Stabiliser Composition for Chlorine-Containing Polymers

Technical Field

The present invention generally relates to a stabiliser composition for chlorine-containing polymers.

Background Art

Chlorine-containing polymers such as polyvinyl chloride (PVC) may be thermally unstable. PVC is one of the most important large-volume thermoplastics available in the market. It is also one of the least thermally stable polymers in commercial use. In PVC processing and the subsequent end uses of PVC, heat stabilisers are needed.

A range of additives can be used to stabilise PVC and such PVC stabilisers can be classified into four categories, namely:

- lead stabilisers;
- tin stabilisers;
- mixed metal stabilisers; and
- organic stabilisers.

Lead stabilisers are stabilisers having lead derivatives as the primary stabilising ingredients, which include inorganic salts such as lead tribasic sulfate, lead dibasic phosphite, etc, and lead soaps, such as, for example, stearates, laurates, etc. Lead stabilisers are currently the market dominant stabilisers for PVC.

Tin stabilisers are stabilisers containing alkyl-tin mercaptides or carboxylates as the primary stabilising ingredients. The tin stabilisers are commonly used in stabilising rigid PVC.

Mixed metal stabilisers are stabilisers containing a combination of metal carboxylates such as barium-zinc or calcium-zinc carboxylates. The mixed metal stabilisers containing calcium-zinc carboxylates are an alternative to lead stabilisers and/or tin compound.

Organic stabilisers are stabilisers containing metal-free organic compounds as the primary stabilising agents. Organic stabilisers are free of lead, cadmium, tin, barium, antimony, zinc and other heavy metals.

Commercially, lead is still today's worldwide dominant PVC stabiliser for due to the properties of lead. Due to environmental regulations prohibiting lead, it is desirable that lead be phased out from application in lead stabilisers. Lead-substitutes, which are environmentally friendly and acceptable, fall under two categories, that is calcium-zinc (Ca/Zn) and heavy-metal-free organic based stabilisers. However, zinc chloride, which is generated in PVC stabilised by a Ca/Zn stabiliser in the PVC processing step, is regarded as a toxic substance.

In view of the above, there is a need to provide a stabiliser for thermally stabilising chlorine-containing polymers.

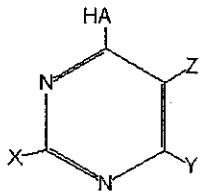
There is also a need to provide a stabiliser that overcomes or at least ameliorates one or more of the disadvantages described above.

There is a need to provide an organic based stabiliser for chlorine-containing polymers such as PVC,

which is free from lead, cadmium, tin, barium, antimony, zinc and any other heavy metals.

Summary of invention

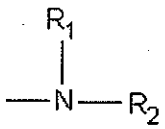
According to a first aspect of the invention, there is provided a stabiliser composition for chlorine-containing polymers comprising compounds represented by the general formula (I):



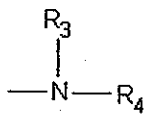
wherein X, Y, and Z are each selected independently of the other,

wherein

X is hydrogen or

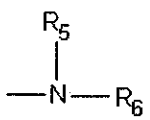


Y is hydrogen or



and

Z is hydrogen or



wherein

R1, R2, R3, R4, R5, and R6 are each independently a hydrogen, alkyl, alkenyl, cycloalkyl, cycloalkenyl, phenylalkyl and aryl group, and

wherein

A is oxygen (O) or sulfur (S).

According to a second aspect of the invention, there is provided a polymer composition comprising:

a chlorine-containing polymer; and

a stabiliser composition as defined in the first aspect.

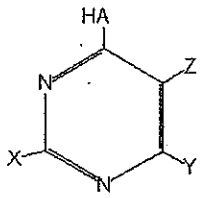
According to a third aspect of the invention, there is provided a polyvinyl chloride resin composition comprising polyvinyl chloride resin and a heat stabilising effective amount of a stabiliser composition according to the first aspect.

According to a fourth aspect of the invention, there is provided a method of preparing a stabilised chlorine-containing polymers comprising the steps of:

mixing a material comprising chlorine-containing polymer resin and a stabiliser composition as defined in the first aspect; and

heating the mixed material for a period so as to at least partially bind the polyvinyl chloride resin and stabiliser composition.

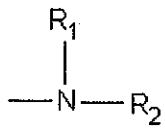
According to a fifth aspect of the invention, there is provided a method for stabilising a chlorine-containing polymer comprising mixing said polymer with a compound represented by the general formula (I):



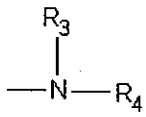
wherein X, Y, and Z are each selected independently of the other,

wherein

X is hydrogen or

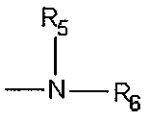


Y is hydrogen or



and

Z is hydrogen or



wherein

R1, R2, R3, R4, R5, and R6 are each independently a hydrogen, alkyl, alkenyl, cycloalkyl, cycloalkenyl, phenylalkyl and aryl group, and

wherein

A is oxygen (O) or sulfur (S).

