one compound of the general formula (II) with at least one other conventional additive or stabilizer. Preference is given to phosphites, polyols and disaccharide alcohols, glycidyl compounds, hydrotalcites, zeolites (alkali metal aluminosilicates and alkaline earth metal aluminosilicates), fillers, metal soaps, alkali metal and alkaline earth metal compounds, lubricants, plasticizers, pigments, epoxidized fatty esters and other epoxy compounds, antioxidants, UV absorbers, light stabilizers, optical brighteners and blowing agents.

Particular preference is given to epoxidized fatty acid esters and other epoxy compounds, polyols, alkaline earth metal soaps, zeolites, hydrotalcites and phosphites. Very particular preference is given to phosphites and phosphites in combination with polyols, and also to anhydrous hydrotalcites and zeolites.

The possible reaction of products of the components used are also encompassed.

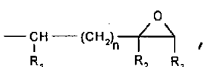
Preference is also given to stabilizer mixtures which additionally comprise an aminouracil, enamine, an indole, or a urea. Examples of suitable compounds are 1,3-dimethyl-4-aminouracil, 1,4-butanediol bis(β -aminocrotonate), thiodiethylene glycol bis(β -aminocrotonate), 2-phenylindole, 2-phenyllaurylindole, N,N'-diphenylthiourea. Other examples are described in the applicant's German patent application 101 07 329.

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

Polyols and disaccharide alcohols

Examples of possible compounds of this type are: pentaerythritol, dipentaerythritol, tripentaerythritol, trimethylolethane, bis(trimethylolpropane), polyvinyl alcohol, bis(trimethylolethane), trimethylolpropane, sugars, sugar alcohols. Of 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 amounts of the polyols used 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.

Glycidyl compounds

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

bonded directly to carbon, oxygen, nitrogen or sulphur atoms, either where both of R_1 and R_3 are hydrogen, R_2 is hydrogen or methyl and $n = 0$ or where R_1 and R_3

together are $-\text{CH}_2-\text{CH}_2-$ or $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$, R_2 then being hydrogen and n being 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.

Use is predominantly made of diglycidyl compounds having aromatic groups.

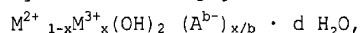
The amounts used of the terminal epoxy compounds are preferably at least 0.1 part, preferably from 0.1 to 50 parts by weight, advantageously from 1 to 30 parts by weight and in particular from 1 to 25 parts, based on 100 parts by weight of PVC.

15

Hydrotalcites

The chemical composition of these compounds is known to the skilled worker, e.g. from the patents 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,

A^b an anion of valency n ,

b is a number from 1-2,

$0 < x < 0.5$,

d is a number from 0-20.

Preference is given to compounds with

$\text{A}^b = \text{OH}^-, \text{ClO}_4^-, \text{HCO}_3^-, \text{CH}_3\text{COO}^-, \text{C}_6\text{H}_5\text{COO}^-, \text{CO}_3^{2-}, (\text{CHOHCOO})_2^{2-}, (\text{CH}_2\text{COO})_2^{2-}, \text{CH}_3\text{CHOHCOO}^-, \text{HPO}_3^-$ or HPO_4^{2-} ;

Examples of hydrotalcites are

$\text{Al}_2\text{O}_3 \cdot 6\text{MgO} \cdot \text{CO}_2 \cdot 12\text{H}_2\text{O}$ (i), $\text{Mg}_{4.5}\text{Al}_2(\text{OH})_{13} \cdot \text{CO}_3 \cdot 3 \cdot 5\text{H}_2\text{O}$ (ii), $4\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 9\text{H}_2\text{O}$ (iii), $4\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 6\text{H}_2\text{O}$, $\text{ZnO} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 8-9\text{H}_2\text{O}$ and $\text{ZnO} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 5-6\text{H}_2\text{O}$.

Very particular preference is given to the following

types: Alkamizer 2, Alkamizer P 93-2 (from Kyowa) and L-CAM (lithium-modified hydrotalcite, from Fuji).

Anhydrous hydrotalcites are preferably used.

5 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;

10 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.

