(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 December 2024 (19.12.2024)

WIPO | PCT

(10) International Publication Number
WO 2024/259026 A1

(51) International Patent Classification:
C08K 5/34 (2006.01) *C08L 27/06* (2006.01)

(21) International Application Number:
PCT/US2024/033695

(22) International Filing Date:
13 June 2024 (13.06.2024)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
63/521,125 15 June 2023 (15.06.2023) US

(71) Applicant: **LUBRIZOL ADVANCED MATERIALS, INC.** [US/US]; 9911 Brecksville Road, Cleveland, Ohio 44141-3247 (US).

(72) Inventor: **NIE, Li**; 9911 Brecksville Rd., Cleveland, Ohio 44141 (US).

(74) Agent: **DEMAS, Christopher P.** et al.; The Lubrizol Corporation, 29400 Lakeland Blvd., Wickliffe, Ohio 44092-2298 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*
— *of inventorship (Rule 4.17(iv))*

Published:
— *with international search report (Art. 21(3))*

(54) Title: HEAVY METAL FREE HALOGENATED COMPOSITIONS

(57) Abstract: The disclosed technology relates to chlorine containing polymers, such as polyvinyl chloride and its copolymers being free of heavy metals, particularly heavy metals in the form of stabilizer additives, the most common heavy metal being tin.

WO 2024/259026 A1

TITLE
HEAVY METAL FREE HALOGENATED COMPOSITIONS

BACKGROUND OF THE INVENTION

[0001] The disclosed technology relates to chlorine containing polymers, such as polyvinyl chloride and its copolymers, compounds being free of heavy metals, particularly heavy metals in the form of stabilizer additives, the most common heavy metal being tin.

[0002] Halogen containing polymers tend to degrade or deteriorate when processed. Generally, the difference between the processing temperature and the degradation temperature is very small and there is a risk that the halogen containing polymers will therefore degrade. When such polymers degrade, it is believed that the halide acid generated by the polymer attacks the components of the processing equipment. Also, this acid further catalyzes elimination reactions and additional degradation of the polymer.

[0003] Stabilizers have been developed to help deter such degradation. For example, heavy metal compounds such as tin are commonly used as heat stabilizers. However, heavy metal stabilizers are becoming disfavored as heat stabilizers for halogenated polymers due to environmental concerns.

[0004] It would be beneficial to the industry to prepare an inexpensive and readily available alternative to current stabilizer systems for halogenated resins, such as, for example, polyvinyl chloride ("PVC"), chlorinated polyvinyl chloride ("CPVC") resins, and the like.

SUMMARY OF THE INVENTION

[0005] The disclosed technology, therefore, solves the problem of providing a heavy metal free halogenated resin composition by including in the composition a barbituric acid salt derivative stabilizer.

[0006] In one aspect, the disclosed technology provides a stabilized halogenated resin composition, such as a polyvinyl chloride (PVC) or chlorinated polyvinyl chloride (CPVC) composition. The stabilized composition can comprise (a) a halogenated resin, such as PVC resin, or CPVC resin and (b) a barbituric acid salt derivative stabilizer.

[0007] In an embodiment, the barbituric acid salt derivative stabilizer can be present in the stabilized halogenated resin composition

in an amount of from about 0.1 to about 6.0 parts by weight per 100 parts by weight of said halogenated resin.

[0008] In embodiments, the composition will be substantially free, or even free of heavy metal containing stabilizers.

[0009] In another aspect of the invention, there is provided a pipe or pipe fitting made from a halogenated resin composition according to any of the above embodiments.

[0010] The present invention also provides a method of stabilizing a halogenated resin composition. The method includes employing in a halogenated resin composition a barbituric acid salt derivative stabilizer.

[0011] In an embodiment, the compositions and methods of the present technology exclude heavy metals in general, and heavy metal stabilizers in particular, such as tin stabilizers.

DETAILED DESCRIPTION OF THE INVENTION

[0012] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0013] One aspect of the invention is a rigid halogenated resin composition comprising (a) a halogenated resin, and (b) a stabilizer comprising a barbituric acid salt derivative. “Salt derivatives” is in reference to the fact that the barbituric acid will be in complex with an alkaline or alkaline earth metal.

[0014] Barbituric acid salt derivatives can be, for example, 1,3-disubstituted barbiturates, and 1,3,5-trisubstituted barbiturates. The substituents are hydrocarbyl substituents.

