[54] FIRE RETARDANT AGENT

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Related U.S. Patent Documents

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[51] Int. Cl. ................................. C08C 11/04

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[57] ABSTRACT

A fire retardant agent comprising calcium or magnesium mineral borates or calcium or magnesium metal borate and a halogen source; a method of rendering organic materials generally of a hydrocarbon nature, such as plastic and rubber polymers, cellulose, resins and oils, etc., fire retardant by introducing into said organic materials calcium or magnesium mineral borates or calcium or magnesium metal borate and a halide; articles, laminates, coatings, foams, papers, fabrics, etc., containing calcium or magnesium mineral borates or calcium or magnesium metal borate and a halide of atomic weight greater than 19.

38 Claims, No Drawings
FIRE RETARDANT AGENT

Matter enclosed in heavy brackets [ ] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention is directed to the use of certain specific types of mineral borates, especially calcium or magnesium mineral borates of a generally water-insoluble nature, as flame retardants for organic materials, which borates are employed in a composition containing a source of a halogen of an atomic weight greater than 19. This invention is also directed to imparting to latex foam substances, such as those substances used in carpet backing, increased flame-retardancy by including in the latex foam a water-insoluble mineral borate, such as colemanite or other calcium or magnesium mineral borate. The latex foam contains a source of halide such as chloride, such as provided by polyvinyl chloride, or a chlorinated, brominated, or iodated organic compound.

2. Discussion of the Prior Art

Borates including some of the mineral borates have been used as fire retardant agents in the past, such as in extinguishing forest fires. Borax and the sodium cation containing materials are generally water-soluble, therefore causing incompatibility problems in some systems. There is also another major obstacle to their being used in that they are leached out when in contact with a water environment or as in washing or laundering. Hydrated zinc borates are effective fire retardants. However, due to the cost of manufacturing these products, they find application only in specialty products where their high cost is justified. Halogenated materials have also been used as fire retardant agents. Both borates and halogenated materials, when used alone, however, require large amounts of either to be effective.

What has now been discovered is that a composition comprising a relatively crude, inexpensive mineral borate and a halogenated organic material has a synergistic effect in that when only small amounts of each component are employed, significant effective flame retardancy is provided. Such composition, therefore, is an efficient low-cost flame retardant agent.

Numerous fire retardant agents have been proposed for flammable organic materials. Due to current and anticipated Government regulations on items such as carpets there has been an unprecedented desire and demand for effective, economical fire retardants.

SUMMARY OF THE INVENTION

Broadly, this invention contemplates a composition for imparting fire-retardant properties, which composition comprises a calcium or magnesium mineral borate or a calcium magnesium meta borate and a source of a halogen having an atomic weight greater than 19.

In a particularly desirable embodiment, this invention contemplates a method for rendering a flammable material more fire retardant, which method comprises introducing into said organic material a calcium or magnesium mineral borate or a calcium or magnesium meta borate and a source of a halogen of an atomic weight greater than 19.
in the chain. The halides contemplated within the invention include, specifically, chlorine, bromine and iodine. Additional sources of halogen include halogenated aromatic compounds, especially with aryl groups, such as C6-C18. Included within this group are phenyl naphthyl and anthracenyl compounds. Of these, halogenated phenyl compounds are desired. The phenyl compound can be a polyhalogenated compound which supplies one or more halide atoms to the composition. Indeed, the phenyl compound can supply several types of halides such as would be supplied by 2 bromo, 1,3 dichlorobenzene. It will be realized that the aryl group, especially the phenyl group, can be substituted to any desired extent provided there exists an available halide. Thus the same can have other substituents on the ring, such as amino, imino, alkoxy, nitrite, nitroso, sulfone, alkyl, especially C1-C8, acetyl and the like, including ortho, para and meta directors.

Other halogenated organic compounds useful include:

Halogenated acids where the halogen is an anioncarbon atom especially C3-C24 saturated and unsaturated fatty acids;

Polyethers such as polyethylene glycol derivatives;

Ketones where at least one substituent attached to the carbonyl has at least 4 carbon atoms, preferably 4 to 12;

Aldehydes where the substituent attached to the carbonyl group is at least 4 carbon atoms, especially C4 to C12;

Anhydrides of the halogenated acids;

Alcohols, both primary and secondary, which are the reduction products of the aldehydes or ketones set forth above, i.e., having 4 to 12 carbon atoms or a group attached to the carbon atom bearing the OH radical;

Acid halides, especially C2 to C10 acid halides;

Saccharides, especially mono- di- and polysaccharides, including starch and cellulose.

