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PATENTS ACT 1952

A
APPLICATION BY INVENTOR

DECLARATION IN SUPPORT OF AN APPLICATION FOR A PATENT

no. 19668/88

In support of an application made for a patent for an invention entitled:

TITLE

PROCESS FOR STABILIZING MIXTURES BASED ON HALOGENATED POLYMERS

FULL NAME AND ADDRESS OF SIGNATORY

I, SIMON KORNBAUM,

of 213, rue Benjamin-Delessert, F-69300 Caluire-et-Cuire, France.

do solemnly and sincerely declare as follows:

1. I am the applicant for the patent.

2. I am the actual inventor of the invention.

3. The basic application as defined by Section 141 of the Act was made in my name

COUNTRY

in FRANCE

DATE

on 26th June, 1987

DELETE PARAGRAPHS 3 AND 4 FOR NON CONVENTION APPLICATION

4. The basic application referred to in the preceding paragraph was the first application made in a Convention country for protection in respect of the invention the subject of this application.

PLACE AND DATE OF SIGNING

Declared at Caluire

this 6th (sixth) day at December 1989

Signed

GRIFFITH HACK & CO

PATENT AND TRADE MARK ATTORNEYS

MELBOURNE · SYDNEY · PERTH

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PROCESS FOR STABILIZING MIXTURES BASED ON HALOGENATED POLYMERS

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(57) Claim

1. A process to protect a halogenated polymer and/or copolymer-based resin blend against undesirable effects of heat during passage through a processing machine, comprising adding to the blend at least one organic compound containing one or more -SH functional groups in an amount between 0.1 and 5 parts of weight per 100 parts by weight of the resin and at least one halide chosen from organometallic halides having the following general formula:

$$R_nMe(v)Hal_{v-n}$$

wherein:

- R is a linear or branched aliphatic, cyclic, olefinic or aromatic organic residue optionally containing radicals and/or simple or mixed functional group substituents,

- n indicates the number of R groups linked to the metal represented by Me

- Me is Sn, Al, B, Sb, Fe, Cd, Zn, Cu, Ti, Hg, Bi, Mn or Ga.

... /2

- v is the valency of Me
- Hal is chlorine, bromine, iodine or fluorine

and wherein the amount of halide(s) of the metallic halide or blend of metallic halides expressed as halogen content, is between 0.1 and 30 milliequivalents of halogen per kg of resin.

10. A thermal stabilization system for the protection of a halogenated polymer and/or copolymer-based resin blend against undesirable effects of heat during passage through a processing machine comprising incorporating into the resin blend at least one organic compound containing one or more -SH functional groups in a quantity which is between 0.1 and 5 parts weight for 100 parts weight of resin and at least one halide selected from organo-metallic halides having the following general formula:

$$R_nMe(v)\ Hal_{v-n}$$

wherein:

- R is a linear or branched aliphatic, cyclic, olefinic or aromatic organic residue optionally containing radicals and/or simple or mixed functional substituents
- n indicates the number of R groups linked to the metal represented by Me
- Me is Sn, Al, B, Sb, Fe, Cd, Zn, Cu, Ti, Hg, Bi, Mn or Ga
- v is the valency of the Me
- Hal is chlorine, bromine, iodine or fluorine

and wherein the amount of halide(s) of the metallic halide or blend of halides expressed as halogen content, is between 0.1 and 30 milliequivalents of halogen per kg of resin.

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(54) Title: PROCESS FOR STABILIZING MIXTURES BASED ON HALOGENATED POLYMERS

(54) Titre: PROCEDE DE STABILISATION DES MELANGES A BASE DE POLYMERES HALOGENES

(57) Abstract

In a process for stabilizing mixtures of halogenated polymers, at least one organic compound containing one or more -SH functions and a very small amount of at least one halide chosen from the organometallic halides and/or the metallic halides, or a mixture of these compounds, are added to the mixtures during their preparation. The organic compounds containing one or more -SH functions have the formula $R(R'\text{-}SH_x)_y$ in which: R is the residue of a monohydroxylic alcohol or of a monomeric or polymeric polyol, $R'\text{-}SH_x$ is the residue of a carboxylic monoacid or polyacid containing one or more -SH functions bonded to R by esterification. The organometallic halides have the formula $R_nMe(v)Hal_{v-n}$ in which R is an organic residue, n is the number of R bonded to the metal Me, Me = Sn, Al, B, Sb, Fe, v is the valency of Me. The metallic halides have the formula $Me(v)Hal_v$ in which: Me is a metal whose halide solution containing 35 meq of halide per litre of distilled water has a pH equal ot or less than 5, and preferably equal to or less than 3, at 23°C.