15 Examples of zeolites are sodium aluminosilicates of the formulae

$Na_{12}Al_{12}Si_{12}O_{48} \cdot 27 H_2O$ [zeolite A], $Na_6Al_6Si_6O_{24} \cdot 2 NaX \cdot 7.5 H_2O$, X = OH, halogen, ClO_4 [sodalite]; $Na_6Al_6Si_{30}O_{72} \cdot 24 H_2O$; $Na_8Al_8Si_{40}O_{96} \cdot 24 H_2O$; $Na_{16}Al_{16}Si_{24}O_{80} \cdot 16 H_2O$;

20 $Na_{16}Al_{16}Si_{32}O_{96} \cdot 16 H_2O$; $Na_{56}Al_{56}Si_{136}O_{384} \cdot 250 H_2O$ [zeolite Y], $Na_{86}Al_{86}Si_{106}O_{384} \cdot 264 H_2O$ [zeolite X];

or the zeolites which can be prepared by partial or complete exchange of the Na atoms by Li atoms, K atoms, Mg atoms, Ca atoms, Sr atoms or Zn atoms, for example

25 $(Na, K)_{10}Al_{10}Si_{22}O_{64} \cdot 20 H_2O$; $Ca_{4.5}Na_3[(AlO_2)_{12}(SiO_2)_{12}] \cdot 30 H_2O$; $K_9Na_3[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27 H_2O$.

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

The hydrotalcites and/or zeolites may be used in

30 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.

35 Fillers

Fillers such as calcium carbonate, dolomite, wollastonite, magnesium oxide, magnesium hydroxide, silicates, china clay, talc, glass fibres, glass beads,

wood flour, mica, metal oxides or metal hydroxides, carbon black, graphite, rock flour, heavy spar, glass fibres, talc, kaolin and chalk are used. Preference is given to chalk (HANDBOOK OF PVC FORMULATING E. J.

- 5 Wickson, John Wiley & Sons, Inc., 1993, pp. 393 - 449) and reinforcing agents (TASCHENBUCH der Kunststoffadditive [Plastics Additives Handbook], R. Gächter & H. Müller, Carl Hanser, 1990, pp. 549 - 615).

10

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

- 15 100 parts by weight of PVC.

Metal soaps

Metal soaps are primarily metal carboxylates, preferably of relatively long-chain carboxylic acids.

- 20 Well-known examples of these are stearates and laurates, and also oleates and salts of relatively short-chain aliphatic or aromatic carboxylic acids, such as acetic acid, propionic acid, butyric acid, valeric acid, hexanoic acid, sorbic acid; oxalic acid, 25 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, 30 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 35 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.

The metal soaps or a mixture of these may be used in amounts of, for example, 0.001 to 10 parts by weight, expediently 0.01 to 8 parts by weight, particularly preferably 0.05 to 5 parts by weight, based on
5 100 parts by weight of PVC.

Alkali metal and alkaline earth metal compounds

For the purposes of the present invention, these are mainly the carboxylates of the acids described above,
10 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
15 magnesia alba and huntite), and also fatty-acid salts of Na and of K. In the case of alkaline earth 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
20 the stabilizers according to the invention it is preferable to use alkali metal carboxylates, alkaline earth metal carboxylates and/or aluminium carboxylates.

Lubricants

25 Examples of possible lubricants are: montan wax, fatty acid esters, PE 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. Calcium
30 stearate is preferred.

Plasticizers

Examples of organic plasticizers are those from the following groups:

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

di-2-ethylhexyl phthalate), DINP (diisononyl phthalate), DIDP (diisodecyl phthalate).

- 5 B) Esters of aliphatic dicarboxylic acids, in particular esters of adipic, azelaic or sebacic acid: preferably di-2-ethylhexyl adipate and diisooctyl adipate.
- 10 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
15 (trioctyl trimellitate, tri-2-ethylhexyl trimellitate), TIDTM (triisodecyl trimellitate) and TITDTM (triisotridecyl trimellitate).
- 20 D) Epoxy plasticizers: these are primarily epoxidized unsaturated fatty acids, e.g. epoxidized soybean oil.
- E) Polymeric plasticizers: the commonest starting materials for preparing polyester plasticizers are:
25 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.
- 30 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
35 these phosphoric esters are tributyl phosphate, tri-2-ethylbutyl phosphate, tri-2-ethylhexyl phosphate, trichloroethyl phosphate, 2-ethylhexyl diphenyl phosphate, cresyl diphenyl phosphate, triphenyl phosphate, tricresyl phosphate and

trixylenyl phosphate. Preference is given to 2-triethylhexyl phosphate and Reofos® 50 and Reofos® 95 from Ciba Spezialitätenchemie.