[0015] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

[0016] hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through

another portion of the molecule (e.g., two substituents together form a ring);

[0017] substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);

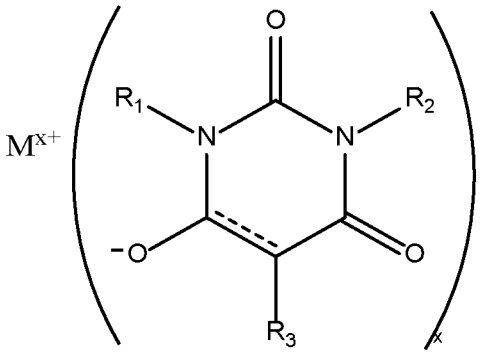
[0018] hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. Heteroatoms include sulfur, oxygen, and nitrogen. In general, no more than two, or no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; alternatively, there may be no non-hydrocarbon substituents in the hydrocarbyl group

[0019] In one embodiment the substituents can, for example, be aliphatic or aromatic substituents and may be alkyl, cycloalkyl, allyl or aryl substituents. In another embodiment, the substituents can include hetero atoms.

[0020] Barbiturates having one substituent each at position 1 and position 3 and one substituent each at positions 1, 3, and 5 may be used. In embodiments, the barbituric acid salt derivative can be a 1,3-disubstituted barbiturate or a 1,3,5-trisubstituted barbiturate, for example a N,N' 1,3-dialkylbarbiturate or a 1,3,5-trialkylbarbiturate. Metal salts are possible.

[0021] In embodiments, the barbituric acid salt derivative stabilizer can be a substituted barbiturate of the structure of Formula I set forth below,

Formula I



where each of R_1, and R_2, individually, can be a hydrocarbyl group of 1 to 18 carbon atoms, or in some cases 1 to 15 carbon atoms, or even 1 to 12 carbon atoms, or 1 to 10 carbon atoms, R_3 can be H or a hydrocarbyl group of 1 to 18 carbon atoms, or in some cases 1 to 15 carbon atoms, or even 1 to 12 carbon atoms, or 1 to 10 carbon atoms, M can be an alkaline or alkaline earth metal, and x is 1 or 2.

[0022] In an embodiment, the hydrocarbyl groups, R_1 to R_3, can be, individually, alkyl groups. The alkyl groups, R, of the barbituric acid salt derivative stabilizer can be straight chain or branched, and can include unsaturation. Often, the R groups can be alkyl groups of 1 to 18 carbon atoms.

[0023] R_1 to R_3 can also, individually, be aromatic groups, such as a benzyl or phenyl group.

[0024] In either case, the hydrocarbyl R groups can include heteroatoms, such as halogens, sulfur, oxygen, or nitrogen, for example.

[0025] The metals of the M group, when present, are not particularly limited from alkaline and alkaline earth metals, but sodium, potassium, magnesium and calcium are most often employed, with sodium more often present than not.

[0026] In an embodiment, the barbituric acid salt derivative stabilizer can include a N,N'-1,3-dimethylbarbiturate salt stabilizer, which encompasses sodium N,N'-1,3-dimethylbarbiturate. Other barbituric acid salt derivative stabilizers can include, for example, N,N'-1,3-dihexylbarbiturate salts, N,N'-1,3-didodecylbarbiturate salts, 1,3-dioctodecylbarbiturate salts, N,N'-1,3-diphenylbarbiturate salts, each

encompassing its branched and unsaturated derivatives, such as, for example, N,N'-1,3-di-*sec*-butyl-barbiturate salt, N,N'-1,3-di-*iso*-octyl-barbiturate salt, N,N'-1,3-di-*tert*-sedecyl-barbiturate salt, and N,N'-1,3-pent-1-ene-barbiturate salt, N,N'-1,3-undec-3-ene-barbiturate salt, and N,N'-1,3-(2-methylprop-1-ene)-barbiturate salt.

[0027] A halogenated polymer resin will be present in the composition at 100 parts by weight, and the concentration of all other ingredients are based on levels per 100 parts by weight of the halogenated polymer resin. The abbreviation "phr" is used in this specification to express the amount of an additive component by weight based on 100 parts by weight of the halogenated resin. The barbituric acid salt derivative stabilizer can be present in the stabilized halogenated resin composition in an amount of from about 0.1 to about 6 phr, or from about 0.1 to about 5 phr, or from about 0.1 to 4 phr. In some embodiments, the barbituric acid salt derivative stabilizer can be present in the stabilized halogenated resin composition in an amount of from about 0.25 to about 3.75, or from about 0.5 to about 3.5 phr, or from about 0.75 to about 3.25 phr, or from about 1 to about 3 phr.

[0028] The halogenated polymer resin employed in the composition is not particularly limited. Halogenated Polymer resins can include polymers used in many different applications, for example, those used in residential and commercial plumbing, such as potable water or drain, waste and vent applications; residential and commercial fire sprinkler systems; residential and commercial profile applications, such as, siding, window framing, cabinet finishes, flooring, aircraft interior, roofing tiles, cap stock and the like; industrial piping, such as chemical processing or wastewater treatment; semiconductor applications; wire and cable applications; electrical conduit; masterbatch applications, and so on, as well as the associated fittings and molded components for each application. Halogenated polymers can include, but are not limited to, for example, polymers of vinyl chloride, including homopolymers of polyvinyl chloride ("PVC") or chlorinated polyvinyl chloride ("CPVC"); copolymers of vinyl chloride with ethylene-type unsaturated compounds, such as PVC-VA (vinyl acetate) copolymers, PVC-acrylate, chlorinated polyethylene ("CPE"), poly-chloroprene and the like.