(57) Abrégé

Selon ce procédé, on ajoute aux mélanges lors de leur préparation au moins un composé organique contenant une ou plusieurs fonctions -SH et une très faible quantité d'au moins un halogénure choisi parmi les halogénures organo-métalliques ou/et les halogénures métalliques, ou un mélange de ces composés. Les composés organiques contenant une ou plusieurs fonction(s) -SH présentent la formule suivante: $R(R'\text{-}SH_x)_y$ dans laquelle: R est le reste d'un alcool monohydroxylique ou d'un polyol monomérique ou polymérique, $R'\text{-}SH_x$ est le reste d'un monoacide ou d'un polyacide carboxylique, contenant une ou plusieurs fonctions -SH liée(s) à R par estérification. Les halogénures organo-métalliques présentent la formule suivante: $R_nMe(v)Hal_{v-n}$ dans laquelle: R est un reste organique, n indique le nombre de R lié au métal Me, Me = Sn, Al, B, Sb, Fe..., v est la valence du Me. Les halogénures métalliques présentent la formule suivante; $Me(v)Hal_v$ dans laquelle: Me est un métal dont le composé halogéné donne en solution aqueuse d'environ 35 meq. d'halogène par litre d'eau distillé, à environ 23°C, un pH égal ou inférieur à 5, de préférence un pH égal ou inférieur à 3.

PROCESS FOR STABILIZING MIXTURES BASED ON HALOGENATED POLYMERS

This invention concerns a stabilization process for halogenated polymer and / or copolymer-based blends during processing as well as the stabilisation systems for this purpose.

The process invented employs stabilizing compositions aimed at protecting polymers and copolymers containing halogens and especially vinyl chloride polymers and copolymers (PVC) from the undesirable effects of heat when they pass through processing machines such as calenders, extruders, mixers, injection-moulding machines and gellation tunnels.

This process allows the initially desired colour to be obtained and colour stability and thermal stability to be maintained for sufficiently long periods.

It is common knowledge that polymers and copolymers containing halogens require the addition of chemical compounds in order to make them suitable for processing with heat. These compounds are commonly called thermal stabilizers, and they have four roles to play:

a) to ensure the desired colour or absence of colour;

b) to maintain the initial colour of the melt, without embarrassing change, for a sufficiently long period;

c) to prevent the thermal degradation of the melt for a sufficiently long period and

d) in the case of finished products which must be transparent, not to alter the intrinsic transparency of the polymer.

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During processing, the temperature of the melt in the case of PVC is between 160°C and 230°C according to different factors: the nature of the PVC (flexible or rigid), the K value of the PVC and finally the shearing rate the melt is subjected to in the machine. In general the temperature of flexible PVC is between 160°C and 190°C and that of rigid PVC between 200°C and 230°C.

The length of colour stability and thermal stability for a given blend is inversely proportional to the temperature of the melt. For every 10°C rise in temperature, the length is reduced approximately by half. This means, for example, that a thermal stabilization system which is adequate for the processing of a flexible PVC at 180°C, can be totally unsuitable for the processing of rigid PVC at 220°C.

These technological particularities and considerations of stabilization cost explain why such a great range of thermal stabilizers is offered by producers in order to satisfy the large and varied market of PVC processing.

The use of organic compounds containing -SH functions as PVC stabilizers in combination with other known thermal stabilizers has been proposed.

For example, they are used:

- in association with Ba, Sr, Ca, Cd, Zn, Pb, Sn, Mg, Co, Al, Ni, Ti salts of phenols, aromatic carboxylic acids, fatty acids and epoxydized fatty acids (US-A-3144 422);
- in association with dialkylated tin carboxylates (US-A-3-063963);
- in association with organo-tin oxides or organo-antimony oxides (DE-C-1 217609).

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US-A-3 715 333 mentions the association of organo-tin trichloride with a thio-organo-tin of general formula $R_2 Sn(SR')_2$.