- 5 G) Chlorinated hydrocarbons (paraffins)
- H) Hydrocarbons
- I) Monoesters, e.g. butyl oleate, phenoxyethyl oleate,
- 10 tetrahydrofurfuryl oleate and alkylsulphonates.
- J) Glycol esters, e.g. diglycol benzoates.

A definition of these plasticizers and examples for the 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

20 mixtures of different plasticizers.

The plasticizers may be used in amounts of, for example, 5 to 20 parts by weight, expediently 10 to 20 parts by weight, based on 100 parts by weight of

25 PVC. Rigid or semirigid PVC comprises preferably up to 10%, particularly preferably up to 5%, of plasticizer, or no plasticizer.

Pigments

30 Suitable substances are known to the skilled worker. Examples of inorganic pigments are TiO_2 , pigments based on zirconium oxide, $BaSO_4$, zinc oxide (zinc white) and lithopones (zinc sulphide/barium sulphate), carbon black, carbon black-titanium dioxide mixtures, iron

35 oxide pigments, Sb_2O_3 , $(Ti,Ba,Sb)O_2$, Cr_2O_3 , spinels, such as cobalt blue and cobalt green, $Cd(S,Se)$, ultramarine blue. Examples of organic pigments are azo pigments, phthalocyanine pigments, quinacridone pigments,

perylene pigments, diketopyrrolopyrrole pigments and anthraquinone pigments. TiO₂ in micronized form is also preferred. A definition and further descriptions are found in the "Handbook of PVC Formulating", E.J.

5 Wickson, John Wiley & Sons, New York, 1993.

Phosphites

Organic phosphites are known costabilizers for chlorine-containing polymers. Examples of these are

10 trioctyl, tridecyl, tridodecyl, tritridecyl, tripentadecyl, trioleyl, tristearyl, triphenyl, trilauryl, tricresyl, tris(nonylphenyl), tris(2,4-tert-butylphenyl) and tricyclohexyl phosphite.

Other suitable phosphites are various mixed aryl

15 dialkyl or alkyl diarylphosphites, such as phenyl dioctyl, phenyl didecyl, phenyl didodecyl, phenyl ditridecyl, phenyl ditetradecyl, phenyl dipentadecyl, octyl diphenyl, decyl diphenyl, undecyl diphenyl, dodecyl diphenyl, tridecyl diphenyl, tetradecyl
20 diphenyl, pentadecyl diphenyl, oleyl diphenyl, stearyl diphenyl and dodecyl bis(2,4-di-tert-butylphenyl) phosphite.

Advantageous use may also be made of phosphites of various di- or polyols: e.g. tetraphenyldipropylene

25 glycol diphosphite, polydipropylene glycol phenyl phosphite, tetraisodecyl dipropylene glycol diphosphite, tris(dipropylene glycol) phosphite, tetramethylolcyclohexanol decyl diphosphite, tetramethylolcyclohexanol butoxyethoxyethyl diphosphite, tetra-
30 methylolcyclohexanol nonylphenyl diphosphite, bis(nonylphenyl) di(trimethylolpropane) diphosphite, bis(2-butoxyethyl) di(trimethylolpropane) diphosphite, tris(hydroxyethyl) isocyanurate hexadecyl triphosphite, didecyl pentaerythrityl diphosphite, distearyl
35 pentaerythrityl diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythrityl diphosphite, and also mixtures of these phosphites and aryl/alkyl phosphite mixtures of empirical composition (H₁₉C₉-

$C_6H_4O)_{1.5}P(OC_{12,13}H_{25,27})_{1.5}$ or $[C_8H_{17}-C_6H_4-O-]_2P[i-C_8H_{17}O]$,
 $(H_{19}C_9-C_6H_4O)_{1.5}P(OC_{9,11}H_{19,23})_{1.5}$.

Example amounts of the organic phosphites used are from 0.01 to 10, advantageously from 0.05 to 5 and in particular from 0.1 to 3 parts by weight, based on 100 parts by weight of PVC.

