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(19)

(54) SELF-EXTINGUISHING POLYMERIC COMPOSITIONS

(71) We, MONTEDISON S.P.A., of Large Donegani 1/2, 20121 Milano, Italy, an Italian Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to self-extinguishing compositions based on polymeric thermo-plastics materials including polymers or copolymers of ethylenically unsaturated materials, such as polypropylene, polyethylene, ethylene-propylene copolymers, EPDM rubbers, polystyrene and ABS resins, polyesters such as polyethylene terephthalate and polybutylene terephthalate, polycarbonates and polyamides.

Various processes for rendering such thermoplastic materials fire-proof are known in the art; such processes are generally based on the use of metal compounds, particularly of antimony, in combination with thermally unstable halogenated compounds, such as chlorinated paraffin waxes.

Such metal compound/halogenated compound combinations provide satisfactory results as regards the self-extinguishing properties they impart to the polymers, but they exhibit serious drawbacks: corrosion phenomena in the machinery where the materials are processed and a strong evolution of toxic fumes and gases in the event of fire. Furthermore, acceptable levels of self-extinguishing power are attained only by employing such combinations at high concentration.

It is an object of the invention to provide self-extinguishing polymeric thermoplastics materials, and additives for imparting self-extinguishing qualities to thermoplastics materials, which are relatively free from the drawbacks described above.

The invention consists in a self-extinguishing thermoplastic composition based on polymeric thermoplastics material, comprising, for 100 parts by weight of the composition, from 5 to 30 parts by weight of an ammonium phosphate and from 3 to 20 parts by weight of one or more nitrogen-containing compounds selected from (a) those containing one or both of the groups

$$>C=O \text{ and } >C=S,$$

together with the group >NH in a cyclic structure; (b) those containing the group

$$—CO—NH—(CH_2)_n—$$

in which n is an integer having a value of at least 1, and (c) the reaction products of compounds (a) or (b) with aldehydes.

The invention also consists in a combustibility-reducing additive for polymeric thermoplastics compositions, comprising an ammonium phosphate mixed with a nitrogen-containing compound selected as defined above, in such proportions that for 5—30 parts by weight of the ammonium phosphate, 3—20 parts by weight of the nitrogen-containing compound are present.

The thermoplastic composition to which the phosphate and nitrogen-containing compound are added may be a polymeric thermoplastics material or such a material with other ingredients, e.g. inert filler, plasticiser, antioxidant, etc.

Among the various ammonium phosphates which may be used, preference is given to the ammonium polyphosphates having the general formula

$$(NH_4)_{n+2}P_nO_{3n+1},$$

wherein n is an integer equal to or higher than 2, the molecular weight preferably being high enough to ensure low solubility in water.

When n is sufficiently high, the material is substantially a metaphosphate $(NH_4PO_3)_n$. An example of such polyphosphates is that known under the trade name "Albaplas AP 95" (produced and sold under Benckiser Knapsack GmbH), having the composition

$(NH_4PO_3)_n$, wherein n is higher than 50; another example is the product known under the trade mark Phos-Chek P/30 (Monsanto Chemical Co.) and having a similar composition.

Some representative examples of suitable nitrogen-containing compounds are: ethylene urea, ethylene thiourea, hydantoin, hexahydropyrimidine-2-one, piperazino-3, 6-dione, barbituric acid, uric acid, indigotin, Nylon 6 and Nylon 66. The nitrogen-containing compounds are preferably employed in the form of reaction products with an aldehyde, in particular with formaldehyde. Such reaction products offer the advantage of being free from bad smells, as well as being relatively water-insoluble and in general more compatible with the polymers to which they are to be added. They may be prepared by known methods.