However, thio-organo-tin type stabilizers occupy a privileged position, especially those which correspond to the following formula:

$R_{1 \text{ or } 2} Sn (SCH_2COOC_8H_{17})_{3 \text{ or } 2}$

wherein R = methyl, butyl or octyl.

At present, this type of stabilizer is the only one able to fulfil in the simplest conditions the four-fold role mentioned above, in the case of rigid PVC processing at temperatures between 200°C and 230°C. These stabilizers are almost exclusively used for the processing of PVC into sheets and transparent rigid films, hollow bodies - except mineral-water bottles for organo-leptic reasons - and rigid tubes in the USA and Japan and partly in Europe, as a substitute for stabilizers containing lead.

The main disadvantages of these stabilizers are the complexity of their manufacture, the high tin content (14% to 20%), and the high cost.

The object of the present invention is to give compositions of thermal stabilizers which are capable of the same performances as thio-organo-tin type stabilizers in the processing of rigid PVC but which offer important advantages: simplicity of manufacture, reduction of the metal content to about 1% and a considerable reduction in the cost of stabilization.

The inventor discovered to his surprise that if a very small quantity

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of metallic or organo-metallic halide was added to blends of rigid PVC containing one or more -SH functions (thiol compound), the result was a remarkable improvement in the initial colour, a lengthening of the colour stability and of the thermal stability. These results were all the more surprising as certain metallic halides are well-known for their negative influence on the thermal stability of PVC.

The inventor found that in the case of organo-metallic halides, the improvements were progressive up to a certain added quantity, beyond which the length of colour and thermal stability both diminished.

These observations lead to a new concept in the field of PVC stabilization, namely that certain metallic halides in the presence of thiol compounds have a contrasting action which can help or hinder PVC colour and thermal stability according to the quantity added.

Furthermore, metallic halides - without organic radicals - added in very small quantities to PVC blends containing thiol compound, produce effects which are similar to those of organo-metallic halides, but the intensity of these effects depends on the degree of acidity of the metallic halide.

The stabilization process for halogenated resins according to the invention is characterized by the addition to the polymer to be protected of a system consisting of at least one organic compound containing one or more -SH functions and a very small quantity of at least one halide chosen from metallic and organo-metallic halides.

The halogenated resins the invention concerns are the homopolymers and/or copolymers of vinyl chloride, vinylidene chloride, fluoroethylene chloride with the following comonomers: vinyl acetate, acrylonitrile, maleic anhydride, ethylene, propylene, and any other monomer which is

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copolymerizable with the aforementioned vinyl halides, as well as halogenated polyolefins and other halogenated natural or synthetic polymers and elastomers.

The thiol compounds used in the process concerned by the invention have the following general formula:

$$R(R' - SH_x)_y \qquad (I)$$

wherein:

- R is a residual radical formed by the removal of the -OH group from either a monohydroxylic alcohol of any chemical nature such as: aliphatic, olefinic, cyclic, heterocyclic, aromatic, or a monomeric polyol such as: glycerine, glycol, pentaerythrite, sorbitol, pentites, hexites, monosaccharides, or a polymeric polyol such as : polyethylene-glycol, polypropylene-glycol, polyvinylic alcohol, cellulose, starch or other polysaccharides; R may include various functions such as etheroxide, and carboxylic, thiocarbonic, sulfonic ester and/or esters of other anorganic acids.

- R' $-SH_x$ is a residual radical formed by the removal of a -H group from a mono- or poly-carboxylic acid containing one or more -SH functions linked to R by esterification such as for example thioglycolic, mercapto-propionic, mercaptosuccinic, dimercaptosuccinic, or thiosalicylic acid.

- x is the number of -SH linked to R'.

- y is the number of R' $-SH_x$ linked to R.

The added quantity of organic compound containing one or more -SH functions is between 0.1 and 5 parts weight for 100 parts weight of resin and preferably between 0.3 and 1.5 parts weight for 100 parts weight of resin.

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The organo-metallic halides used in the process concerned by the invention present the following general formula:

$R_n Me(v) Hal_{v-n}$ (II)

wherein:

- R is an aliphatic, cyclic, heterocyclic, aromatic organic rest with or without radicals and/or simple or mixed functions.
- n is the number of R linked to the metal Me.
- Me = Sn, Al, B, Sb, Fe, Cd, Zn, Ti, Hg, Bi, Mn, or Ga.
- v is the valency of the Me
- Hal = chlorine, bromine, iodine, fluorine.