According to a sixth aspect of the invention, there is provided a method for stabilising a chlorine-containing polymer comprising mixing said polymer with a stabiliser composition as defined in the first aspect.

According to a seventh aspect of the invention, there is provided a stabiliser composition as defined in the first aspect when used for stabilising a chlorine-containing polymer.

According to an eighth aspect of the invention, there is provided a stabilised chlorine-containing polymer when made by the method of the fifth aspect.

Definitions

The following words and terms used herein shall have the meaning indicated:

The term 'stabilised chlorine-containing polymer' or 'stabilised polymer' is to be interpreted broadly to include any chlorine-containing polymer that includes the stabiliser composition disclosed herein.

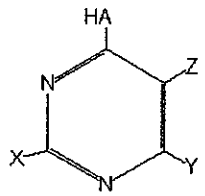
The term 'unavoidable impurities' is to be interpreted broadly to include material that does not include chlorine-containing polymer material or stabiliser composition constituent material that may be present during the manufacturing process of the stabiliser composition or the stabilised chlorine-containing polymer material.

Disclosure of embodiments

The present invention is further described in the following embodiments, which are included for purpose of illustration and not for limitation of the scope of that which the applicants claim to be the invention.

An exemplary non-limiting embodiment of a stabiliser composition for thermally stabilising chlorine-containing polymers will now be disclosed.

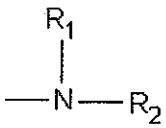
The disclosed embodiments describe a novel stabiliser composition comprising compounds represented by formula (1):



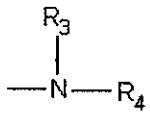
wherein X, Y, and Z are each selected independently of the other,

wherein

X is hydrogen or

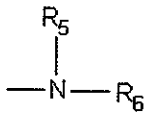


Y is hydrogen or



and

Z is hydrogen or



wherein

R1, R2, R3, R4, R5, and R6 are each independently a hydrogen, alkyl, alkenyl, cycloalkyl, cycloalkenyl, phenylalkyl and aryl group, and

wherein

A is oxygen (O) or sulfur (S).

The stabiliser composition may be used as a thermal stabiliser for stabilising a chlorine-containing polymer.

The stabiliser composition may comprise two or more compounds of formula 1 that are linked together by a covalent bond between the atoms A or the nitrogen atoms of X, Y, or Z.

The stabiliser composition may comprise two or more compounds of formula 1 that are linked together by a covalent bond.

The stabiliser may comprise one or more additive compounds. The stabiliser may also comprise one or more lubricants.

The stabiliser composition may be mixed with a chlorine-containing polymer to form a stabilised chlorine-containing polymer. The stabilised chlorine-containing polymer may contain compounds of formula 1 in an amount by weight selected from the group consisting of: 0.01% to 16%; 0.1% to 15%; 0.15% to 10%; 0.2% to 8%; 0.2% to 6%; and 0.2% to 4%.

In one embodiment, the chlorine-containing polymer may undergo extrusion to form a pipe made from the chlorine-containing polymer having compounds of formula 1 in an amount by weight between the range of about 0.05% to about 2%.

In another embodiment, the chlorine-containing polymer may undergo injection molding to form a molded shape made from the chlorine-containing polymer having compounds of formula 1 in an amount by weight between the range of about 0.1% to about 3.5%.

The stabilised chlorine-containing polymer may comprise one or more additive compounds in an amount by weight selected from the group consisting of: 0.09% to 16%; 0.1% to 15%; 0.15% to 10%; 0.2% to 8%; 0.2% to 6%; and 0.2% to 4%.

In one embodiment, the chlorine-containing polymer may undergo extrusion to form a pipe made from the chlorine-containing polymer having one or more additive compounds in an amount by weight between the range of about 0.1% to about 2%.

In another embodiment, the chlorine-containing polymer may undergo injection molding to form a molded shape made from the chlorine-containing polymer having one or more additive compounds in an amount by weight between the range of about 0.3% to about 3%.

The stabilised chlorine-containing polymer may comprise one or more lubricants in an amount by weight selected from the group consisting of: 0.09% to 21%; 0.1% to 20%; 0.15% to 10%; 0.2% to 8%; 0.3% to 6%; and 0.4% to 4%.

In one embodiment, the chlorine-containing polymer may undergo extrusion to form a pipe made from the chlorine-containing polymer having one or more lubricants

in an amount by weight between the range of about 0.5% to about 2%.

In another embodiment, the chlorine-containing polymer may undergo injection molding to form a molded shape made from the chlorine-containing polymer having one or lubricants in an amount by weight between the range of about 0.8% to about 3%.

Amino-substituted pyrimidine compounds

The amino-substituted pyrimidine compounds may be amino-substituted hydroxy-pyrimidines or amino-substituted mercapto-pyrimidines.