There are also contemplated derivatives of the above, such as the esters of the acids and the thio derivatives of the acids, aldehydes, ketones and alcohols set forth above.

Additionally, the following aryhyl compounds in halogenated form can be employed:

Aryl compounds having C6 to C12 aryl radicals, especially phenyl. These can be substituted as follows or can be unsubstituted (aside from the halogen): Substitutes include:

Either especially where the organic group attached to the oxygen contains at least 4 carbon atoms; or

Aldehyde especially where the organic radicals attached to the oxygen atom contains at least 4 carbon atoms, e.g., C4-C12;

Ketone, especially where at least one organic group attached to the oxygen atom has at least 4 carbon atoms, e.g., C4-C12;

Alkenyl, especially C4-C12;

Alcohol, especially C4-C12, whether primary or secondary;

Hydroxy, e.g., 1 hydroxy 2 chloro phenyl;

Sulfonate

Nitrate

Acid radical, especially C2-C10 acid halide

Cya

 Mercapto

Amine

Dicarboxylic acid and its anhydride, especially phthalic acid anhydride.

Other agents hexachloro and hexabromo benzene. Especially contemplated are materials which are at least 50% halogenated by weight. Decabromodiphenyl oxide [Dow FR-300-BA] a new fire retardant agent. Especially included is hexachlorocyclopentadene and chloroprene.

Additionally, the following can be employed:

its acids, mixed acids, bi-acids, mixed esters, biesters and anhydrides.

In the formula R can be H, C1-C12 alkyl or a halogenated derivative thereof.

Examples of particularly suitable highly chlorinated materials useful in the present invention include:

1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene

1,2,3,4-tetrachlorocyclopentadiene nonachlorobicyclo[3.2.0]heptane-2

1,2-dichloro-3,4,5,5-hexafluorocyclopentadiene decachloropentacyclo[5.3.0.0^2,5.0^4,9]decan-3-one octachlorocyclopentene bis(pentachloro-2,4-cyclopentadien-1-yl)

1,2,3,5,5,6-hexachloro-4-(dichloromethylen)cyclopentene

perchloropentacyclo[5.2.1.0^2,5.0^3,0^5,9]decane

2,3,4,4,5-pentachloro-2-cyclopentene-1-one

1,2,4-trichlorocyclopentene-3,5-dione

1,2,3,4,7,7-hexachlorobicyclo[2.2.1]2-5 heptadiene

1,4,5,6,7,7-hexachlorobicyclo[2.2.1]5-heptene-2,3-dicarboxylic acid

1,4,5,6,7,7-hexachloro-2,3-bis(chloromethyl)biclyclo[2.2.1]-5-heptene

1,4,5,6,7,7-hexachloro-2-(1,2-dichloroethyl)-biclyclo[2.2.1]-5-heptene

1,4,5,6,7,7-hexachloro-2-carboxy-bicyclo[2.2.1]-5-heptene

1,4,5,6,7,7-hexachloro-2,3-bis(hydroxyethyl)methylbiclyclo[2.2.1]-5-heptene

undecachloropentacyclo[5.3.0^2,4,0^6,6,0^9,3]-decylochlorosulfonate

4,5,6,7,8,8-hexachloro-3a, 7a-dihydro-4,7-methanodine

1,2,3,4,10,10-hexachloro-1,4,4a, 5,8,8a-hexahydro-1,4-endo, exo, 5,8-dimethanonaphthalene

1,4,5,6,7,7-hexachloro-2-formylbicyclo[2.2.1]-5-heptene

1,4,5,6,7,7-hexachloro-2-cyanobicyclo[2.2.1]-5-heptene

Hexachlorocyclopentenes

Halogenated heterocyclics, especially those containing between 5 and 8 members in the ring and containing, as a component of the ring, a nitrogen, sulfur or oxygen atom, can be suitably employed. Contemplated within these definitions are included materials such as furan, pyridine and other nitrogen-containing heterocyclics such as pyrimidin.