The metallic halides preferred in the process concerned by the invention present the following general formula:

$Me(v)Hal_v$ (III)

wherein:

- Me is a metal the halogenated salt of which, in a solution of about 35 milliequivalents of halogen per litre of distilled water at about 23°C, gives a pH which is equal to or below 5, preferably a pH equal to or below 3.
- v is the valency of the Me
- Hal = chlorine, bromine, iodine, fluorine.

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An organo-metallic or metallic halide of a single chemical species can be used, or a mixture of at least one organo-metallic halide and/or at least one metallic halide.

Because only a very small quantity is necessary, the halide should be easy to measure and disperse homogeneously in the PVC mixture. Consequently, the halide should be diluted in a solvent or an appropriate medium, for example, in one or more of the constituents of the mixture.

In the present description, the term 'blend' corresponds to the matter destined for processing, obtained by homogenization of several constituents, and whose basic constituent is one or more halogenated polymers and/or copolymers and which also contains, besides the additives I, II and/or III described above, one or more other ingredients such as: impact modifiers, processing aids, known PVC stabilizers, plastifiers, fillers, pigments, anti-static additives and any other ingredients.

The present invention will be better understood and its advantages will be made clear in the light of the following examples which are non-limitative illustrations.

PVC blends whose ingredients are given for each example are prepared in a high-speed laboratory mixer. The quantities of the ingredients are indicated in weight parts per 100 weight parts of PVC (phr). The quantities of organo-metallic and metallic halides are moreover given in brackets by the halogen content, expressed in milliequivalents of halogen per kg of PVC.

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Test method allowing the initial colour and colour and thermal stability to be determined.

A 60-gramme portion of mixture is malaxed on a two-roll laboratory mill whose rolls are heated to 210°C by the circulation of oil. The two rolls are 250 mm in diameter. During the test the distance between the rolls is kept constant at 0.6 mm. The rotation speed of the rolls is 18 r.p.m. and 20 r.p.m. respectively. A small rectangular sample is taken every minute. The samples are attached successively to a cardboard display-board. The initial colour is judged visually on the sample taken after two minutes. Colour stability is determined by the malaxing-time resulting in a change in the initial colour visible to the naked eye. The thermal stability is determined by the malaxing-time resulting in a change in colour to dark brown or dark red.

The thiol compound, pentaerythrite tetra- mercaptoacetate, is prepared in the laboratory by esterification of a mole of pentaerythrite containing about 49% of -OH functions, with four moles of mercaptoacetic acid, of an iodometric purity of 99%.

First, the acid with 2% water and 0.25% sulfonic para-toluene acid is put into the reactor. At 80°C, the pentaerythrite is added; then, the temperature is maintained at 145°C until no more water is eliminated. Then 0.25% of calcium carbonate is added and a filtration is carried out while it is hot.

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Example 1

Constituents	Blends A	Blends B
PVC "Lacqvyl S 071 s", K = 58 from ATOCHEM	100	100
Impact Modifier BTA III F from ROHM and HAAS	7	7
Lubricant AC 316 A from ALLIED CHEMICAL	0.3	0.3
Lubricant Lacer BH from LA CERESINE	0.45	0.45
Epoxydized soya bean oil	1	1
Pentaerythrite tetra mercaptoacetate	1	1
Tin mono-n-octyl trichloride (MOTCl) from SCHERING	--	0.017 (1.45)

Test results

Blend	Initial Colour	Colour Stability	Thermal Stability
A	yellowish	under 2 minutes	between 3 and 4 minutes
B	yellowish	9 minutes	12 minutes

The addition of a very small quantity of the tin mono-n-octyl trichloride quadruples the colour and thermal stability.