The amino-substituted pyrimidine compounds may be selected from the list consisting of: 2-Amino-6-hydroxypyrimidine, 2-amino-6-mercaptopyrimidine, 2-*N*-methylamino-6-hydroxypyrimidine, 2-*N*-2-propylamino-6-hydroxypyrimidine, 4-amino-6-hydroxypyrimidine, 4-amino-6-mercaptopyrimidine, 4-*N*-phenylamino-6-hydroxypyrimidine, 4-methylamino-6-hydroxypyrimidine, 4-octylamino-6-hydroxypyrimidine, 5-amino-6-hydroxypyrimidine, 5-amino-6-mercaptopyrimidine, 5-*N*-butylamino-6-hydroxypyrimidine, 5-*N*-methyl amino-6-mercaptopyrimidine, 2,4-diamino-6-hydroxypyrimidine, 2,4-diamino-6-mercaptopyrimidine, 2,4-*N,N'*-dimethyldiamino-6-hydroxypyrimidine, 4,5-diamino-6-hydroxypyrimidine, 4,5-diamino-6-mercaptopyrimidine, 4,5-*N,N'*-dipropyldiamino-6-hydroxypyrimidine, 4-*N*-methylamino-5-*N*-octylamino-6-hydroxypyrimidine, 2,6-diamino-6-hydroxypyrimidine, 2,6-diamino-6-mercaptopyrimidine, 2,6-*N,N'*-dibutyldiamino-6-hydroxypyrimidine, 2-*N*-butylamino-6-*N*-phenylamino-6-hydroxypyrimidine, 2,4,5-triamino-6-hydroxypyrimidine, 2,4,5-triamino-6-mercaptopyrimidine, 2-

N-methylamino-4-*N*-butylamino-5-*N*-phenylamino-6-hydroxypyrimidine and one or more combinations thereof.

Additive compounds

The stabiliser composition may further comprise one or more additives selected from the group consisting of: polyols, alkali or alkaline earth metal compounds, alkali or alkaline earth carboxylates, alkali aluminosilicates, hydrotalcite ($Mg_6Al_2(CO_3)(OH)_{16}.4H_2O$), perchlorate compounds, phosphites and hypophosphites, β-diketones, sterically hindered amines, phenolic antioxidants and one or more combinations thereof.

The amount of additive compounds present in a stabilised chlorine-containing polymer may be selected from the group consisting of: 0.001% to 15%; 0.01% to 10%; 0.1% to 8%; 0.1% to 6%; 0.1% to 5%; 0.1% to 4%; 0.1% to 3%; 0.1% to 2% and *0.1% to 0.6%*.

The polyols

The polyols may be selected from the group consisting of: pentaerythritol, dipentaerythritol, tripentaerythritol, bistrimethylolpropane, bistrimethylolethane, trismethylolpropane, polyvinylalcohol, sorbitol, mannitol, tetramethylolcyclohexanol, tetramethylolcyclopentanol, tetramethylolcyclopyranol, glycerol, diglycerol, polyglycerol, thiodiglycerol, tris(hydroxyethyl) isocyanurate; tris(hydroxypropyl) isocyanurate and one or more combinations thereof.

The alkali or alkaline earth metal compounds

The alkali or alkaline earth metal compound may be selected from the group consisting of: oxides, hydroxides,

sulfides, silicates, phosphates, borates, and carbonates of alkali metals and alkaline earth metals, and one or more combinations thereof.

The alkali metals may be selected from the group consisting of: lithium, sodium, and potassium and one or more combinations thereof.

The alkaline earth metals may be selected from the group consisting of: magnesium, calcium, strontium, and barium and one or more combinations thereof.

The alkali or alkaline earth metal compounds may be basic alkali or alkaline earth metals selected from the group consisting of: calcium hydroxide, magnesium hydroxide, lithium hydroxide, sodium borate, sodium silicate and one or more combinations thereof.

The alkali or alkaline earth carboxylates

The alkali or alkaline earth carboxylates may be selected from the group consisting of: sodium palmitate, potassium palmitate, magnesium palmitate, sodium hydroxystearate, calcium hydroxystearate, magnesium hydroxystearate, sodium stearate, lithium stearate, potassium stearate, magnesium stearate, calcium stearate and one or more combinations thereof.

The alkali aluminosilicates

The alkali aluminosilicates may be selected from the group consisting of: sodium aluminosilicate, potassium aluminosilicate, lithium aluminosilicate and one or more combinations thereof.

The perchlorate compounds

The perchlorate compounds may be selected from compounds having the formula $M(ClO_4)_n$, wherein M is selected from the group consisting of: Li, Na, K, Mg, Ca, Sr, Zn, Al, La or Ce, and wherein n is 1, 2 or 3.

The perchlorate compounds may be complexed with alcohols (polyols, cyclodextrins) or ether alcohols or ester alcohols. The ester alcohols include also the polyol partial esters. Also suitable in the case of polyhydric alcohols or polyols are their dimers, trimers, oligomers and polymers, such as di-, tri-, tetra- and poly-glycols, and di-, tri- and tetra-pentaerythritol or polyvinyl alcohol in various degrees of polymerisation.

The perchlorate compounds can be introduced in various known forms, for example in the form of a salt or an aqueous solution applied to a substrate, such as PVC, calcium silicate, zeolites or hydrotalcites, or bound in a hydrotalcite by chemical reaction.