Thus, for instance, to prepare the ethylene thiourea/CH_2O reaction product, ethylene thiourea is dissolved in water in an amount of 50 g/liter, acidified to pH 2 by adding a dilute acid (for example sulphuric or phosphoric acid), heated to 90°C and an aqueous solution of 37% w/w formaldehyde is added dropwise to the solution, kept at 90°C and stirred intensively, until a CH_2O/ethylene-thiourea molar ratio of 2 is reached. The resulting precipitate, in the form of a very fine powder, is filtered, washed with water and dried.

To prepare the hexahydropyrimidine-2-one/CH_2O reaction product, hexahydropyrimidine-2-one and an aqueous solution of 37% w/w formaldehyde are introduced into the flask of a rotary evaporator at a molar ratio CH_2O/hexahydropyrimidine-2-one of 2, the mixture is acidified as indicated above up to pH 2 and is then heated in an oil bath kept at 120°C whilst evaporating the water present under reduced pressure and in a stream of nitrogen. The bath temperature is raised progressively to 180°C until any remaining moisture is removed (including water of reaction), the resulting dry product is ground to a fine-grain powder and is washed with water until neutral.

The thermoplastic compositions according to the present invention can be prepared by conventional methods: for instance, the polymer and the flame-proofing additives may be mixed in a blade mixer of the Banbury type at the polymer plasticizing temperature, the resulting mix then being extruded in a DOLCI type extruder (screw diameter 20 mm; screw length/diameter ratio 23; screw speed 20 r.p.m.) at the appropriate temperature to give a granulated product, such temperature varying with the nature of the polymer composition.

To determine the self-extinguishing properties of the polymeric compositions of this invention (and any control samples), the following procedure is adopted: The granular product is moulded to sheets of 3 mm thickness by means of a small press of the CARVER type ("CARVER" is a Registered Trade Mark), working for 7 minutes at a pressure of 40 kg/cm² and at a suitable temperature, according to the polymer composition being tested. The level of the self-extinguishing power is determined on the sheets so prepared either by measuring (according to standard ASTM D—2863) the oxygen index, which expresses the minimum percentage of O_2 in a O_2/N_2 mixture required by the sample to burn continuously, or by applying standards UL—94 (published by the "Underwriters Laboratories"—U.S.A.), which provide an evaluation of the self-extinguishing degree of plastics materials.

Standards UL—94 provide for different, more or less severe test conditions and permit classification of the sample at different self-extinguishing levels. In the tests set out in Tables I and II hereinafter, the "Vertical Burning Test" has been adopted, which permits classification of the material at the decreasing levels 94V—0, 94V—1 and 94V—2.

Each test is conducted on a group of 5 specimens that may have a thickness of ¼", 1/8 or 1/16". The specimen, kept in a vertical position by means of a suitable stand, is primed with a flame at its lower end, and two ignition attempts are effected (at the two ends of the specimen), each attempt lasting 10 seconds.

The three above-mentioned self-extinguishing levels may be defined briefly as follows:

94V—0 No specimen burns for more than 10 seconds after each application of the flame or drops burning particles. Moreover, the total combustion time does not exceed 50 seconds for the 10 attempts made on the 5-specimen group.

94V—1 Combustion times up to 30 seconds for an individual specimen and up to 250 seconds for the 10 attempts made on the 5-specimen group are allowable. Also at this level no specimen drops burning particles.

94V—2 The allowable combustion times are the same as for level 94V—1, but the fall of burning particles is allowed.

The two following Tables show the results achieved in tests carried out with polypropylene, polyethylene, polystyrene, an ABS resin, a polyamide and a blend of polypropylene/EPDM rubber.