The synergistic composition of the present invention is useful in a wide variety of flammable materials. Generally speaking, the composition is useful in all organic materials which are flammable. Most polymeric and resinous compositions are organic and are therefore flammable.
The resinous compositions can be of any resin, including polymers of alpha olefins, especially polyethylene, polypropylene, polybutene-1, polyisobutylene, vinyl polymers, including polymers of vinyl chloride, methyl methacrylate, ethyl methacrylate, acrylonitrile, vinyl alcohol, vinyl acetal, vinyl butyral and styrene, polyamide, especially nylon 6 and nylon 6/6, polycetals, polyurethanes, polyesters; also polymers classified as rubbers or latexes such as natural rubber, polystyrene-butanediene-acrylonitrile; acrylic, chlorosulfonated polyethylene, ethylene-propylene, ethylene-propylene-diene terpolymers, polyisoprene-acrylonitrile, polybutadienes, polychloroprenes, polyprene, polyisoprene, and polyurethanes.

There are also included condensation polymers such as phenol-formaldehyde and urea-formaldehyde polymers, polycarbonates and, for that matter, all organic thermoplastic and thermosetting resins and polymers such as epoxy resins.

A particular use of the composition of the present invention is in the field of latex foams. Thus, it has been discovered a styrene-butadiene rubber latex foam can be rendered flame-retardant by removing a portion of the SBR latex and substituting for such portion a polyvinyl chloride latex material. Such material not only is compatible with the SBR latex to accomplish the purposes for which the latex is used, but also the polyvinyl chloride contributes the desired source of halogen, so that no additional halide need be added to the composition. The composition is complete when it contains the added calcium or magnesium mineral borate. Latex foams which contain, initially, an adequate amount of chlorine, bromine, or iodine need not have added thereto a material which acts as a source of a halogen, it being sufficient that the mineral borate be added thereto. Other latex materials which can be treated include natural rubber, acrylic, isoprene, acrylonitrile, nitrile, polybutadiene, polyisobutylene, polyisoprene, vinyl pyridine, especially when they contain a source of halogen of atomic weight of at least 19.

Other organic materials which can be rendered more flame-retardant include fibrous materials such as cotton, polyester, nylon, acrylics, non-woven and woven fabrics of natural and synthetic fibers, paper, Kraft cardboard, adhesives, molded plastics, compressed paper employed in the building industry in lieu of plywood sheathing, and egg cartons.

The amount of mineral and source of halogen will vary depending upon the type of mineral and the type of halogen source employed. Generally speaking, the mineral will be present in the material to be protected in an amount between 2 and 400 phr (parts per hundred of organic material, e.g., resin) preferably in an amount between 5 and 50 phr. The parts are on a weight basis. Similarly, the source of halogen will be present, such that the halogen itself is present in an amount between 1 and 100 phr, preferably between 2 and 20 phr, based upon the weight of the resin being rendered flame retardant. The relation of mineral borate and halogen generally satisfy the following ratios: 1 to 8 parts by weight mineral borate; 1 part by weight halogen. Preferably the ratio is 1 to 4:1. Naturally, these ratios are satisfied in different manners by different materials, owing to their different polymer systems, the purity of the borate ore, and the atomic weight and effectiveness of the different halogens and the number of halogen atoms on the compound supplying the same.

It has been found, surprisingly, that mixed mineral borates having a relatively high concentrate of nonbo rate materials can be used as such, i.e., in a nonrefined state, pursuant to the present invention. The concentration of borates are normally reported as to their percentage of boric oxide (B₂O₃). Thus it has been found that the borate can be present together with other minerals in an amount between 15 and 55 percent by weight, based upon the weight of the boric oxide. For example, gangue materials which can be present together with the borate include earth (soil), bentonite clay, and other normally associated mineral silicates and carbonates.

However, in certain instances, it is preferred that the mixed mineral borate be refined, so that it has a purity of at least 45 percent B₂O₃. Different mineral types and grades to be employed are dependent on such factors as type of borate ore, mine location, purity and assay of ore, as well as other processing refinements.