Phosphites and Hypophosphites

The phosphites may be selected from the group consisting of: triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris-(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl-pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecylpentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)-pentaerythritol diphosphite, bis-isodecyloxy-pentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl)pentaerythritol diphosphite, bis(2,4,6-tri-tert-butylphenyl)pentaerythritol diphosphite, tristearyl-

sorbitol triphosphite, bis(2,4-di-tert-butyl-6-methylphenyl)methyl phosphite, bis(2,4-di-tert-butyl-6methylphenyl)ethyl phosphite, phenyldidecyl phosphite, (2,4-di-tert-butylphenyl)-di-dodecyl phosphite, (2,6di-tert-butylphenyl)-di-dodecyl phosphite distearylpentaerythritol diphosphite and one or more combinations thereof.

The hypophosphite may be selected from the group consisting of: sodium hypophosphite, lithium hypophosphite, sodium hypophosphite, potassium hypophosphite, magnesium hypophosphite, calcium hypophosphite, zinc hypophosphite, titanium hypophosphite, vanadium hypophosphite, molybdenum hypophosphite, manganese hypophosphite, cobalt hypophosphite, ammonium hypophosphite, butylammonium hypophosphite, tetraethylammonium hypophosphite, N-cetylpyridinium hypophosphite and tetraphenylphosphonium hypophosphite, and one or more combinations thereof.

The β-diketones

The β-diketones may be selected from the group consisting of: dibenzoylmethane; stearoylbenzoylmethane, benzoyl 2,4-methylenedioxy benzoylmethane; benzoyl 3,5-dimethylbenzoyl methane; benzoyl 3-methylbenzoylmethane; benzoyl 4-methyl benzoylmethane; 3-methylbenzoyl 4-methylbenzoylmethane; benzoyl 4-chlorobenzoylmethane; benzoyl 2-bromobenzoylmethane; benzoyl 3,5-dichlorobenzoylmethane; benzoyl 2-nitrobenzoylmethane; benzoyl-2,3,4-trimethylbenzoylmethane; benzoyl-2,3,5-trichlorobenzoylmethane; benzoylstearoylmethane; 3-methylbenzoylstearoylmethane 3,4-dichlorobenzoylstearoylmethane benzoyl heptadecanoylmethane; 3-

methylbenzoyltetradecanoylmethane;; 2-methylbenzoylauroylmethane; 3-nitrobenzoylmyristoylmethane; 2,3-ethoxybenzoyl palmitoylmethane; 2-methoxy benzoylstearoylmethane, and one or more combinations thereof.

The sterically hindered amines

The sterically hindered amines may be selected from the group consisting of: bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(2,2,6,6-tetramethyl-4-piperidyl)succinate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl) n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, the condensate of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, the condensate of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octyl-amino-2,6-dichloro-1,3,5-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl)nitrilotriacetate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butanetetracarboxylate, 1,1'-(1,2-ethanediyl)-bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyloxy-2,2,6,6-tetramethylpiperidine, bis(1,2,2,6,6-pentamethylpiperidyl)-2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl)malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)succinate, the condensate of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensate of 2-chloro-4,6-bis(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, the condensate of 2-chloro-4,6-

bis(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidine-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidine-2,5-dione, a mixture of 4-hexadecyloxy- and 4-stearyloxy-2,2,6,6-tetramethylpiperidine, a condensation product of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, a condensation product of 1,2-bis(3-aminopropylamino)ethane and 2,4,6-trichloro-1,3,5-triazine as well as 4-butylamino-2,2,6,6-tetramethylpiperidine; N-(2,2,6,6-tetramethyl-4-piperidyl)-n-dodecylsuccinimide, N-(1,2,2,6,6-pentamethyl-4-piperidyl)-n-dodecylsuccinimide, 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4,5]decane, and one or more combinations thereof.

The phenolic antioxidant

The phenolic antioxidant may be selected from the group consisting of: 2,2-bis(4-hydroxyphenyl)propane, esters of 3,5-di-tert-butyl-4-hydroxyphenylpropionic acid with octadecanol or pentaerythritol, and tris(2,4-di-tert-butylphenyl)phosphite, tetrakis[methylene 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methane, octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate, octadecyl-3,5-di-tert-butyl-4-hydroxyhydrocinnamate, di-n-octadecyl-3,5-di-tert-butyl-4-hydroxybenzyl phosphonate, 2,6-di-t-butyl-4-methylphenol, and tris-2,4,6-(3,5-di-t-butyl-4-hydroxybenzyl)isocyanurate and one or more combinations thereof.

Commercially available phenolic antioxidants that may be used are available form Great Lakes Chemical

Corporation of Indianapolis, Indiana USA and are available under the brand names Anox™ and Lowinox™.