[0029] The halogenated resin can be, for example, polyvinyl chloride ("PVC"), including homopolymers of polyvinyl chloride resin(s), copolymers of polyvinyl chloride resin(s), and mixtures thereof. Copolymers of vinyl chloride are formed by the copolymerization of vinyl chloride and other monomers or monomer blends. Suitable monomers include vinyl acetate, ethylene, propylene, maleate, methacrylate, acrylate, high alcohol vinyl ester, urethane, chlorinated urethane, methylmethacrylate, and mixtures thereof.

[0030] A particular halogenated polymer for the composition can be CPVC resin, also referred to simply as CPVC. For a typical pipe or fitting resin, CPVC according to the present invention can contain less than about 11.0 mole %, or from about 1.0 to about 10.0 mole %, or from about 3.0 to about 9.0 mole % of CCl_2. In general, lower amounts of CCl_2 are desirable for a CPVC resin. In another embodiment, CPVC according to the invention can contain from about 52.0 to about 66 mole %, or from about 54.0 to about 60.0 mole % CHCl.

[0031] It is further contemplated in the present invention that the CPVC resin can contain some unsaturation (i.e., double bonds) along the backbone. CPVC according to one aspect of the invention can contain from about 0.0 to about 4.0 mole%, or from about 1.0 to about 3.0 mole%. For example, for every 100 carbon bonds in the CPVC backbone, from average of about 0.0 or 1.0 to an average of about 4.0 of the bonds can be unsaturated.

[0032] In contrast to CPVC, PVC contains only about 50% CH_2 and about 50% CHCl moieties, with no CCl_2 moieties and very near 0% unsaturation. -

[0033] CPVC can be prepared by chlorinating poly(vinyl chloride) (PVC) polymer. There are considerations pertaining to the precursor PVC from which are derived the post polymerization chlorination product (CPVC) employed in this invention. The molecular weight of PVC as indicated by intrinsic viscosity (I.V.) measurement per ASTM D1243 should generally range from about 0.4 to about 1.4 dL/g at the extremes. Desirably, the I.V. of precursor PVC employed falls within a range of from about 0.6 to about 1.4 dL/g for pipe and fittings, generally pipe is about 0.90 to about 1.05 dL/g and generally fittings are about 0.6 to about 0.8 dL/g. The preferred polymerization method for preparing said PVC is the aqueous suspension method. This is the

predominant method used in the art. A detailed description of the suspension process is beyond the scope of the invention and therefore will not be disclosed. The suspension process for polymerization of PVC is described in The Encyclopedia of PVC, Marcel Decker, Inc. (1976).

[0034] CPVC suitable for use in the instant invention may be derived from a PVC copolymer having about 5 parts or less of a co-monomer. Where the precursor PVC contains less than about 5 parts total of one or more co-monomers per 100 parts of vinyl chloride, the chlorinated version of this polymer will also be referred to herein as CPVC.

[0035] Co-monomers for both PVC and CPVC can include esters of acrylic acid wherein the ester portion has from 1 to 12 carbon atoms, for example, methyl acrylate, ethyl acrylate, butyl acrylate, octyl acrylate, cyano-ethyl acrylate, and the like; vinyl acetate; esters of methacrylic acid wherein the ester portion has from 1 to 12 carbon atoms, such as methyl methacrylate (MMA), ethyl methacrylate, butyl methacrylate, and the like; acrylonitrile, and methacrylonitrile; styrene derivatives having a total of from 8 to 15 carbon atoms such as alpha-methylstyrene, vinyl toluene, chlorostyrene; vinyl naphthalene; diolefins having a total of from 4 to 8 carbon atoms such as isoprene, and including halogenated olefins such as chlorobutadiene, monoolefins such as ethylene and propylene and having from 2 to 10 carbon atoms, desirably 2 to 4 carbon atoms and preferably 4 carbon atoms, with isobutylene being highly preferred. If co-monomers are used, preferred are MMA, co-polymerizable imides such as N-cyclohexyl maleimide and co-monomers known to co-polymerize with vinyl chloride monomer and yield a copolymer having a Tg equal to or higher than homo-PVC. The preferred CPVC is derived from a PVC homopolymer. It is also contemplated that a small portion of the solvent in which the PVC is polymerized can copolymerize therewith. For example, vinyl chloride can advantageously be prepared in the presence of a chain modifying co-reactant solvents such as, for example, THF, an ethylenically unsaturated alkylene such as an alpha olefin or a reactive mercaptan such as 2-mercapto ethanol, and small portions thereof may be present as co-monomer in the resultant PVC.