TABLE I

Self-extinguishing compositions based on polypropylene

Ingredients	Parts by Weight														
	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14	Ex. 15
Polypropylene	75	75	75	80	70	70	75	80	75	70	75	73	73	75	70
Albaplas AP 95 (ammonium polyphosphate)	17	17	17	17	15	15	17	15	15	18	17	17	20	17	15
Hexahydropyrimidine-2-one	8	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Hydantoin	–	8	–	–	–	–	–	–	–	–	–	–	–	–	–
Hexahydropyrimidine-2-one/formaldehyde	–	–	8	3	–	–	–	–	–	–	–	–	–	–	–
Nylon 6, ground	–	–	–	–	15	–	–	–	–	–	–	–	–	–	10
Nylon 66, ground	–	–	–	–	–	15	–	–	–	–	–	–	–	–	–
Ethylene-thiourea/formaldehyde	–	–	–	–	–	–	8	5	–	–	–	–	–	–	–
Ethylene-thiourea	–	–	–	–	–	–	–	–	10	12	–	–	–	–	–
Ethyleneurea/formaldehyde	–	–	–	–	–	–	–	–	–	–	8	10	7	8	5
Oxygen Index	28	27	32.5	29.5	27	27	32	28.5	28	31	32.5	33.5	30.5	33.5	35
UL–94 (1/8")	–	–	–	–	–	–	V–O	V–O	V–O	V–O	V–O	V–O	V–O	V–O	V–O

TABLE II

Self-extinguishing compositions based on polyethylene or polystyrene or ABS resin or polyamide or blend polypropylene/EPDM rubber

Ingredients	Parts by Weight							
	Ex. 16	Ex. 17	Ex. 18	Ex. 19	Ex. 20	Ex. 21	Ex. 22	Ex. 23
Polyethylene	65	–	–	–	75	–	–	–
Polystyrene	–	65	–	–	–	–	–	75
ABS resin	–	–	65	–	–	–	75	–
Polyamide from caprolactam	–	–	–	80	–	–	–	–
Blend polypropylene/EPDM rubber	–	–	–	–	–	75	–	–
Albaplas AP 95 (ammonium polyphosphate)	20	20	20	15	17	17	17	17
Ethylene-thiourea	15	15	15	–	–	–	–	–
Hexahydropyrimidine-2-one/formaldehyde	–	–	–	5	–	–	–	–
Ethyleneurea/formaldehyde	–	–	–	–	8	8	8	8
Oxygen Index	28	27	28.5	27.5	27.5	26.5	28.5	32
UL–94 (1/8")	V–O	V–O	V–O	V–O	V–O	V–O	V–O	V–O

WHAT WE CLAIM IS:—

1. A self-extinguishing thermoplastic composition based on polymeric thermoplastics material comprising, for 100 parts by weight of the composition, from 5 to 30 parts by weight of an ammonium phosphate and from 3 to 20 parts by weight of one or more nitrogen-containing compounds selected from (a) those containing one or both of the groups

$$>C=O \text{ and } >C=S,$$

together with the group >NH in a cyclic structure; (b) those containing the group

$$—CO—NH—(CH_2)_n—$$

in which n is an integer having a value of at least 1, and (c) the reaction products of compounds (a) or (b) with aldehydes.

2. A composition according to claim 1, in which a polyphosphate having the composition $(NH_4PO_3)_n$, wherein n is higher than 50, is employed as ammonium phosphate.

3. Polymeric compositions according to claim 1 or 2, in which the nitrogen containing compound is ethylene urea, ethylene thiourea, hexahydropyrimidine-2-one, hydantoin, Nylon 6 or Nylon 66.

4. A composition according to claim 1 or 2, in which a reaction product of formaldehyde with a nitrogen containing compound as set forth in claim 3 is employed as nitrogen containing compound.

5. A composition according to claim 1 or 2 in which the nitrogen-containing compound used is one of those hereinbefore specifically referred to.

6. A composition according to any preceding claim, in which the polymeric material is polypropylene, polyethylene, polystyrene, an ABS resin, a polyamide or a polypropylene EPDM rubber blend.

7. Polymeric compositions according to claim 1, substantially as hereinbefore exemplified.

8. A combustibility-retarding additive for thermoplastics materials, comprising an ammonium phosphate mixed with a nitrogen-containing compound as hereinbefore defined, in proportions such that for 5—30 parts by weight of the former there are 3—20 parts by weight of the latter.

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