The Lubricants

The phenolic antioxidant may be selected from the group consisting of: glycerol monooleate, glycerol dioleate, glycerol monostearate; fatty alcohols having chain lengths in the range from C_{16} to C_{18}; phthalic acid esters of fatty alcohols having chain lengths in the range from C_{16} to C_{18} and hydrogenated castor oil such as the glycerol ester of 12-hydroxystearic acid; esters of polyhydric alcohols and short chain monocarboxylic acids such as glycerol monostearate; ethylene glycol dilaurate; 2-ethylhexane diol-1,3-distearate; ethylene glycol di-2-ethylhexanoate and octylene glycol dicaprylate; and esters of dicarboxylic acids with short chain monohydroxy-alcohols, such as diisooctyl sebacate; dilauryl azelate; oxidised polyethylene waxes, polyethylene waxes; paraffin waxes; carboxylic acids such as stearic acid, 12-hydroxystearic acid and montanic acid; carboxylates such as calcium stearate, magnesium stearate and sodium stearate; amides such as ethylene bis-stearamide and one or more combinations thereof.

The lubricants present in a stabilised halogen containing polymer, may be selected from the group consisting of: 0.01% to 2%; 0.05% to 1.8%; 0.1% to 1.5%; 0.15% to 1.45%; 0.2% to 1.4%; 0.5% to 1.35%; 1% to 1.3%; 1.1% to 1.3%; 1.2% to 1.3% and 1.25% to 1.28%.

The chlorine-containing polymer

The chlorine-containing polymer that may be stabilised by the disclosed stabiliser composition may be selected from the group consisting of: chlorinated

polyolefin, chlorinated polyolefin copolymers; polymer blends containing a chlorinated polyolefin homopolymer or copolymer; vinyl chloride homopolymers; vinylidene chloride homopolymers; vinyl chloride copolymers; vinylidene chloride copolymers and polymer blends containing vinyl chloride homopolymer or copolymers and one or more combinations thereof.

The vinyl chloride homopolymers, vinyl chloride copolymers and polymer blends containing vinyl chloride homopolymers or vinyl chloride copolymers may be selected from the group consisting of: polyvinyl chloride; polyvinylidene chloride; copolymers of vinyl chloride with a copolymerizable ethylenically unsaturated monomer such as vinylidene chloride; methyl alpha chloracrylate; vinyl chloroethyl ether; 1-fluoro-1-chloroethylene; chloroacrylonitrile; allylidene diacetate; chloroallylidene diacetate; and polymer blends such as blends of polyvinyl chloride and polyethylene; polyvinyl chloride and chlorinated polyethylene; polyvinyl chloride and polymethyl methacrylate; polyvinyl chloride and polybutylmethacrylate; polyvinyl chloride and polystyrene; polyvinyl chloride and acrylonitrile-butadiene-styrene copolymer; and polyvinyl chloride and polyethylene and polymethy methacrylate, and one or more combinations thereof.

The vinyl chloride copolymers may be selected from the group consisting of: vinyl chloride-vinyl acetate copolymer, vinyl chloride-vinylidene chloride copolymer, vinyl chloride-trichloroethylene copolymer and vinyl chloride-2-ethylhexyl acrylate copolymer.

Preparation of the stabilised chlorine-containing polymer

The stabiliser composition and a chlorine-containing polymer such as polyvinyl chloride (PVC) are mixed in a mixing device to form a substantially homogenous mixture.

The amount of stabiliser composition present in the homogenous mixture may be in the range selected from the group consisting of: 0.5% to 10%; 1% to 7.5%; 1.2% to 6%; 1.5% to 5%; 1.7% to 4.5%; 2% to 4%; 2% to 3.5%; 2% to 3% and 2.3% to 2.7%. In one embodiment, the amount of stabiliser composition present in the homogenous mixture is about 2.4%.

The stabiliser composition and the chlorine-containing polymer may initially be in the form of a powder that may be substantially homogeneously mixed.

The homogenous mixture may be heated at an elevated temperature to cause the stabiliser composition powder and the chlorine-containing polymer powder to at least partially bind. The heating temperature may be in the range between 90°C to 120°C or 100°C to 110°C.

The heating may occur for a period of time selected from the group consisting of: 10 minutes to 1000 minutes; 20 minutes to 800 minutes; 25 minutes to 600 minutes; 30 minutes to 400 minutes; 35 minutes to 300 minutes; 40 minutes to 200 minutes; 45 minutes to 120 minutes; and 50 minutes to 90 minutes.

The stabilised chlorine-containing polymer is allowed to cool and may be used as a material for further processing.

In one embodiment, the stabilised chlorine-containing polymer is placed within an extrusion device such as TWP-110-PVC twin screw extruder manufactured by Foshan Plastic Machinery Co., Ltd of Foshan, Guangdong province, China.

In another one embodiment, the stabilised chlorine-containing polymer is placed within an injection molding device such as IS-GS/GT injection molding machine manufactured by Toshiba Machine Co., Ltd. of Numazu-shi, Shizuoka-ken, Japan.

Modes for Carrying Out the Invention

Non-limiting examples of the invention will be further described.

Detailed Description of Figures

Figure 1 shows a picture of a chlorine-containing polymer (PVC 1A) with a stabilised composition next to a lead chlorine-containing polymer (comparative PVC 1B) that has been stabilised with lead.