Epoxidized fatty acid esters and other epoxy compounds

The stabilizer combination of the invention may additionally and preferably comprise at least one epoxidized fatty acid ester. Possible compounds here are especially esters of fatty acids from natural sources (fatty acid glycerides), such as soya oil or rapeseed oil. However, it is also possible to use synthetic products, such as epoxidized butyl oleate. Use may also be made of epoxidized polybutadiene and polyisoprene, if desired also in a partially hydroxylated form, or of glycidyl acrylate and glycidyl methacrylate as homo- or copolymer. These epoxy compounds may also have been applied to an alumino salt compound; in this connection see also DE-A-4 031 818.

Antioxidants

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 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'-tetratert-butyl-4,4'-dihydroxydibenzyl ether, hydroxybenzylated malonates, e.g. dioctadecyl 2,2-bis(3,5-di-tert-butyl-2-hydroxybenzyl) malonate, hydroxybenzyl aromatics, e.g. 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, triazine compounds, e.g. 2,4-bis(octylmercapto-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, phosphonates and

phosponites, e.g. dimethyl 2,5-di-tert-butyl-4-hydroxybenzylphosphonate, acylaminophenols, e.g. 4-hydroxylauranilide, esters of beta-(3,5-ditert-butyl-4-hydroxyphenyl)propionic acid, beta-(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid, beta-(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid, esters of 3,5-ditert-butyl-4-hydroxyphenylacetic acid with mono- or polyhydric alcohols, amides of beta-(3,5-ditert-butyl-4-hydroxyphenyl)propionic acid, such as, for example, N,N'-bis(3,5-ditert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine, vitamin E (tocopherol) and derivatives.

Examples of the amounts of the antioxidants used are 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 parts by weight of PVC.

UV absorbers and light stabilizers

Examples of these are: 2-(2'-hydroxyphenyl)benzotriazoles, 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, acrylates, nickel compounds, oxalamides, such as 4,4'-dioctyloxyoxanilide, 2,2'-dioctyloxy-5,5'-ditert-butylloxanilide, 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-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.

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

and sodium bicarbonate and also mixtures of these.

Definitions for and examples of impact modifiers and processing aids, gelling agents, antistats, biocides, metal deactivators, optical brighteners, flame retardants, antifogging agents and compatibilizers are given in "Kunststoffadditive" ["Plastics Additives"], R. Gächter/H. Müller, Carl Hanser Verlag, 3rd Ed., 1989, and 4th Edition, 2001, and in "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 "Impact Modifiers for PVC", J. T. Lutz/D. L. Dunkelberger, John Wiley & Sons, 1992.

The invention also provides compositions which comprise a chlorine-containing polymer and a stabilizer mixture of the invention.

The amounts of the compounds of the general formula (II) present for stabilization in these chlorine-containing polymer compositions are advantageously from 0.01 to 10 parts by weight, preferably from 0.05 to 5 parts by weight, based on 100 parts by weight of PVC.

Examples of the amount used of the sulphate ester salts and/or sulphonate salts are from 0.001 to 10 parts by weight, advantageously from 0.01 to 5 parts by weight, particularly preferably from 0.01 to 3 parts by weight, based on 100 parts by weight of PVC.

Preference is given to compositions in which the ratio of the compound of the general formula (II) to the sulphate ester salt and/or sulphonate salt, based on weight, is in the range of from 1.5:1 to 10:1.

Examples of the chlorine-containing polymers to be

stabilized are: 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, 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 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 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 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 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 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.

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 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, 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; EVA: ethylene-vinyl acetate. Other possible polymers are in particular styrene-acrylonitrile copolymers based on acrylate (ASA).
- 15 A preferred component in this context is a polymer composition which comprises, as components (i) and (ii), a mixture of 25-75% by weight 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 NBR, NAR and/or EVA, but in particular EVA.
- 25 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 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 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 Ed., 1989; in DE 197 41 778 and in EP-A 0 967 245, which are incorporated herein by way of reference.

The inventive stabilization is suitable for chlorine-containing polymer compositions that are non-plasticized or plasticizer-free or substantially plasticizer-free compositions, and also as for plasticized compositions.

The compositions of the invention are useful in particular, in the form of rigid formulations, for hollow articles (bottles), packaging films (thermoformable films), blown films, crash pad films (cars), tubes, foams, heavy profiles (window frames), translucent-wall profiles, building profiles, films (including Luvitherm films), PVC tubes, profiles, sidings, fittings, office films and equipment housings (computers and domestic appliances).

Preferred other compositions, in the form of flexible formulations, are for wire sheathing, cable insulation, decoration sheeting, roofing films, foams, agricultural sheeting, hoses, sealing profiles, floorcoverings, motor vehicle parts, flexible films, injection mouldings, office films and films for air halls.