[0036] CPVC resin can include CPVC having a specified weight percent (wt%) of chlorine from about 57.0 to about 70.0 wt%, more

preferably, from about 60.0 to about 69.0 wt%, and even more preferably from about 63.0 to about 68.0 wt%, and most preferably between about 64.0 or 65.0 and 67.5 wt%. The wt% chlorine is based on the weight of the CPVC resin.

[0037] The halogenated polymer can also be chlorinated polyethylene (CPE). The CPE is a rubbery material resulting from the chlorination of polyethylene having a substantially linear structure. The polyethylene can be chlorinated by various methods including aqueous suspension, solution or gas phase methods. An example of a method for preparing CPE can be found in U.S. Pat. No. 3,563,974. Preferably, the aqueous suspension method is used to form the CPE. If used as an impact modifier, the CPE material contains from 5 to 50% by weight of chlorine. Preferably, the CPE contains from 25 to 45% by weight of chlorine. However, the CPE can comprise a mixture of chlorinated polyethylenes, provided that the overall mixture has a chlorine content in the range of about 25 to 45% by weight chlorine.

[0038] In an embodiment, the halogenated resin can be rigid. Rigid CPVC in this specification can be defined according to ASTM D883. More specifically, a rigid polymer as used herein means a polymer having a either a flexural or tensile modulus of elasticity of 700 MPa (100,000 psi) or more measured at a temperature of 23°C in an atmosphere of 50 % relative humidity when tested in accordance with Test Methods ASTM D747, D790, D638, or D882.

[0039] The halogenated polymer composition in addition to the halogenated polymer and barbituric acid salt derivative, may also include other ingredients typically added to halogenated polymer compositions. The amount and nature of these ingredients is dependent upon the end use of the composition. The ingredients and their amount can be tailored to meet the end-use needs by one of ordinary skill in the art. Examples of additives which can be used include other stabilizers, antioxidants, lubricants, other impact modifiers, pigments, glass transition enhancing additives, processing aids, fusion aids, fillers, fibrous reinforcing agents and antistatic agents.

[0040] For example, in addition to barbituric acid salt derivative stabilizers, the compositions can include other stabilizers known for halogenated polymer compositions. For example, the compositions

can include organic based stabilizers, zeolites and carboxylates, which are known stabilizers.

[0041] In simplest terms, organic based stabilizers (OB-Stabilizers) are non-metal containing stabilizers based on organic chemistry. While the OB-Stabilizers suitable for the stabilizer system herein are not particularly limited, the most prevalent OB-Stabilizer compounds today include uracil and its derivatives. A common derivative of uracil suitable as an OB-Stabilizer for the composition herein is 6-amino-1,3-dimethyluracil. Other commercially available OB-Stabilizers suitable for the present composition include, for example, the Mark™ OBS™ line of stabilizers available from Galata™.

[0042] In general, the OB-Stabilizers can be included in the composition at levels required to meet physical properties, such as color. The OB-Stabilizers can be present in an amount of from about 0.05 or 0.1 to about 2.0 parts by weight per 100 parts by weight of said CPVC resin. In some embodiment, the OB-Stabilizers can be present from about 0.15 to about 1.75 phr, or from about 0.2 to about 1.5 phr, or even from about 0.25 or 0.5 to about 1.25 phr.

[0043] Zeolites comprise basically a three dimensional framework of SiO_4 and AlO_4 tetrahedra. The tetrahedra are crosslinked through the sharing of oxygen atoms so that the ratio of oxygen atoms to the total of the aluminum and silicon atoms is equal to 2. This relationship is expressed as O/(Al+Si)=2. The electrovalence of the tetrahedra containing aluminum and silicon is balanced in the crystal by the inclusion of a cation. For example, the cation can be an alkali or alkaline earth metal ion. The cation can be exchanged for another depending upon the final usage of the aluminosilicate zeolite. The spaces between the tetrahedra of the aluminosilicate zeolite are usually occupied by water. Zeolites can be either natural or synthetic.

[0044] The basic formula for all aluminosilicate zeolites is represented as follows:

$$M_{2/n}O:[Al_2O_3]_x:[SiO_2]_y:[H_2O]_z$$

wherein M represents a metal, n represents the valence of the metal and X and Y and Z vary for each particular aluminosilicate zeolite. Essentially it is believed that any aluminosilicate zeolite can be used

as a stabilizer in the instant invention, provided that the ratio of the silicon to aluminum in such aluminosilicate zeolite is less than 3.0 and that the aluminosilicate zeolite can be incorporated into the halogenated composition. Preferably, the zeolite ratio of silicon to aluminum in such aluminosilicate zeolite is less than 1.5. Most preferably, the ratio of silicon to aluminum in such aluminosilicate zeolite is about 1.