The organic stabiliser compound

The amino-substituted pyrimidine compounds are commercially available from Sigma-Aldrich Company of St. Louis, Missouri, United States of America and include: 2-Amino-6-hydroxypyrimidine, 2-amino-6-mercaptopyrimidine, 2-*N*-methylamino-6-hydroxypyrimidine, 2-*N*-2-propylamino-6-hydroxypyrimidine, 4-amino-6-hydroxypyrimidine, 4-amino-6-mercaptopyrimidine, 4-*N*-phenylamino-6-hydroxypyrimidine, 4-methylamino-6-hydroxypyrimidine, 4-octylamino-6-hydroxypyrimidine, 5-amino-6-hydroxypyrimidine, 5-amino-6-mercaptopyrimidine, 5-*N*-butylamino-6-hydroxypyrimidine, 5-*N*-methyl amino-6-mercaptopyrimidine, 2,4-diamino-6-hydroxypyrimidine, 2,4-diamino-6-mercaptopyrimidine, 2,4-

N,N'-dimethyldiamino-6-hydroxypyrimidine, 4,5-diamino-6-hydroxypyrimidine, 4,5-diamino-6-mercaptopyrimidine, 4,5-*N,N'*-dipropyldiamino-6-hydroxypyrimidine, 4-*N*-methylamino-5-*N*-octylamino-6-hydroxypyrimidine, 2,6-diamino-6-hydroxypyrimidine, 2,6-diamino-6-mercaptopyrimidine, 2,6-*N,N'*-dibutyldiamino-6-hydroxypyrimidine, 2-*N*-butylamino-6-*N*-phenylamino-6-hydroxypyrimidine, 2,4,5-triamino-6-hydroxypyrimidine, 2,4,5-triamino-6-mercaptopyrimidine, 2-*N*-methylamino-4-*N*-butylamino-5-*N*-phenylamino-6-hydroxypyrimidine.

Example 1

A stabiliser composition was made by stirring together the following components in the amounts indicated below:

0.3 parts of 2,4-diamino-6-hydroxypyrimidine obtained from ScienceLab.com, Inc. of Kingwood, Texas, United States of America;;

0.2 parts pentaerythritol additive stabiliser from US Petrochemical Industries, Inc., of Houston, Texas, United States of America;

0.45 parts hydrotalcite additive stabiliser from Minerals Technologies Inc. of New York, United States of America;

0.05 parts octadecyl-3,5-di-tert-butyl-4-hydroxyhydrocinnamate additive stabiliser obtained from Ciba Specialty Chemicals Corporation of Tarrytown, New York, United States under the brand name Irganox 1076™;

0.1 part oxidized polyethylene wax from Clariant Corporation, of Charlotte, North Carolina, United States of America;

1.0 part polyethylene wax from Clariant Corporation, of Charlotte, North Carolina, United States of America;

0.4 parts calcium stearate from Astro Chemicals, Inc, of Springfield Massachusetts; and

0.4 parts glyceryl mono stearate from Acme-Hardesty of Blue Bell, Pennsylvania, United States of America.

The stabiliser composition was prepared by mixing the mixture in a mixer for 30 minutes under ambient temperature and atmospheric pressure. The stabiliser composition was then mixed with 100 parts by weight PVC resin, 3.0 parts of $CaCO_3$, 1.2 parts of TiO_2, and 0.001 parts of pigment at 105°C to produce a PVC compound (PVC 1A). A comparative PVC without the stabiliser composition was and with Pb stabiliser was also prepared (comparative PVC 1B) and mixed at 105 degree C.

The compositions of PVC 1A and comparative PVC 1B are shown in Table I below:

Composition	**PVC 1A**	**Comparative PVC 1B**
PVC Resin K66	100 parts	100 parts
2,4-diamino-6-hydroxypyrimidine	0.3 parts	-
Pentaerythritol	0.2 parts	-
Hydrotalcite	0.45 parts	-
Octadecyl-3,5-di-tert-butyl-4-hydroxyhydrocinnamate	0.05	-
Oxidized Polyethylene wax	0.1	-
Polyethylene wax	1.0	-
Calcium Stearate	0.4	-
Gylcerol Mono Stearate	0.4	-

Pb stabilizer composition	-	2.7 parts
$CaCO_3$	3.0 parts	3.0 parts
TiO_2	1.2 parts	1.2 parts
Pigment	0.001 parts	0.001 parts

TABLE I

PVC 1A and comparative PVC 1B underwent a plant trial for rigid pipe extrusion to produce 40mm (diameter) pressure pipes using a KMD2-90 extruder manufactured by Krauss-Maffei Process Technology AG of Munich, Germany, under the process parameters shown in Table II.

Process Parameters	PVC 1A	Comparative PVC 1B
Screw Speed (1/min)	25	25
Mass Temperature (c)	188	187
Screw Torque (%)	60	60
Output (M/min.)	4.38	4.37
Visual Appearance of the Product	Good	Good

Table II

The visual appearance of the PVC 1A and comparative PVC 1B is shown in Figure 1. Fig. 1 shows that the PVC 1A had good colour hold and was comparable to the PVC 1B, which contains lead.