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Example 2

Ingredients	Blend C	D	E	F
PVC "Lacqvyl S 071 s"	100	100	100	100
BTA III F	7	7	7	7
AC 316 A	0.3	0.3	0.3	0.3
Lacer BN	0.45	0.45	0.45	0.45
Calcium Stearate	0.2	0.2	0.2	0.2
Zinc Stearate	0.2	0.2	0.2	0.2
Epoxydized soya bean oil	1	1	1	1
Pentaerythrite tetra mercaptoacetate	1	1	1	--
Tin mono-n-octyl trichloride	--	0.017 (1.45)	--	--
Tin di-n-octyl dichloride (DOTCl) from SCHERING	--	--	0.017 (0.82)	--
Thio-organo-tin stabilizer Irgastab 17 MOK from CIBA-GEIGY	--	--	--	1

Test results

Blend	Initial Colour	Colour Stability	Thermal Stability
C	yellow	8 minutes	14 minutes
D	almost colourless	11 minutes	11 minutes 30 seconds
E	light yellow	11 minutes	12 minutes
F	almost colourless	11 minutes	14 minutes

On the one hand, we can see the very clear improvement in the initial colour thanks to the addition of organo-tin chloride, and on the other, the result obtained with the D blend which is comparable to that obtained with the Irgastab 17 MOK stabilizer.

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Example 3

Ingredients	Blend			
	G	H	I	J
PVC "Lacqvyl S 071 s"	100	100	100	100
BTA III F	7	7	7	7
AC 316 A	0.3	0.3	0.3	0.3
Lacer BN	0.45	0.45	0.45	0.45
Calcium stearate	--	--	0.2	0.2
Zinc stearate	0.2	0.2	--	--
Epoxydized soya bean oil	1	1	1	1
Pentaerythrite tetra mercaptoacetate	1	1	1	1
Tin mono-n-octyl trichloride	0.017 (1.45)	0.051 (4.35)	0.017 (1.45)	0.034 (2.90)

Test results

Blend	Initial Colour	Colour Stability	Thermal Stability
G	almost colourless	8 minutes	9 minutes
H	almost colourless	5 minutes	6 minutes
I	yellowish	9 minutes	19 minutes
J	light yellow	13 minutes	19 minutes

Visibly:

- there exists a limit to the amount of organo-tin chloride to be added, beyond which colour and thermal stability diminishes.
- even in the presence of calcium soap, without addition of zinc stearate, light initial colours and excellent colour and thermal stability are obtained.

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Example 4

Ingredients	Blends				
	K	L	M	N	O
PVC "Lacqvyl S 071 s"	100	100	100	100	100
BTA III F	7	7	7	7	7
AC 316 A	0.3	0.3	0.3	0.3	0.3
Lacer BN	0.45	0.45	0.45	0.45	0.45
Epoxydized soya bean oil	1	1	1	1	1
Pentaerythrite tetra mercaptoacetate	1	1	1	1	1
Tin tetra chloride RPE from CARLO ERBA	--	0.0095 (1.45)	0.0285 (4.35)	--	--
Cadmium dichloride RPE from CARLO ERBA	--	--	--	0.0133 (1.45)	0.0399 (4.35)

The metallic halide is added to the blend as a diluted solution obtained by dissolving in 250 cc of distilled water 0.33 grammes of $SnCl_4 5H_2O$ or one gramme of $CdCl_2 2,5H_2O$, both chemically pure. The tin tetrachloride solution shows a pH value of 1.5 at 23°C and that of the cadmium dichloride a pH value of 5. Before the test on the two-roll mill, the blends were dried at 110°C for 10 minutes in an oven.

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Test results

Blend	Initial Colour	Colour Stability	Thermal Stability
K	yellowish	under 2 minutes	4 minutes
L	yellowish	between 8 and 9 minutes	11 minutes
M	almost colourless	8 minutes	between 9 and 10 minutes
N	yellowish	under 2 minutes	between 5 and 6 minutes
O	yellowish	between 4 and 5 minutes	10 minutes

It can be seen that:

- tin tetrachloride results in colour and thermal stability which are close to those obtained by tin mono-n-octyl trichloride, with the same chlorine content.
- the efficiency of cadmium dichloride is, for an equal halogen content, far below that of tin tetrachloride, doubtless because of its less acidic nature.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process to protect a halogenated polymer and/or copolymer-based resin blend against undesirable effects of heat during passage through a processing machine, comprising adding to the blend at least one organic compound containing one or more -SH functional groups in an amount between 0.1 and 5 parts of weight per 100 parts by weight of the resin and at least one halide chosen from organometallic halides having the following general formula:

$$R_nMe(v)Hal_{v-n}$$

wherein:

- R is a linear or branched aliphatic, cyclic, olefinic or aromatic organic residue optionally containing radicals and/or simple or mixed functional group substituents,
- n indicates the number of R groups linked to the metal represented by Me
- Me is Sn, Al, B, Sb, Fe, Cd, Zn, Cu, Ti, Hg, Bi, Mn or Ga.
- v is the valency of Me
- Hal is chlorine, bromine, iodine or fluorine

and wherein the amount of halide(s) of the metallic halide or blend of metallic halides expressed as halogen content, is between 0.1 and 30 milliequivalents of halogen per kg of resin.