Examples of the use of the compositions according to the invention as plastisols are synthetic leather, floorings, textile coatings, wallcoverings, coil coatings and underfloor sealing for motor vehicles.

Examples of sintered PVC applications of the compositions according to the invention are slush, slush mould and coil coatings and also in E-PVC for Luvitherm films.

The stabilizers may advantageously be incorporated by the following methods: as emulsion or dispersion (one possibility is, for example, the form of a pasty mixture, an advantage of the combination of the invention in the case of this administration form is the stability of the paste); as a dry mixture during the mixing of added components or polymer mixtures; by

direct addition into the processing apparatus (e.g. calender, mixer, kneader, extruder or the like) or as a solution or melt or, respectively, as flakes or pellets in a dust-free form as one-pack.

5

The PVC stabilized according to the invention, which is also provided by the invention, may be prepared in a manner known per se, by using equipment known per se, such as the abovementioned processing apparatus, to mix the stabilizer mixture of the invention and, if desired, other additives, with the PVC. The stabilizers here may be added individually or in a mixture, or else in the form of what are known as masterbatches.

10

The PVC stabilized as in the present invention may be brought into the desired shape in a known manner.

15

Examples of processes of this type are grinding, calendering, extruding, injection moulding and spinning, and also extrusion blowmoulding. The stabilized PVC may also be processed to give foams. The invention therefore also provides a process for stabilizing chlorine-containing polymers by adding of the stabilizer mixture according to the invention to a chlorine-containing polymer, and also provides products comprising PVC stabilized by the stabilizer mixture according to the invention.

20

25

A PVC stabilized according to the invention is, for example, particularly suitable for hollow articles (bottles), packaging films (thermoformed films), blown films, pipes, foams, heavy profiles (window frames), translucent-wall profiles, construction profiles, films (including Luvitherm films), PVC tubes, profiles, sidings, fittings, office sheeting and apparatus housings (computers, household devices).

30



The PVC of the invention is suitable particularly for semirigid and flexible formulations, especially in the form of flexible formulations for wire sheathing, cable insulation, floorcoverings, wallcoverings, motor

35

vehicle parts, flexible films, injection mouldings or hoses which are particularly preferred. In the form of semirigid formulations the PVC of the invention is particularly suitable for decorative films, foams, agricultural films, hoses, sealing profiles and office films.

- 5 Examples of the use of the PVC according to the invention as plastisol are synthetic leather, floor coverings, textile coatings, wall coverings, coil coatings and underfloor sealing for motor vehicles.
- 10 Examples of sintered PVC applications of the PVC stabilized according to the invention are slush, slush mould and coil coatings for plastisol, semirigid and flexible formulations.
- 15 For more detail in this connection see "Kunststoffhandbuch PVC" ["Plastics Handbook PVC"], Vol. 2/2, W. Becker/H. Braun, 2nd Ed., 1985, Carl Hanser Verlag, pp. 1236 - 1277.
- 20 The examples below illustrate the invention but do not restrict the same. As in the remainder of the description, parts and percentages given are based on weight.

25 Table 1: Stabilizers (I)

Stabilizer	Formula
1	$\text{CH}_3\text{-O-SO}_3\text{Na}$ (50% strength in H_2O)
2	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{CH}_3(\text{CH}_2)_3\text{-CH-CH}_2\text{-O-SO}_3\text{Na} \end{array}$ (50% strength in H_2O)
3	$\text{CH}_3(\text{CH}_2)_{11}\text{O-SO}_3\text{Na}$
4	$\text{CH}_3(\text{CH}_2)_{11}\text{SO}_3\text{Na}$
5	$\text{CH}_3(\text{CH}_2)_{11}$ —  — SO_3Na
6	CH_3 —  — $\text{SO}_3\text{Na} \times \text{H}_2\text{O}$

Example 1: Static heat test

A mixture composed of

5

100.0 parts of Evipol (trademark of EVC)
SH 7020 - PVC K value 70

47.0 parts of dioctyl phthalate

3.0 parts of ESO = epoxidized soya bean oil

10 0.3 part of Loxiol® G 71 S = pentaerythritol
adipate complex ester - lubricant

0.1 part of calcium stearate

x parts of a stabilizer given in Table 1

15 and 0.6 part of triethanolamine (TEA) were rolled for 5
minutes at 180°C on mixing rolls. Test strips of film,
thickness 0.5 mm, were removed from the milled sheet
formed. The film specimens were exposed to heat at
190°C in an oven (= Mathis Thermo-Takter). The

20 Yellowness Index (YI) was determined at 3 minute
intervals to ASTM D1925-70. The results are reported in
Table 2. Where appropriate, 0.6 part of CH 300 = mixed
aryl/alkyl phosphite from Crompton was added to the
mixture (cf. Table 2). Low YI values indicate good
25 stabilization.