[0045] The preferred zeolites can include, alone or in combination with another Group I metal, hydrated silicates of aluminum incorporating sodium, of the type $mNa_2O{\cdot}xAl_2O_3.ySiO_2{\cdot}zH_2O$. These preferred zeolites include zeolites A, P, X, and Y.

[0046] In the prior art, it is preferable to include the zeolite at sub-micron particle sizes (e.g., D50 by volume of less than 1 micron). However, it has been found that the at least one zeolite can be employed at any particle size distribution, particle size, and water content as a sole stabilizer, or in combination with a C_6 to C_{12} metal carboxylate and OB-Stabilizer.

[0047] In some embodiments, the zeolite can be present from about 0.25 to about 3.5 phr, or 0.5 to about 3.0 phr. In a preferred embodiment, the zeolite can be present from about 0.75 to about 1.5 or 2.5 phr.

[0048] The halogenated polymer (e.g., CPVC) compositions may also include acrylic impact modifiers. U.S. Pat. No. 3,678,133 describes the compositions conventionally referred to as acrylic impact modifiers. Generally, the acrylic impact modifier is a composite interpolymer comprising a multi-phase acrylic base material comprising a first elastomeric phase polymerized from a monomer mix comprising at least 50 wt. % alkyl methacrylate having 1-4 carbon atoms in the alkyl group and having a molecular weight of from 50,000 to 600,000 Daltons. Further, the patent states that the polymerization of the rigid thermoplastic phase is preferably conducted in such a fashion that substantially all of the rigid phase material is formed on or near the surface of the elastomeric phase. Acrylic impact modifiers are polyacrylates including (C_4-C_{12}) acrylate homo or copolymers, second stage graft copolymerized with methyl methacrylate and styrene, poly(ethylhexyl acrylate-co-butyl-acrylate) graft copolymerized with styrene, and/or acrylonitrile and/or methyl methacrylate; polybutyl

acrylate graft polymerized with acrylonitrile and styrene. Examples of suitable acrylic impact modifiers include Paraloid™ EXL-2330, KM™ 330, 334, and 365; all of which are available from Rohm and Haas. Paraloid is a trademark of the Rohm & Haas Company. Additionally, Durastrength™ 200, available from Elf Atochem, and Kane Ace™ FM-10 and FM-25, available from Kaneka, are examples of commercially available acrylic impact modifiers.

[0049] Methyl butadiene styrene ("MBS") impact modifiers can also be added to the compounds of the present invention. MBS polymers are graft polymers. Generally, MBS impact modifiers are prepared by polymerizing methyl methacrylate or mixtures of methyl methacrylate with other monomers in the presence of polybutadiene or polybutadiene-styrene rubbers. Further information on MBS impact modifiers can be found in the Second Edition of the Encyclopedia of PVC, edited by Leonard I. Nass, Marcel Dekker, Inc. (N.Y. 1988, pp. 448-452). Examples of commercially available MBS impact modifiers include Paraloid KM™ 680, BTA™ 733, 751, and 753 available from Rohm & Haas, Kane Ace™ B-22 impact modifier and Kane Ace™ B-56 impact modifier available from Kaneka.

[0050] Typical of the graft copolymer impact modifiers are those generally referred to as "ABS" resins, which may generally be described as copolymers of styrene and acrylonitrile on butadiene containing rubber. ABS modifiers are usually prepared by polymerizing styrene and acrylonitrile in the presence of polybutadiene rubber. Examples of commercially available ABS impact modifiers which can be used in the instant invention include Blendex 338, Blendex 310 and Blendex 311; all available from GE Plastics. If used as the impact modifier of choice, approximately 5 parts to about 15 parts of ABS impact modifier are used. Preferably, 6 parts of the ABS impact modifier are used.

[0051] Chlorinated polyethyelene (CPE), as discussed above, can also be employed in the composition at levels sufficient to act as an impact modifier.

[0052] Exemplary lubricants are polyglycerols of di- and trioleates, Fischer-tropsch waxes, polyolefins such as polyethylene, polypropylene and oxidized polyolefins such as oxidized polyethylene and high molecular weight paraffin waxes. Since several lubricants can be combined in countless variations, the total amount of lubricant can

vary from application to application. Optimization of the particular lubricant composition is not within the scope of the present invention and can be determined easily by one of ordinary skill in the art. Preferably, an oxidized polyethylene is used. An example of an oxidized polyethylene is AC 629A, sold by Allied Signal. In addition to the oxidized polyethylene, preferably a paraffin wax may also be included in the compounds of the instant invention. An example of a paraffin wax is Paraffin 160F Prill from Witco.