2. A process as defined by claim 1, wherein the amount of halide(s) added to the blend, expressed as halogen content, is between 0.3 and 10 milliequivalents per kg of resin.

3. A process as defined in claim 1 or 2, wherein the metallic halides have the following general formula:

$$Me(v)Hal_v$$

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wherein:

- Me is a metal whose halogenated compound in a solution of about 35 milliequivalents of halogen per litre of distilled water at about 23°C has a pH of 5 or below,
- v is the valency of the Me
- Hal is chlorine, bromine, iodine or fluorine.

4. A process as defined by claim 3 in which the solution has a pH of 3 or below.

5. A process as defined by any one of claims 1 to 4 wherein the metal is tin.

6. A process as defined by any one of the preceding claims wherein the organic compound containing the one or more -SH functional groups has the following general formula:

$$R(R'\text{-}SH_x)_y$$

wherein:

- R is a residual radical formed by the removal of the -OH group from either a monohydroxylic alcohol selected from amongst aliphatic, olefinic, cyclic, heterocyclic or aromatic alcohols, or a monomeric polyol selected from amongst glycerine, glycol, pentaerythrite, sorbitol, pentites, hexites or monosaccharides, or a polymeric polyol selected from amongst polyethylene-glycol, polypropylene-glycol, polyvinylic alcohol, cellulose, starch or other polysaccharides optionally containing functional groups chosen amongst etheroxide, carboxylic ester, thiocarbonic ester, sulfonic ester and/or esters of other organic acids.
- R' $-SH_x$ is a residual radical formed by the removal of the -H group from either a mono- or poly-carboxylic acid, containing one or more -SH functional groups linked to R by esterification, selected from thioglycolic, mercaptoproprionic, mercaptosuccinic, dimercaptosuccinic or thiosalycilic acids.
- x indicates the number of -SH functional groups

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linked to R'.

- y indicates the number of R'-SH linked to R.

7. A process as defined in any one of the preceding claims wherein the amount of organic compound containing one or more -SH functional groups added to the resin is between 0.3 and 1.5 parts by weight per 100 parts by weight of resin.

8. A process as defined by any one of the preceding claims wherein the resin blend to be protected is based on halogenated natural or synthetic resins and/or elastomers based on homopolymers and/or copolymers of vinyl-chloride, vinylidene chloride or fluorethylene chloride, wherein the comonomers of the copolymers are chosen from amongst vinyl acetate, acrylonitrile, maleic anhydride, ethylene, propylene and/or any other monomer which is copolymerizable with the aforementioned vinyl halides, or halogenated polyolefins.

9. A process as defined in any one of the preceding claims, wherein the resin blend further comprise usual additives such as impact modifiers, plasticizers, processing aids, lubricants, fillers pigments, known thermal stabilizers or anti-static agents.

10. A thermal stabilization system for the protection of a halogenated polymer and/or copolymer-based resin blend against undesirable effects of heat during passage through a processing machine comprising incorporating into the resin blend at least one organic compound containing one or more -SH functional groups in a quantity which is between 0.1 and 5 parts weight for 100 parts weight of resin and at least one halide selected from organo-metallic halides having the following general formula:

$$R_nMe(v)\ Hal_{v-n}$$

wherein:

- R is a linear or branched aliphatic, cyclic,

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olefinic or aromatic organic residue optionally containing radicals and/or simple or mixed functional substituents

- n indicates the number of R groups linked to the metal represented by Me
- Me is Sn, Al, B, Sb, Fe, Cd, Zn, Cu, Ti, Hg, Bi, Mn or Ga
- v is the valency of the Me
- Hal is chlorine, bromine, iodine or fluorine

and wherein the amount of halide(s) of the metallic halide or blend of halides expressed as halogen content, is between 0.1 and 30 milliequivalents of halogen per kg of resin.