Example	13	14	15
Stabilizer according to Table 1	5	6	6
Parts	0.6	0.3	0.3
Parts of CH 300	0.6	-	0.6
Min	YI value		
0	14.51	15.09	12.66
3	16.77	21.14	20.61
6	25.03	28.61	28.34
9	41.94	45.65	26.97
12	57.97	65.39	39.41
15	68.11	84.69	50.49
18	64.91	108.96	66.41
21	80.17		87.72
24	113.52		101.22
27			

* does not comprise TEA

Example 2: Static heat test

5 A mixture composed of

100.0 parts of Evipol (trademark of EVC)
SH 7020 - PVC K value 70

47.0 parts of dioctyl phthalate

10 3.0 parts of ESO = epoxidized soya bean oil
0.3 part of Loxiol[®] G 71 S = pentaerythritol
adipate complex ester - lubricant

0.1 part of calcium stearate

x parts of a stabilizer given in Table 1

15

and 0.3 part of triethanolamine (TEA) was rolled for 5 minutes at 180°C on mixing rolls. Test film strips of thickness 0.5 mm were taken from the resultant milled sheet. The film specimens were subjected to heat in an oven (= Mathis-Thermo-Takter) at 190°C. At 3 minute intervals the Yellowness Index (YI) was determined to

20

ASTM D1925-70. The results are seen in Table 2. Where appropriate, 0.6 part of CH 300 = mixed aryl/alkyl phosphite from Crompton was added to the mixture (cf. Table 3). Low YI values indicate good stabilization.

5

Table 3

Example	16	17*	18	19
Stabilizer according to Table 1	-	3	3	3
Parts	-	0.15	0.15	0.15
Parts of CH 300	-	0.6	-	0.6
	YI value			
0	18.81	22.77	13.33	10.62
3	22.51	24.91	14.53	10.5
6	32.57	29.29	22.53	12.39
9	47.33	36.67	31.69	15.97
12	68.18	51.94	48.96	24.38
15	99.19	70.81	77.07	49.93
18	124.85	85.81	109.68	84.83
21		99.95		117.19
24		114.17		
27				

* does not comprise TEA

10 Example 3: Pressed PVC sheet

A mixture composed of

- 100.0 parts of Evipol (trademark of EVC)
- 15 SH 7020 = PVC with K value 70
- 47.0 parts of dioctyl phthalate
- 3.0 parts of ESO = epoxidized soya bean oil
- 0.3 part of Loxiol[®] G 71 S = pentaerythritol adipate complex ester - lubricant
- 20 0.1 part of calcium stearate
- 0.3 part of triethanolamine (TEA)
- x parts of a stabilizer given in Table 1

was rolled at 180°C for 5 minutes on mixing rolls. A pressed sheet was produced from the resultant milled sheet in a preheated multisheet press. Pressed sheet thickness 2 mm, pressing time 2 minutes. The Yellowness Index (YI) of this pressed sheet was determined to ASTM D1925-70 and the transparency was measured in % to ASTM D2805-80. The results are seen in Table 4. Low YI values mean good stabilization or initial colour. High percentages mean good transparency.

Table 4

Example	20	21*	22	23
Stabilizer (I) according to Table 1	-	3	3	3
Parts	-	0.15	0.15	0.15
Parts of CH 300	-	0.6	-	0.6
YI value	88.3	70.6	50.3	29.7
Transparency	83.1	92.4	94.3	96.3

* does not comprise TEA

The use of sulphate ester salt/sulphonate salt (formula I) combined with triethanolamine (formula II) is seen to give good stabilization. Stability can be further increased via combination with phosphite (CH 300).