[0053] Suitable processing aids include acrylic polymers such as methyl acrylate copolymers. Examples of process aids include Paraloid K-120ND, K-120N, K-175; all available from Rohm & Haas. A description of other types of processing aids which can be used in the compound can be found in The Plastics and Rubber Institute: International Conference on PVC Processing, Apr. 26-28 (1983), Paper No. 17.

[0054] An example of antioxidants to be used in the halogen containing compounds include Irganox 1010 (tetrakis[methylene(3,5-ditert-butyl-4-hydroxy-hydrocinnamate)]methane) sold by BASF, if used at all.

[0055] Suitable pigments include among others titanium dioxide, and carbon black. Examples of titanium dioxide is Tiona RCL-6 and RCL-4 from Millennium Inorganics. An example of carbon black is Raven 410, available from Columbian Chemicals.

[0056] Suitable inorganic fillers include talc, clay, mica, wollastonite, silicas, and other filling agents.

[0057] The components of the unique compound can be made in any manner wherein the various components are added together and mixed under heat. For example, the appropriate amount of the halogenated polymer (e.g., CPVC) resin can be added to a vessel such as Henschel mixer or a ribbon blender. The remaining ingredients of the compound can then be added thereto and mixed until the blend is homogeneous. If pellets are to be formed, the compound can be melt mixed. Melt mixing can generally occur in the temperature range of about 150 to about 250°C. Once the blend is formed, it can be processed further depending upon the desired application in any conventional manner, using extrusion or molding techniques.

[0058] If extrusion techniques are used to process the composition of the present invention, generally conventional extrusion

machinery such as a multi-screw extruder or a single screw extruder are used. An extruder generally has conveying means, an intermediate screw processing means and a final die through which the material is discharged in the form of an extrudate. Generally, a multi-screw extruder is used for the extrusion of pipe. Examples of possible conventional extruders to be used to process the CPVC and PVC compounds containing the modified zeolite include the following twin screw counterrotating extruder models from Cincinnati Milacron: CM 35HP, CM 55HP, CM 65HP, CM 80HP, CM 92HP. Examples of suitable conical twin screw extruders from Krauss Maffei include KMD-2/40KK and KMD-2/50KK.

[0059] The halogenated polymer (e.g., CPVC) composition made according to the instant invention has the following characteristics: a tensile strength in the range of about 5,000 to about 10,000 psi (as measured according to ASTM D 638-95); a Notched Izod in the range of about 1.0 to about 20 ft.lb. per inch of notch (as measured according to ASTM D 256-93A); a dynamic thermal stability of greater than 14 minutes, such as, for example, in the range of about 14 to about 60 minutes as measured by ASTM D 2538), unless otherwise specified:

1) Counter rotating batch mixing bowl is set at 190°C depending on formulations, 75 grams sample is charged to the batch mixer unless otherwise specified;
2) 1 minute sample loading at 10 rpm, followed by 0.5 minutes gentle mixing at 1 rpm, followed by 35 rpm run until sample degrades. Stability timing starts at 35 rpm;
3) A small pinch sample is taken at 6 minutes after 35 rpm is achieved from the start of sample loading, and then every two minutes thereafter.

a heat distortion temperature in the range of about 80 to about 140°C. (as measured by ASTM D 648-95). This novel compound can be formed into any article desired. Examples include but are not limited to sheet, pipe, ducts, fittings, valves, injection molded and thermoformed industrial parts, appliance housing, fabricated parts, and different containers.

[0060] In a preferred embodiment, the halogenated composition can be employed to prepare pipe or pipe fitting.

[0061] Pipe or pipe fitting prepared from the halogenated compositions can meet the cell class specifications for their respective chemistries. For instance, pipes or pipe fitting made with CPVC formulations can meet a cell class of 23447 and can also be adjusted to meet 24448 cell class rating. The first numeral "2" in the cell class designation specifies the resin type, in the case of "2" the resin is for CPVC pipe or pipe fitting; the second numeral (whether "3" or "4") specifies the level of notched Izod impact strength where "3" indicates at least 80.1 J/m (1.5 ft.lb/in) of notch, and "4" indicates at least 266.9 J/m (5 ft.lb/in) of notch; the third numeral "4" specifies tensile strength of at least 48.3 MPa (7,000 psi); the fourth numeral "4" specifies tensile modulus of at least 2482 MPa (360,000 psi); and the fifth numeral (whether "7" or "8") specifies the level of DTUL or HDT measured under 1.82 MPa (264 psi) load. Numeral "7" indicates DTUL or HDT of at least 100 C, and "8" indicates DTUL or HDT of at least 110 C (see ASTM D1784).

[0062] Pipes or pipe fitting made of PVC can meet cell class 12444. The first numeral "1" in the cell class designation specifies the resin type is PVC; the second numeral specifies the level of notched Izod impact strength where "2" indicates at least 34.7 J/m (0.65 ft.lb/in) of notch; the third and fourth numeral are the same as for CPVC above; and the fifth numeral "4" indicates DTUL or HDT of at least 70 C (see ASTM D1784).