11. A blend based on halogenated natural or synthetic resins and/or elastomers based on homopolymers and/or copolymers of vinyl chloride, vinylidene chloride, fluorethylene chloride, wherein the comonomers of the copolymers are chosen from amongst vinyl acetate, acrylonitrile, maleic anhydride, ethylene, propylene and/or any other monomer which is copolymerizable with the aforementioned vinyl halides, or halogenated polyolefins, which blend has been protected against the effects of heat during processing by using thermal stabilizing systems containing at least one organic compound containing one or more -SH functional groups in an amount between 0.1 and 5 parts by weight per 100 parts by weight of the resin and at least one halide chosen from organo-metallic halides having the following general formula:

$$R_nMe(v)Hal_{v-n}$$

wherein:

- R is a linear or branched aliphatic, cyclic, olefinic, aromatic residue optionally containing radicals and/or simple or mixed functional substituents
- n indicates the number of R linked to the metal represented by Me
- Me is Sn, Al, B, Sb, Fe, Cd, Zn, Cu, Ti, Hg, Bi, Mn, or Ga

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- v is the valency of the Me
- Hal is chlorine, bromine, iodine or fluorine

and wherein the amount of halide(s) of the metallic halide or mixture of halides expressed as halogen content, is between 0.1 and 30 milliequivalents of halogen per kg of resin.

12. A process to protect a halogenated polymer and/or copolymer-based resin blend against undesirable effects of heat during passage through a processing machine substantially as hereinbefore described with reference to any one of the foregoing examples.

13. A thermal stabilization system for the protection of a halogenated polymer and/or copolymer-based resin blend against undesirable effects of heat during passage through a processing machine substantially as hereinbefore described with reference to any one of the foregoing examples.

14. A blend based on halogenated natural or synthetic resins and/or elastomers substantially as hereinbefore described with reference to any one of the foregoing examples.

Dated this 7th day of April, 1992
SIMON KORNBAUM
By his Patent Attorneys:
GRIFFITH HACK & CO.
Fellows Institute of Patent Attorneys of Australia.

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INTERNATIONAL SEARCH REPORT

International Application No PCT/FR 88/00332

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC C 08 K 5/00;
Int. Cl.[4] C 08 K 13/02; C 08 L 27/02; C 08 L 27/06;//(C 08 K 5/00, 5:37; 5:56);(C 08 K 5/00, 5:37, 5:57);(C 08 K 13/02, 3:16, 5:37)

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
Int. Cl.[4]	C 08 K; C 08 L

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	US, A, 3063963 (W. WOOTEN et al.) 13 November 1962, see claims (cited in the application)	1
X	US, A, 4021407 (R. GOUGH et al.) 3 May 1977, see claims; table 2, examples 21,23,25	1-3,6-11

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
3 October 1988 (03.10.88)	25 October 1988 (25.10.88)
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. FR 8800332 SA 23170

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 13/10/88
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3063963		FR-A- 1304800	
		GB-A- 1012231	
US-A- 4021407	03-05-77	DE-A,B,C 2703904	29-12-77
		AU-A- 2274977	07-09-78
		AU-B- 497668	21-12-78
		JP-A- 53007754	24-01-78
		GB-A- 1570812	09-07-80
		CA-A- 1084691	02-09-80

RAPPORT DE RECHERCHE INTERNATIONALE

Demande internationale N° PCT/FR 88/00332

I. CLASSEMENT DE L'INVENTION (si plusieurs symboles de classification sont applicables, les indiquer tous) [7]

Selon la classification internationale des brevets (CIB) ou à la fois selon la classification nationale et la CIB C 08 K 5/00; CIB[4]: C 08 K 13/02; C 08 L 27/02; C 08 L 27/06;//(C 08 K 5/00, 5:37; 5:56);(C 08 K 5/00, 5:37, 5:57);(C 08 K 13/02, ./.