In order to more fully illustrate the nature of the invention and the manner of practising the same, the following examples are presented:

**EXAMPLE 1**

**FIRE RETARDANT NO GEL LATEX FOAM**

<table>
<thead>
<tr>
<th>FOR-</th>
<th>MULA</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Pliolite LPE3717E) (NO GEL)</td>
<td>129.0</td>
<td>129.0</td>
<td></td>
</tr>
<tr>
<td>(SBR latex)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Geon 354 (Q) (polyvinyl)</td>
<td>19.0</td>
<td>19.0</td>
<td></td>
</tr>
<tr>
<td>(latex)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Super GLS (6) (alkyl sulfonate) (s</td>
<td>3.75</td>
<td>3.75</td>
<td></td>
</tr>
<tr>
<td>(wetting agent)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Sodium tripolyphosphate</td>
<td>4.0</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>(NH₄OH)</td>
<td>5.0</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>(Acrylod G5 (1) (polycrylamide</td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>(thickener)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Spata fill (7) (Feltonpare</td>
<td>200.0</td>
<td>160.0</td>
<td></td>
</tr>
<tr>
<td>(II) (Colemanite = calcium borate of</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(formula 2 CaO B₂O₃ 3H₂O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(III) (Care Paste (sulfur &amp; rubber</td>
<td>10.0</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>(accelerators)</td>
<td>370.75</td>
<td>370.75</td>
<td></td>
</tr>
</tbody>
</table>

**NO GEL LATEX FOAM PROCEDURE**

Mixed slowly part IA until thoroughly blended. Added part IB, thickeners, to desired viscosity. Added Part II, fillers, flame retarders, and pigments with intermediate stirring until dispersed. Added Part III, with stirring. Foamed with 6 minutes at high speed on blender, poured out onto substrate and drawn down to desired thickness, generally three eights inches thick. Cured 20 min. at 150° C.

**FIRE RETARDANT TEST - HORIZONTAL MATCH TEST**

Foam samples of the above materials, 1 inch x 5 inches x 1 inch, were supported horizontally and a burning match was positioned under the leading edge of the foam samples for 5 seconds. Failure to self-extinguish within 1 inch of the edge is considered failing.

**TEST RESULTS:**

The A samples had to be extinguished after burning for more than 1 inch and therefore failed. The B samples self-extinguished in less than 1 inch and therefore passed.
EXAMPLE II

<table>
<thead>
<tr>
<th>FIRE RETARDANT TYPE LATEX FOAM</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Pholite 5532D (5) (SBR Latex)</td>
<td>119.0</td>
<td>119.0</td>
<td>119.0</td>
</tr>
<tr>
<td>(Geon 354 (2) (PVC copolymer)</td>
<td>27.0</td>
<td>27.0</td>
<td>27.0</td>
</tr>
<tr>
<td>(PTPP (potassium triphosphate)</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>(Alipal CD436 (8) (Wetting agent)</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>(50% K2CO3)</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>10% KOH</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

II

| (Cure Paste (Sulfur & rubber accelerators) | 20.5 | 20.5 | 20.5 |
| (20% Potassium oleate)                    | 20.0 | 20.0 | 20.0 |
| (Water to Balance)                        | 2.0  | 2.0  | 2.0  |
| (Spartacil (7) (Feldspar)                 | 160.0| 179.0| 197.0|

III

| (Colameinate)                          | 40.0 | 20.0 |      |
| (Thermogard S (SbO3)2 (21))            |      | 1.0  | 3.0  |
| (NH4O2H)                               | 2.0  | 2.0  | 2.0  |
| (Alquart 750 g (Quaternary Ammonium Compound) | 3.0  | 3.0  | 3.0  |

IV

| (Water)                                | 4.0  | 4.0  | 4.0  |
| (20% Potassium Oleate)                 | 3    | 3    | 3    |

V

| (25% Ammonium Acetate)                  | 10.0 | 10.0 | 10.0 |

416.5 416.5 416.5

PROCEDURE FOR LATEX FOAM

Part I was stirred slowly as Part II was added and mixed in. Part III was then added gradually, and foamed for 2 minutes at high speed.

Part IV is added and mixed one minute, then Part V is added and mixed for 40 seconds.

The foam is poured onto the substrate, drawn down, gelled for 30 seconds under heat lamps, and then cured for 20 min. at 150° C.

TEST AND RESULTS

Samples from A, B, and C were exposed to the 5 second horizontal match test.