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Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" or "comprising", will be understood to imply the inclusion of a
5 stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

The reference in this specification to any prior publication (or information derived from it), or to any
10 matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

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- heterocyclic ring of carbon atoms optionally containing up to 2 heteroatoms, or when $x = 2$, R^1 may be a C_2-C_{18} alkylene which may be OH-substituted at both β -carbon atoms and/or may be interrupted by one or more O-atoms and/or one or more
- 5 NR^2 groups, or a dihydroxy-substituted tetrahydrodicyclopentadienylene, dihydroxy-substituted ethylcyclohexanylene, dihydroxysubstituted 4,4'-(bisphenol A dipropyl ether)ylene, isophoronylene, dimethylcyclohexanylene, dicyclohexylmethanylene, or 3,3'-
- 10 dimethyldicyclohexylmethanylene, and if $x = 3$, R^1 may be a trihydroxysubstituted (tri-N-propyl isocyanurate) triyl;
- R^3_a and R^3_b independently are a 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 $-CO-O-$;
- 15 R^4 is a C_1-C_{18} alkyl/alkenyl or phenyl, and R^5 is H, C_1-C_{22} alkyl, C_2-C_{22} alkenyl or C_6-C_{10} aryl.

2. Stabilizing mixture according to claim 1, wherein in the compound of formula II, R^3_a and R^3_b are, independently of one another, H or CH_3 , and y is 1.

- 20 3. Stabilizing mixture according to claim 1 or claim 2, wherein in the compound of formula II $R^1 = R^2 = CH_2-CHR^3_b-OH$.

4. Stabilizing mixture according to any one of claims 1 to 3, wherein the compounds of formula II are selected
- 25 from the group consisting of: tris(2-hydroxy-1-propyl)amine, tris(2-hydroxyethyl)amine, bis(2-hydroxyethyl)(2-hydroxy-1-propyl)amine or alkyl/alkenylbis(2-hydroxyethyl)-amine, N-oleylbis(2-hydroxyethyl)amine, N-soyabis(2-

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hydroxyethyl)amine, alkyl/alkenyl(2-hydroxy-1-propyl)amine, N-(2-hydroxyhexadecyl)-diethanolamine, N-(2-hydroxy-3-octyloxypropyl)-diethanolamine, N-(2-hydroxy-3-decyloxypropyl)-diethanolamine and mixtures thereof.

5 5. Stabilizing mixture according to any one of claims 1 to 4, wherein in the sulphate ester salt and/or sulphonate salt, M is Li, Na, K, Mg, Ca, Sr, Ba, Zn, Al, La, Ce or a hydrotalcite layer-lattice cation; t is 1, 2 or 3, and in the case of a hydrotalcite layer-lattice cation, $0 < t \leq 1$.

10 6. Stabilizing mixture according to any one of claims 1 to 5, wherein in the sulphate ester salt and/or sulphonate salt, M = Na or K and t = 1.

 7. Stabilizing mixtures according to any one of claims 1 to 6, further comprising an aminouracil, enamine,
15 indole or urea.

 8. Stabilizing mixture according to any one of claims 1 to 7, further comprising an anhydrous hydrotalcite or a zeolite.

 9. Stabilizing mixture according to any one of claims
20 1 to 8, further comprising metal soaps, polyols, disaccharide alcohols, glycidyl compounds, hydrotalcites, alkali metal/alkaline earth metal aluminosilicates, alkali metal/alkaline earth metal hydroxides/oxides, or alkali metal/alkaline earth metal (hydrogen)carbonates, or
25 carboxylates, fillers/pigments, plasticizers, antioxidants, light stabilizers, optical brighteners, lubricants, epoxidized fatty esters and mixtures thereof.

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10. Stabilizing mixture according to any one of claims 1 to 9, further comprising a phosphite or a reaction product of a phosphite with component a) and/or b).

11. Stabilizing mixture according to any one of claims 1 to 10, wherein the phosphite is selected from the group consisting of: distearyl pentaerythritol diphosphite, triphenyl phosphite, trisonylphenyl phosphite, phenyl didecyl phosphite, polydipropylene glycol phenyl phosphite, tetraphenyl dipropylene glycol diphosphite, tetraisodecyl dipropylene glycol diphosphite, tris (dipropylene glycol) phosphite, decyl diphenyl phosphite, trioctyl phosphite, trilauryl phosphite or (nonylphenyl_{1.5} C₁₂/C₁₃alkyl)_{1.5} phosphite and mixtures thereof.