[0063] In another aspect, the invention includes a method of stabilizing a halogenated polymer (e.g., CPVC) composition. The method comprises the step of employing in the halogenated polymer composition a barbituric acid salt derivative.

[0064] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic or anionic sites of other molecules. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present

invention encompasses the composition prepared by admixing the components described above.

[0065] The invention herein is useful for preparing stable halogenated compositions and particularly halogenated compositions that can be extruded into pipe or molded into pipe fitting, which may be better understood with reference to the following examples.

EXAMPLES

[0066] Sample Preparation Procedure - Resin wet coated with stabilizers - For stabilizers that are water soluble, the resin is wet blended and dried. 1.5 phr stabilizer is dissolved into a 15 phr total water solution as a stabilizer solution. A 15 phr water solution is added to 100 phr PVC with a blender and mixed into a wet cake with uniform mixing. The wet resin cake obtained is dried in a flat tray at room temperature overnight inside a natural vent hood to reach equilibrium moisture state (naturally dried).

[0067] Stabilizers - Sodiumdimethylbarbiturate is prepared by neutralizing 1,3-dimethylbarbituric acid with equal molar amount of NaOH. 15 phr water solution containing 1.5 phr sodiumdimthylbarbiturate is blended with 100 phr PVC following the above wet blend method.

[0068] Other stabilizers are available as powders. All powder ingredients are mixed together using a Ware blender.

[0069] DTS Measurement - The Dynamic Thermal Stability (DTS) is measured according to ASTM D 2538. A longer DTS time is indicative of a compound with enhanced stability.

[0070] The Brabender™ DTS batch mixer is used to study melt stability. One way to determine stability time is with visual inspection of the melt appearance, indicates degradation time. At the point of melt color degradation, the melt color typically will show a very visible pinkish, brown or even darkened color starting with a white or tan white color. Monitoring color change is also a good way to study melt stability by pinching out a small melt chip for the color record at selected time intervals. Higher DTS stability is preferred.

[0071] The DTS procedure used herein is as follows, unless otherwise specified:

1) Counter rotating batch mixing bowl is set at 190°C depending on formulations, 75 grams sample is charged to the batch mixer unless otherwise specified
2) 1 minute sample loading at 10 rpm, followed by 0.5 minutes gentle mixing at 1 rpm, followed by 35 rpm run until sample degrades. Stability timing starts at initial sample loading ;
3) A small pinch sample is taken at 6 minutes from the start of operation, and then every 2 minute thereafter.

Example 1 Tan color hold stability using DTS sample pinching method

[0072] Table 1 below shows formulations containing various amounts of acid scavenging stabilizers and 0.25 phr of an OB-Stabilizer 6-amino-1,3-dimethyluracil, blended together in a compound with a 0.92 IV PVC resin, along with other additives. The amount of stabilizer is fixed at 1.5 phr per 100 phr of PVC. 101.5 indicates the PVC is wet coated with 1.5 phr stabilizer. Otherwise, 1.5 phr stabilizer is shown separately in the formulation examples.

[0073] Table 1 also provides the color stability time. The formulations presented above are tested for color hold stability in a tan colored compound.

[0074] Color hold stability is another measure of melt stability. A small sample of the compound is taken using a sampling plier during DTS melt mixing. No more than 0.5 gram melt is pinched out at a time. Trimmed color chip is typically at 0.25-0.3 gram.

Table 1 Stabilizer performance Examples

	exam-ple 1	exam-ple 2	exam-ple 3	exam-ple 4	exam-ple 5	ex-am-ple 6
PVC (0.92IV)			100	100	100	100
PVC (0.92IV) wet coated with 1.5 phr Na dimethylbarbiturate	101.5					
PVC (0.92IV) wet coated with 1.5 phr Na barbiturate		101.5				
Beta-diketone co-stabilizer						1.5
tin stabilizer				1	1.25	
zeolite			1.5			
Uracil derivative stabilizer	0.25	0.25	0.25			0.25
TiO2	3.5	3.5	3.5	3.5	3.5	3.5
MBS impact modifier	7	7	7	6	6	6

oxidized polyethylene	0.9	0.9	0.9	1	1	1
Fischer Tropsch wax	1.5	1.5	1.5	1.3	1.3	1.3
Anti-Oxidant	0.25	0.25	0.25	0.25	0.25	0.25
color stability time (mins)	14	< 6	8	12	13	8

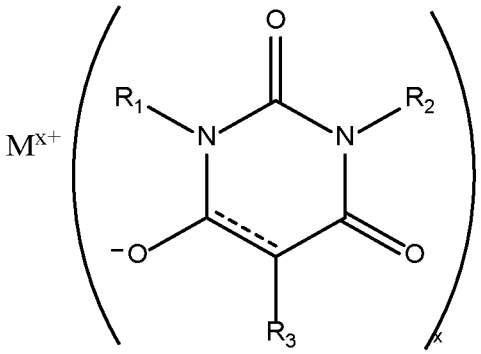
[0075] Each of the documents referred to above is incorporated herein by reference, including any prior applications, whether or not specifically listed above, from which priority is claimed. The mention of any document is not an admission that such document qualifies as prior art or constitutes the general knowledge of the skilled person in any jurisdiction. Except in the examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements.