Sample A (Colameinate and PVC) Passed Sample B (Colameinate, Sb2O3 and PVC) Passed Sample C (Sb2O3 and PVC) Failed

EXAMPLE III

<table>
<thead>
<tr>
<th>FLAME RETARDANT PLASTISOL</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Dioctyl) phthalate</td>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td>(Paraplex G62 (3) epoxy plasticizer)</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>(Nuostab V1216 (4) (Ba &amp; Cd) (fatty acid stabilizer))</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>(Alcolex S (Sulfonated wetting agent))</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>(Cerystil Boracite (1) (Ulexite &amp; (Colameinate)</td>
<td>—</td>
<td>75</td>
</tr>
</tbody>
</table>

II

| (Atomite (22) (Calcium Carbonate)) | 75   | —    |
| (Geon 121 (2) (Polyvinyl chloride) (dispersion grade)) | 500  | 500  |

IV

| (30% CaO paste) | 5    | 5    |

975 grams 975 grams

PLASTISOL PROCEDURE

Part II was added to Part I and dispersed with a Cowles Dissoverter. Part III was then added and dispersed followed by Part IV. The plastisol was evacuated, drawn down, and fused.

TEST AND RESULTS:

Film samples of the above materials 0.5 inches wide and 0.14 inches thick, were supported horizontally and a burning match was positioned under the leading edge of the plastisol samples for 5 seconds. Upon removal of the flame, the B samples self-extinguished within 8 seconds, and burned less than 1/16 inch, passing the test.

The A samples burned over 1 inch (completely) and were considered to have failed.

EXAMPLE IV

<table>
<thead>
<tr>
<th>FLAME RETARDANT POLYESTER FORMULAS</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyfit 31-586 (polyester resin)</td>
<td>34.1</td>
<td>34.1</td>
</tr>
<tr>
<td>Dione BR 6399 (chlorinated polyester resin)</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>BPO Paste (Benzyol peroxide)</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>80 WSA (Talc) (16)</td>
<td>60.0</td>
<td>35.0</td>
</tr>
<tr>
<td>Colameinate</td>
<td>25.0</td>
<td>—</td>
</tr>
</tbody>
</table>

100.0 100.0

PROCEDURE:

The materials were mixed, molded into one quarter inch rods, cured for 15 min. at 300° F.

The samples were exposed to a modified match test. The samples were positioned at 45° down from the horizontal to increase the severity of the flame test. Otherwise the match was again held at the leading edge of the sample for 20 seconds.

The sample passes if it self-extinguishes before burning 1 inch.

RESULTS:

Formula A failed the match test. Formula B passed.
EXAMPLE V
Flame Retardance and Prevention of Dripping of Polypropylene

Polyolefins are very flammable due to their wax like structure. Also, when they are ignited they melt and run or drip, thereby carrying and spreading the flame.

It is therefore advantageous that where flame retardance is necessary that the resin also be prevented from running and spreading the flames.

The following compositions were tested:

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 g</td>
<td>100 g</td>
<td>100 g</td>
<td>100 g</td>
</tr>
<tr>
<td>CHEX BC 26 (20) (Organic Chemical containing Cl and Br)</td>
<td>3 g</td>
<td>3 g</td>
<td>6 g</td>
</tr>
<tr>
<td>COLEMANITE</td>
<td>40 g</td>
<td>-</td>
<td>40 g</td>
</tr>
<tr>
<td>80 WSA TALC (16)</td>
<td>100 g</td>
<td>103 g</td>
<td>143 g</td>
</tr>
</tbody>
</table>

PROCEDURE
The extruded samples were cut into strips, held in a vertical position and the top edge was ignited by holding a match to it for 20 seconds. Failure results from not self-extinguishing within an inch.

RESULTS
Sample A failed and ran.
Sample B failed and ran.
Sample C passed and no running.
Sample D failed and ran.

CONCLUSIONS:
The addition of the Citex at this level was not sufficient to make the polypropylene flame retardant and non-dripping. The addition of the Colemanite effected both desired results. The addition of the inert talc effected neither of the desired results when added with double the amount of Citex, which is an organic chemical containing both aliphatic bromine and chlorine.

EXAMPLE VI
Flame Retardant Paper

Brown Kraft paper was made flame retardant and self-extinguishing by the addition of Colemanite and vinyl chloride-vinylidene chloride copolymer, whereas the paper containing double the amount of either material alone remains flammable.