In view of the above, it is concluded that the visual appearance of the product is the same as the PVC containing lead as stabiliser. Accordingly, the stabiliser composition that was used in PVC 1A provides a substituted stabiliser to the use of lead as a stabiliser.

Product Test Results

The trial pipe product made from PVC 2A was tested according to standard methods known in the art and the results of the test were shown in Table III below:

Tests	Results	Parameter Requirements
Heat Reversion Test	3.1%	Maximum 5%
Impact Test	Passed	Maximum 3 failures among 14 samples
Hydrostatic Test	Passed	No cracks
Resistance to Acetone	Passed	No delamination
Softening Point Test	80C	Minimum 75 degree C
Opacity Test	0.08%	Maximum 0.2%

Table III

Example 2

Rigid injection molding was carried out to demonstrate the performance of the stabiliser composition compared to commercially available Pb stabilisers.0.5 parts of 2,4-diamino-6-hydroxypyrimidine obtained from ScienceLab.com, Inc. of Kingwood, Texas, United States of America was mixed with the following:

0.3 parts pentaerythritol additive stabiliser from US Petrochemical Industries, Inc., of Houston, Texas, United States of America;

0.7 parts hydrotalcite additive stabiliser from Minerals Technologies Inc. of New York, United States of America;

0.8 parts Zeolite additive stabiliser from Zeolite Australia Ltd of South Melbourne, Victoria, Australia; and

0.1 parts octadecyl-3,5-di-tert-butyl-4-hydroxyhydrocinnamate additive stabiliser obtained from Ciba Specialty Chemicals Corporation of Tarrytown, New York, United States under the brand name Irganox 1076™;

0.3 part oxidized polyethylene wax from Clariant Corporation, of Charlotte, North Carolina, United States of America;

1.5 part polyethylene wax from Clariant Corporation, of Charlotte, North Carolina, United States of America; and

0.8 parts calcium stearate from Astro Chemicals, Inc, of Springfield Massachusetts.

A heat stabiliser composition was made by stirring together the following components in the amounts indicated in Table IV below:

Composition	PVC 2A	PVC 2B
PVC K58	100 parts	100 parts
Processing aid	1.0 parts	1.0 parts
TiO_2	1.5 parts	1.5 parts
$CaCO_3$	3.0 parts	3.0 parts
2,4-diamino-6-hydroxypyrimidine	0.5 parts	-
Pentaerythritol	0.3 parts	-
Hydrotalcite	0.7	-
Zeolite	0.8	-
Irganox	0.1	-
Polyethylene wax	0.3	-
Calcium stearate	1.5	-
Glyceryl mono stearate	0.8	-
Pb stabilizer composition	-	5.0 parts

Table IV

The Composition 2A and Composition 2B were mixed in a stirred tank reactor for 5 minutes at 105°C temperature and atmospheric pressure to respectively form PVC polymers 2A and 2B.

PVC polymers 2A and 2B were subjected to rigid injection molding using an injection molding machine (NC-8300) supplied by NISSEI Plastic Industrial Co.Ltd.

Injection Molding Trial Run

The trial run of the PVC polymers 2A and 2B results are tabulated in Table V as follows:

Results	PVC 2A	PVC 2B
Process Parameters		
Total Cycle Time (sec.)	58	57
Black Pressure (Mpa)	1.0	1.0
Peak Injection Pressure (Mpa)	120	122
Injection Time (sec.)	8.8	8.4
Screw Back Time (sec.)	33	33
Molded Part		
'a	0.21	0.24
'b	2.36	2.29
Charpy Impact (KJ/m2)	5.6	5.4
Vicat Softening Point (deg o)	81	80

Table V

It can be seen from Table V that PVC 2A has similar mechanical stability properties to PVC 2B. Accordingly, the stabilizer composition that is contained within PVC 2A can be used as a direct commercial substitute for PVCs that have been stabilised using lead.

Applications

The disclosed stabiliser compositions provide a stabiliser for thermally stabilising chlorine-containing polymers such as polyvinyl chloride.

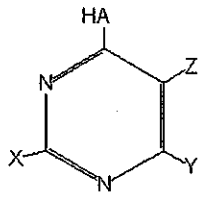
The disclosed stabiliser composition is free from metals such as lead, cadmium, tin, barium, antimony, and zinc.

The disclosed stabiliser composition may be used as a substitute for lead stabilisers, tin stabilisers, mixed metal stabilisers and known organic stabilisers.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

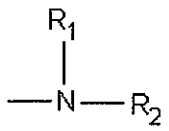
1. A stabiliser composition for chlorine-containing polymers comprising compounds represented by the general formula (I):



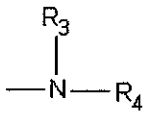
wherein X, Y, and Z are each selected independently of the other,

wherein

X is hydrogen or

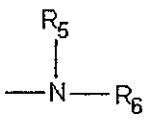


Y is hydrogen or



and

Z is hydrogen or



wherein

R1, R2, R3, R4, R5, and R6 are each independently a hydrogen, alkyl, alkenyl, cycloalkyl, cycloalkenyl, phenylalkyl and aryl group, and

wherein

A is oxygen (O) or sulfur (S).

