LOW MOLECULAR WEIGHT BROMINATED POLYMERS AND THEIR USE IN THERMOPLASTIC FORMULATIONS

TECHNICAL FIELD

[0001] This invention relates to flame retardant compositions containing brominated anionic, chain transfer, vinyl aromatic polymers, hereinafter brominated "ACTVAP". The compositions can accommodate high bromine content while still exhibiting a low thermally labile bromine content. The compositions have glass transition temperatures, T_g that are predictive of acceptable melt flows in high impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene (ABS) based formulations. Articles produced from such formulations have good heat distortion temperatures. The compositions, are suitable flame retardant candidates for use in thermoplastic formulations, *e.g.* HIPS and ABS formulations.

BACKGROUND

[0002] Brominated polystyrenic (styrenic polymer) compositions have long been used as flame retardants in thermoplastic formulations. Brominated polystyrenes can be produced by bromination of polystyrenes, the polystyrenes being derived by free-radical or anionic polymerization of styrenic monomer, see for example, commonly-owned U.S. Pat. Nos. 5,677,390, 5,686,538, 5,767,203, 5,852,131, 5,852,132, 5,916,978, ~~6,113,381,~~ 6,207,765, 6,232,393, 6,232,408, 6,235,831, 6,235,844, 6,326,439, and 6,521,714.

[0003] While the forgoing compositions have and are meeting considerable commercial success, the skilled artisan is always searching for the next generation product that shows commercial promise.

SUMMARY OF THE INVENTION

[0004] This invention relates to flame retardant compositions comprising a brominated anionic, chain transfer, vinyl aromatic polymer (ACTVAP), wherein the compositions: (i) contain at least about 72 wt% bromine; and (ii) contain less than about 1,000 ppm (weight/weight) thermally labile Br, the wt% and ppm values being based upon the total weight of the composition. Within the invention scope are compositions in which the brominated ACTVAP is brominated anionic, chain transfer styrene polymer (ACTSP).

[0005] ACTVAP and ACTSP, as used herein, are acronyms for, in the first case, vinyl aromatic polymer, and, in the second case, styrene polymer that have been anionically

reduced heat distortion temperature (HDT) for articles produced from the flame-retarded HIPS or ABS.

[0016] In the following "Detailed Description of the Invention" further description is given for the compositions of this invention. The compositions to which the description applies, in part or in whole, are within the scope of the inventions disclosed herein.

[0017] Thermoplastic articles containing any one or more of the compositions of this invention are within the scope of the invention.

DETAILED DESCRIPTION OF THE INVENTION

Compositions of this Invention

[0018] Compositions of this invention are predominant in brominated ACTVAP or ACTSP. Generally, the compositions will contain at least about 97 wt% brominated ACTVAP or ACTSP, with the remainder being by-product impurities. Such impurities are, for the most part, by-products of either the polymerization or bromination processes used to ultimately obtain the brominated ACTVAP or ACTSP. Most preferred flame retardant compositions of this invention contain from about 99 to about 99.95^{+} wt% polymer based on the total weight of the composition.

[0019] Base ACTVAP can be represented by the formula:

$$Ar\text{-}CRH[\text{-}CH_2CH(Ar)]_{n\ average}\text{-}CH_2CH_2\text{-}Ar,$$

~~wherein Ar is an aryl group, R is a C_1—C_4 alkyl group and $n_{average}$ is the average number of repeating units and is based on the number average molecular weight, M_n, of the ACTVAP distribution. $n_{average}$ is calculated:~~

~~$n_{average}=(M_n - \text{formula wt ArCRH} - \text{formula wt ArCH}_2\text{CH}_2)/(\text{formula wt ArCH}_2\text{CH}_2)$~~

[0020] Base ACTSP are those having the structure:

$$C_6H_5\text{-}CH_2[\text{-}CH_2CH(C_6H_5)]n_{average}\,CH_2CH_2\text{-}C_6H_5$$

wherein the average $n_{\ average}$ value is determined by the formula:

$$n_{\ average} = (M_n - 196.29) / 104.15.$$

[0021] The method of determining the M_n for ACTVAP and ACTSP is described in the "Analytical Methods" section hereof.

to about 5 bromine substituents per aryl group (on an individual not average aryl group basis). The term "polymer distribution" means the total polymer constituents as measured by GPC analysis of the flame retardant composition and includes any brominated monoadducts present as a polymer constituent of the distribution. It does not include residual chain transfer agent or styrene monomer if present. As mentioned previously, since the compositions of this invention are very high in brominated ACTVAP or ACTSP, the number of bromine constituents in the compositions of this invention is essentially the same as for the brominated ACTVAP or ACTSP. The average number of bromine substituents is calculated by a combination of wt% bromine via XRF and GPC measurement for M_n. The calculation is illustrated as follows:

For 1 mole of material with the formula,

~~$C_6H_{(5-x)}Br_xCH_2(C_6H_{(5-x)}Br_xCHCH_2)CH_2CH_2C_6H_{(5-x)}Br_x$~~

where x is the average number of bromine atoms per phenyl group.

then,

$x = Br_{moles} / Phenyl_{average}$

Total moles of Bromine (Br_{moles}) is given by:

$Br_{moles} = (M_{n\,(brominated)}) \cdot (wt\%\ Br / 80)$

The average number of phenyl rings in one mole ($Phenyl_{average}$) is given by

$Phenyl_{average} = 2 + n_{average}$

where:

$n_{average} = (M_{n\,(unbrominated)} - 196.29) / 104.15$

and:

$M_{n\,(unbrominated)} = M_{n\,(brominated)} \cdot (1 - wt\%\ Br/100)$,

therefore x is given by

$x = Br_{moles} / Phenyl_{average} = M_{n\,(brominated)} \cdot (wt\%\ Br / 80) / 2 + n_{average}$

$x = M_{n\,(brominated)} \cdot (wt\%\ Br / 80) / (2 + [(M_{n\,(unbrominated)} - 196.29) / 104.15])$

$x = M_{n\,(brominated)} \cdot (wt\%\ Br /80)/(2 + [(M_{n\,(brominated)} \cdot (1 - wt\%\ Br/100) - 196.29) / 104.15])$

The x values are given for each of the Brominated Examples in Table I.

[0029] The wt% bromine is affected by selection of the process parameters for the bromination of the base ACTVAP or ACTSP. Parameters, such as, bromination time, catalyst used, catalyst amount, reaction solvent, reaction temperature and the amount of

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