PROCEDURE FOR SAMPLE PREPARATION:
3 grams of brown kraft paper was rederbized with 450 cc of water in a Waring Blender. Two coats of the paper was then reformed on a screen, press dried on felt and finally dried in an oven for 30 min. at 100° C. and stored in a dessicator until testing for flame resistance. Three other papers were made by adding the following per coat:

<table>
<thead>
<tr>
<th>MATERIALS</th>
<th>CONTROL</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft Paper</td>
<td>3 g</td>
<td>3 g</td>
<td>3 g</td>
<td>3 g</td>
</tr>
<tr>
<td>Colemanite</td>
<td>2.4 g</td>
<td>1.2 g</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Geon 652 (2) (s)</td>
<td>-</td>
<td>2.4 g</td>
<td>4.8 g</td>
<td></td>
</tr>
</tbody>
</table>

TEST PROCEDURE:
The dry paper sample materials are cut into 1 inch wide strips. These strips are suspended horizontally in a draft free hood and the leading edge of each strip when tested is ignited with a burning match. The material passes if the sample self-extinguishes within an inch of the ignited edge. The material fails if it's samples do not extinguish themselves within this limit.

EXAMPLE VII
Flame Retardance of Polystyrene

The following materials were heated, blended, molded, and cooled. They were then exposed to the 20 second horizontal match test.

<table>
<thead>
<tr>
<th>MATERIALS</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Piccolastic D 150 (10)(Polystyrene Resin)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Hexabromobenzene (II)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Colemanite</td>
<td>-</td>
<td>10</td>
</tr>
</tbody>
</table>

Match test results
Failed | Passed

EXAMPLE VIII
Flame Retardance of Rubber

The following formulas were made by combining their ingredients on a 2-roll rubber mill, calendaring and curing in a mold for 20 min. at 300° F. The cured rubber specimens were cut into 1 inch x 6 inch x 1 inch samples and were exposed to flame tests.

<table>
<thead>
<tr>
<th>MATERIALS</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Rubber (NR)</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Polyflex 1502 (SBR/5)</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Epsin 40 (BDPDM) (12)</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Chlorobutyl 10-68 (HR)</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Chlorowax 70 (14)(Chlorinated Paraffin)</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>P-S 166 (XxO) (15)</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Colemanite</td>
<td>-</td>
<td>60</td>
</tr>
</tbody>
</table>

The flame test consisted of laying the samples flat horizontally and lighting the leading edge of the sample with a match held to the sample for 20 seconds.
sample is judged to pass if itself extinguishes within one inch of the edge.

RESULTS:
Formul A consistently failed the flame test, whereas Formula B passed.

RAW MATERIAL SUPPLIERS

1. U.S. Borax & Chemical Corp.
2. B. F. Goodrich Chemical Co.
3. Rohm and Haas Co.
4. Tenneco Chemicals Inc.
5. Goodyear Co.
6. Alcolac Chemical Corp.
7. Spartan Minerals Co.
8. GAF
9. Armak Company
10. Pennsylvania Industrial Chemical Corp.
11. East Coast Chemicals Inc.
12. Copolymer Rubber and Chemical Corp.
13. Enjay Chemical Co.
14. Diamond Shamrock Chemical Co.
15. New Jersey Zinc Co.
16. International Talc Co., Inc.
17. E. I. du Pont de Nemours and Co.
18. Stauffer Chemical Co.
19. Pennsalt Chemical Corp.
20. Cities Service Co.
22. Reichhold Chemicals Co.
23. Thompson, Weinman and Co.
24. Hercules Inc.

What is claimed is:

1. A fire retardant agent comprising a calcium [or magnesium] mineral borate or a calcium [or magnesium] borate and a halogen source, said halogen having an atomic weight greater than 19.

2. A composition according to claim 1 wherein the calcium [or magnesium] borate is selected from the group consisting of 2CaO·B₄O₇·H₂O; CaO·B₂O₅·H₂O; CaO·B₂O₅·3H₂O; 2CaO·B₂O₅·13H₂O; 2CaO·B₂O₅·5H₂O; 2CaO·B₂O₅·2H₂O; CaO·B₂O₅·2H₂O; Colemanite, [Boracite, [Sassolite, Ulexite, Tertschite, Pro- briteite, Princeite, Pandermite, Inyoite, Meyerhoffiterite, Nobleite, Gowerite, Ginorite, Calchborite, Inderborite, Hydroborocite,] K₂O·CaO·4B₂O₅·12H₂O; (NH₄)₂·CaO·4B₂O₅·12H₂O and Na₂O·CaO·5B₂O₅·16H₂O; Pinnoite, Ascherite, Szabiehite, Inderite, Kurnakovite, Preobrazhenskite, MgO·2B₂O₅·8·5H₂O; MgO·3B₂O₅·7·5H₂O; MgO·3B₂O₅·5H₂O; Smantanite, (NH₄)₂O·MgO·3B₂O₅·15H₂O and (NH₄)₂O·MgO·3·B₂O₅·7H₂O.