12. The stabilizer mixture according to claim 10, wherein the phosphite is selected from the group consisting of: aryl dialkyl phosphite and alkyl diarylphosphite.

13. The stabilizer mixture according to claim 1, wherein in the sulphate ester salt and/or sulphonate salt, M is Ca and t is 2.

14. Stabilizing mixture for stabilizing chlorine-containing polymers against thermal-induced degradation, comprising

a) at least one sulphate ester salt and/or sulphonate salt of the formula (I), as defined in claim 1,

b) at least one alkanolamine of the formula (II), as defined in claim 1, substantially as hereinbefore described with reference to the Examples.

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15. A composition comprising a chlorine-containing polymer and a stabilizer mixture according to any one of claims 1 to 14.

16. The composition according to claim 15, comprising
5 from 0.01 to 10 parts by weight of the compound of the general formula (II) and from 0.001 to 10 parts by weight of the compound of general formula (I) and, optionally, from 0.05 to 5 parts by weight of a phosphite, based on 100 parts by weight of the chlorine-containing polymer.

10 17. Composition according to claim 15, wherein the chlorine-containing polymer is selected from the group consisting of: a polymer of vinyl chloride, polymer of vinylidene chloride, polymer of a vinyl resin containing vinyl chloride units, copolymer of vinyl chloride with a
15 diene compound and an unsaturated carboxylic acid or anhydride thereof, post chlorinated polymer of copolymer of vinyl chloride, copolymer of vinyl chloride and vinylidene chloride with an unsaturated aldehyde or ketone, polymer of vinyl chloroacetate and a dichlorodivinyl ether, chlorinated
20 polymer of vinyl acetate, chlorinated polymeric ester of acrylic acid and an alpha-substituted acrylic acid, polymer of a chlorinated styrene, chlorinated rubber, chlorinated polymer of ethylene, polymer or postchlorinated polymer of chlorobutadiene or a copolymer thereof with vinyl chloride
25 or a chlorinated natural or synthetic rubber and mixtures thereof.

18. A process for stabilizing chlorine-containing polymers against thermal-induced degradation by adding the

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stabilizer mixture according to any one of claims 1 to 14 to a chlorine-containing polymer.

19. Process for stabilizing chlorine-containing polymers against thermal-induced degradation according to claim 18, wherein the chlorine-containing polymer is plasticized polyvinyl chloride.

20. Process for stabilizing chlorine-containing polymers against thermal-induced degradation according to claim 19, wherein the chlorine-containing polymer is useful in flooring, motor vehicle parts, plasticized films, tubing, injection mouldings, wire sheathing or plastisols.

21. Process for stabilizing chlorine-containing polymers against thermal-induced degradation according to claim 18, wherein the chlorine-containing polymer is unplasticized polyvinyl chloride.

22. Process according to claim 18, wherein the chlorine-containing polymer is selected from the group consisting of: a polymer of vinyl chloride, polymer of vinylidene chloride, polymer of a vinyl resin containing vinyl chloride units, copolymer of vinyl chloride with a diene compound and an unsaturated carboxylic acid or anhydride thereof, post chlorinated polymer of copolymer of vinyl chloride, copolymer of vinyl chloride and vinylidene chloride with an unsaturated aldehyde or ketone, polymer of vinyl chloroacetate and a dichlorodivinyl ether, chlorinated polymer of vinyl acetate, chlorinated polymeric ester of acrylic acid and an alpha-substituted acrylic acid, polymer of a chlorinated styrene, chlorinated rubber, chlorinated

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polymer of ethylene, polymer or postchlorinated polymer of chlorobutadiene or a copolymer thereof with vinyl chloride or a chlorinated natural or synthetic rubber and mixtures thereof.

5 23. A consumer article comprising a polyvinyl chloride stabilized against thermal-induced degradation by the stabilizer mixture according to any one of claims 1 to 14.

 24. A composition comprising a chlorine-containing polymer and a stabilizer mixture according to any one of
10 claims 1 to 14, substantially as hereinbefore described with reference to the Examples.

 25. A process for stabilizing chlorine-containing polymers against thermal-induced degradation by adding the stabilizer mixture according to any one of claims 1 to 14 to
15 a chlorine-containing polymer, said process being substantially as hereinbefore described with reference to the Examples.

 26. A stabilized chlorine-containing polymer whenever prepared by the process of any one of claims 18 to 22 or 25.