[0076] As used herein, the transitional term “comprising,” which is synonymous with “including,” “containing,” or “characterized by,” is inclusive or open-ended and does not exclude additional, un-recited elements or method steps. However, in each recitation of “comprising” herein, it is intended that the term also encompass, as alternative embodiments, the phrases “consisting essentially of” and “consisting of,” where “consisting of” excludes any element or step not specified and “consisting essentially of” permits the inclusion of additional un-recited elements or steps that do not materially affect the basic and novel characteristics of the composition or method under consideration.

[0077] While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of the subject invention. In this regard, the scope of the invention is to be limited only by the following claims.

What is claimed is:

1. A halogenated polymer (e.g., chlorinated polyvinyl chloride (CPVC, PVC) composition comprising (a) a halogenated polymer (e.g., PVC, CPVC resin), and (b) barbituric acid salt derivative.
2. The halogenated polymer composition of claim 1, wherein the barbituric acid salt derivative comprises a compound of Formula I,



where each of R_1, and R_2, individually, is a hydrocarbyl group of 1 to 18 carbon atoms, R_3 is H or a hydrocarbyl group of 1 to 18 carbon atoms, M is an alkaline or alkaline earth metal, and x is 1 or 2.

3. The composition of any previous claim, wherein said barbituric acid salt derivative stabilizer is present in an amount of from about 0.1 to about 6.0 parts by weight per 100 parts by weight of said PVC and CPVC resins.

4. The composition of any previous claim wherein said composition is substantially free of or free of heavy metal containing stabilizers.

5. The composition of any previous claim further comprising a co-stabilizer selected from the group consisting of organic based stabilizers, zeolite, and combinations thereof.

6. The halogenated polymer composition of any previous claim wherein the halogenated polymer is a PVC resin having about 57 weight% chlorine.

7. The halogenated polymer composition of any previous claim wherein the halogenated polymer is a CPVC resin having from about 64 to 68 weight% chlorine.

8. A pipe or pipe fitting comprising a halogenated polymer (e.g., PVC, CPVC) composition according to any previous claim.

9. The pipe or pipe fitting of claim 7, wherein said pipe or pipe fitting meets cell class 23447 to24448.

10. The pipe or pipe fitting of claim 7, wherein said pipe or pipe fitting meets cell class 12444 to 14454.

11. A method of stabilizing a halogenated polymer composition comprising employing in the composition a barbituric acid salt derivative.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/033695

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K5/34 C08L27/06
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 105 802 067 A (GUANGZHOU HUANGLONG BIOTECHNOLOGY CO LTD) 27 July 2016 (2016-07-27) claims 1-6 -----	1-4,11
X	US 4 105 627 A (SEKIGUCHI TETSUO ET AL) 8 August 1978 (1978-08-08) example 5 table 1 claims 1-20 ----- -/--	1,3-5,11

[x] Further documents are listed in the continuation of Box C.

[x] See patent family annex.

* Special categories of cited documents :

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

"E" earlier application or patent 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 when the document is taken alone

"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

Date of the actual completion of the international search	Date of mailing of the international search report
24 September 2024	02/10/2024

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Neumeier, Michael

2

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/033695

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SHUMIN LI ET AL: "Effect of thermal stabilizers composed of zinc barbiturate and calcium stearate for rigid poly(vinyl chloride)", POLYMER DEGRADATION AND STABILITY, BARKING, GB, vol. 96, no. 4, 27 December 2010 (2010-12-27), pages 637-641, XP028365408, ISSN: 0141-3910, DOI: 10.1016/J.POLYMDEGRADSTAB.2010.12.011 [retrieved on 2011-01-13] bullet poins 2.3 and 3.3	1,3-11

A	MOHAMED N A ET AL: "Organic thermal stabilizers for rigid poly(vinyl chloride) I. Barbituric and thiobarbituric acids", POLYMER DEGRADATION AND STABILITY, BARKING, GB, vol. 70, no. 1, 1 January 2000 (2000-01-01), pages 5-10, XP004295012, ISSN: 0141-3910, DOI: 10.1016/S0141-3910(00)00054-9 table 2	1-11

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2024/033695

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 105802067 A	27-07-2016	NONE	
US 4105627 A	08-08-1978	NONE	