2. A stabiliser composition as claimed in claim 1, further comprising one or more additives selected from the group consisting of: polyol compounds, alkali or alkaline earth metal compounds, alkali or alkaline earth carboxylate compounds, alkali aluminosilicate compounds, hydrotalcite ($Mg_6Al_2(CO_3)(OH)_{16}.4H_2O$) compounds, perchlorate compounds, phosphite and hypophosphite compounds, β-diketone compounds, sterically hindered amine compounds, phenolic antioxidant compounds and one or more combinations thereof.

3. A stabiliser composition as claimed in claim 1 or claim 2, further comprising a lubricant.

4. A stabiliser composition as claimed in claim 3, wherein the lubricant is selected from the group consisting of: glycerol monooleate; glyceryl mono stearate, glycerol dioleate; glycerol monostearate; fatty alcohols having chain lengths in the range from C_{16} to C_{18}; phthalic acid esters of fatty alcohols having chain lengths in the range from C_{16} to C_{18}; hydrogenated castor oil; esters of polyhydric alcohols; monocarboxylic acids; ethylene glycol dilaurate; 2-ethylhexane diol-1,3-distearate; ethylene glycol di-2-ethylhexanoate; octylene glycol dicaprylate; esters of dicarboxylic acids with short chain monohydroxy-alcohols; polyethylene waxes; paraffin waxes; carboxylic acids; stearic acid; carboxylates calcium stearate; magnesium stearate; sodium stearate; amides and one or more combinations thereof.

5. A stabiliser composition as claimed in any one of the preceding claims, wherein two or more compounds of formula 1 are linked together by a covalent bond.

6. A stabiliser composition as claimed in claim 5, wherein the two or more compounds of formula 1 are linked by a covalent bond between the A atoms.

7. A stabiliser composition as claimed in claim 5, wherein the two or more compounds of formula 1 are linked by a covalent bond between the nitrogen atoms of X, Y, or Z.

8. A stabiliser composition as claimed in any one of the preceding claims, wherein the compound of formula 1 is an amino-substituted 6-hydroxy pyrimidine compound.

9. A polymer composition comprising:

a chlorine-containing polymer; and

a stabiliser composition as defined in any one of claims 1 to 8.

10. A polymer composition as claimed in claim 9, wherein the compounds of formula 1 are present in the polymer composition within the range of about 0.1% to about 15% by weight.

11. A polymer composition as claimed in claim 9 or claim 10, wherein the compounds of formula 1 are present in the polymer composition within the range of about 0.5% to about 1%.

12. A polymer composition as claimed in any one of claims 9 to 11, when the stabiliser composition is as defined in any one of claims 2 to 8, wherein the additives are present in the polymer composition within the range of about 0.1% to 15%.

13. A polymer composition as claimed in any one of claims 9 to 12, when the stabiliser composition is as defined in any one of claims 2 to 8, wherein the lubricants are present in the polymer composition within the range of about 0.1% to 20%.

14. A polymer composition as claimed in any one of claims 9 to 13, wherein the chlorine-containing polymer is polyvinyl chloride.

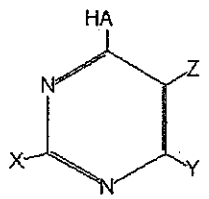
15. A polyvinyl chloride resin composition comprising polyvinyl chloride resin and a heat stabilising effective amount of a stabiliser composition according to any one of claims 1 to 8.

16. A method of preparing a stabilised chlorine-containing polymers comprising the steps of:

mixing a material comprising chlorine-containing polymer resin and a stabiliser composition according any one of claims 1 to 8; and

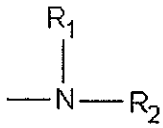
heating the mixed material for a period so as to at least partially bind the polyvinyl chloride resin and stabiliser composition.

17. A method for stabilising a chlorine-containing polymer comprising mixing said polymer with a compound represented by the general formula (I):



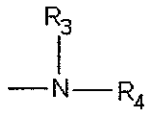
wherein X, Y, and Z are each selected independently of the other,

wherein



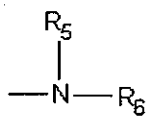
X is hydrogen or

Y is hydrogen or



and

Z is hydrogen or



wherein

R1, R2, R3, R4, R5, and R6 are each independently a hydrogen, alkyl, alkenyl, cycloalkyl, cycloalkenyl, phenylalkyl and aryl group, and

wherein

A is oxygen (O) or sulfur (S).

18. A method for stabilising a chlorine-containing polymer comprising mixing said polymer with a stabiliser composition as claimed in any one of claims 1 to 8.

19. A stabiliser composition as claimed in any one of claims 1 to 8 when used for stabilising a chlorine-containing polymer.

20. A stabilised chlorine-containing polymer when made by the method of claim 16.