II. DOMAINES SUR LESQUELS LA RECHERCHE A PORTÉ

Documentation minimale consultée [8]

Système de classification	Symboles de classification
CIB[4]	C 08 K; C 08 L

Documentation consultée autre que la documentation minimale dans la mesure où de tels documents font partie des domaines sur lesquels la recherche a porté [9]

III. DOCUMENTS CONSIDÉRÉS COMME PERTINENTS [10]

Catégorie *	Identification des documents cités,[11] avec indication, si nécessaire, des passages pertinents [12]	N° des revendications visées [13]
A	US, A, 3063963 (W. WOOTEN et al.) 13 novembre 1962, voir revendications cité dans la demande	1
X	US, A, 4021407 (R. GOUGH et al.) 3 mai 1977, voir revendications; table 2, examples 21,23,25	1-3,6-11

* Catégories spéciales de documents cités: [11]

« A » document définissant l'état général de la technique, non considéré comme particulièrement pertinent

« E » document antérieur, mais publié à la date de dépôt international ou après cette date

« L » document pouvant jeter un doute sur une revendication de priorité ou cité pour déterminer la date de publication d'une autre citation ou pour une raison spéciale (telle qu'indiquée)

« O » document se référant à une divulgation orale, à un usage, à une exposition ou tous autres moyens

« P » document publié avant la date de dépôt international, mais postérieurement à la date de priorité revendiquée

« T » document ultérieur publié postérieurement à la date de dépôt international ou à la date de priorité et n'appartenant pas à l'état de la technique pertinent, mais cité pour comprendre le principe ou la théorie constituant la base de l'invention

« X » document particulièrement pertinent: l'invention revendiquée ne peut être considérée comme nouvelle ou comme impliquant une activité inventive

« Y » document particulièrement pertinent; l'invention revendiquée ne peut être considérée comme impliquant une activité inventive lorsque le document est associé à un ou plusieurs autres documents de même nature, cette combinaison étant évidente pour une personne du métier.

« & » document qui fait partie de la même famille de brevets

IV. CERTIFICATION

Date à laquelle la recherche internationale a été effectivement achevée	Date d'expédition du présent rapport de recherche internationale
3 octobre 1988	25 OCT 1988
Administration chargée de la recherche internationale	**Signature du fonctionnaire autorisé**
OFFICE EUROPEEN DES BREVETS	P.C.G. VAN DER PUTTEN

RAPPORT DE RECHERCHE INTERNATIONALE

Demande internationale N° PCT/FR 88/00332

I. CLASSEMENT DE L'INVENTION (si plusieurs symboles de classification sont applicables, les indiquer tous) [7]

Selon la classification internationale des brevets (CIB) ou à la fois selon la classification nationale et la CIB

CIB[4]: 3:16, 5:37)

II. DOMAINES SUR LESQUELS LA RECHERCHE A PORTÉ

Documentation minimale consultée [8]

Système de classification	Symboles de classification
CIB[4]	

Documentation consultée autre que la documentation minimale dans la mesure où de tels documents font partie des domaines sur lesquels la recherche a porté [9]

III. DOCUMENTS CONSIDÉRÉS COMME PERTINENTS [10]

Catégorie *	Identification des documents cités, [11] avec indication, si nécessaire, des passages pertinents [12]	N° des revendications visées [13]

* Catégories spéciales de documents cités: [11]

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« & » document qui fait partie de la même famille de brevets

IV. CERTIFICATION

Date à laquelle la recherche internationale a été effectivement achevée	Date d'expédition du présent rapport de recherche internationale
	25 OCT 1988
Administration chargée de la recherche internationale	**Signature du fonctionnaire autorisé**
OFFICE EUROPEEN DES BREVETS	

ANNEXE AU RAPPORT DE RECHERCHE INTERNATIONALE RELATIF A LA DEMANDE INTERNATIONALE NO.

FR 8800332
SA 23170

La présente annexe indique les membres de la famille de brevets relatifs aux documents brevets cités dans le rapport de recherche international visé ci-dessus.
Lesdits membres sont contenus au fichier informatique de l'Office européen des brevets à la date du 13/10/88
Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsabilité de l'Office européen des brevets.

Document brevet cité au rapport de recherche	Date de publication	Membre(s) de la famille de brevet(s)	Date de publication
US-A- 3063963		FR-A- 1304800	
		GB-A- 1012231	
US-A- 4021407	03-05-77	DE-A,B,C 2703904	29-12-77
		AU-A- 2274977	07-09-78
		AU-B- 497668	21-12-78
		JP-A- 53007754	24-01-78
		GB-A- 1570812	09-07-80
		CA-A- 1084691	02-09-80

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