3. A composition according to claim 2 wherein the calcium [or magnesium] borate preferably has a negligible solubility in water at 25°C.

4. A composition according to claim 2 wherein the halogen source is selected from the group consisting of halogen-containing polymers, halogen-containing rubbers, halogen-containing phenolics, halogenated aliphatic compounds and halogenated aromatic compounds.

5. A composition according to claim 4 wherein the halogen source is selected from the group consisting of halogenated acids where the halogen is on a non-carbonyl atom, said acid having between 3 and 24 carbon atoms and being saturated or unsaturated, polyethers, ketones where at least one substituent attached to the carbonyl has between 4 and 12 carbon atoms, aldehydes where the substituent attached to the carbonyl group has between 4 and 12 carbon atoms, anhydrides of halogenated acids where the halogen is on a non-carbonyl atom and the group attached to the carbonyl atom has between 3 and 24 carbon atoms, primary alcohols in which the group attached to the OH radical has between 4 and 12 carbon atoms, secondary alcohols in which at least one group attached to the carbon atom to which the OH radical is attached has between 4 and 12 carbon atoms, acid halides of C₃ to C₁₂ atoms, monosaccharides, polyaccharides, starch, cellulose, esters of said acids, thio-derivatives of said acids, aldehydes, ketones and alcohols where the sulfur atom replaces the oxygen atom, aryl compounds of C₄ to C₁₈ carbon atoms, aryl ethers where the organic group attached to the oxygen atom contains at least 4 carbon atoms, aryl aldehydes where the organic radical attached to the oxygen atom contains between 4 and 12 carbon atoms, aryl ketones where at one organic group attached to the oxygen atom has between 4 and 12 carbon atoms, alkyl aryl compounds where the alkenyl group contains between 4 and 12 carbon atoms, aryl alcohols where at least one organic radical attached to the carbon bearing the hydroxy group has between 4 and 12 carbon atoms, hydroxy aryl compounds, sulfonated aryl compounds, nitrated aryl compounds, aryl acid halides of C₃ to C₁₂ atoms in the acid halide group, cyano aryl compounds, mercapto aryl compounds, amine aryl compounds, aromatic dicarboxylic acids and their anhydrides, cyclic and heterocyclic organic acids having between 5 and 10 members in the ring.

6. A composition according to claim 2 wherein said halogen source is selected from the group consisting of a compound having the formula

\[
\begin{align*}
\text{O} & \quad \text{C} \\
\text{H} & \quad \text{O} \\
\text{Br} & \quad \text{OH}
\end{align*}
\]

its acids, mixed acids, bi-acids, mixed esters, bi-esters and anhydrides, wherein R can be H, C₁₋C₁₂ alkyl or a halogenated derivative thereof, 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene, 1,2,3,4-tetrachlorocyclopentadiene, nonachlorobicyclo[3.2.0]heptene-2, 1,2-dichloro-3,4,5,5-tetrafluorocyclopentene, deca-chloropentacyclo[5.3.0.0².0⁵.0⁸]decane-3-one, octachloropentacyclo, bis(pentachloro-2,4-cyclohexadiene-1-yl), 1,2,3,4,5,5-hexachloro-4-(dichloromethylene)cyclopentene, perchloropentacyclo[5.2.1.0².0⁵.0⁸]decane, 2,3,4,4,5-pentachloro-2-cyclopentene-1-one, 1,2,4-trichlorocyclopentene-3,5-dione, 1,2,3,4,7-hexachlorobicyclo[2.2.1.1]2,5-heptadiene, 1,4,5,6,7,7-hexachlorobicyclo[2.2.1.1]2,5-heptene-3,2-dicarboxylic acid, 1,4,5,6,7,7-hexachloro-2,3-bis(chloromethyl)-bicyclo[2.2.1]5-heptene, 1,4,5,6,7,7-hexachloro-2-(1,2-dichloroethyl)-bicyclo[2.2.1]5-heptene, 1,4,5,6,7,7-hexachloro-2-carboxybicyclo[2.2.1]5-heptene, undecachloropentacyclo[5.3.0.0².0⁵.0⁸]dec-3-ecyclosulfonate, 4,5,6,7,8,8hexachloro-3a, 7a-dihydro-4,7-methano-indene, 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-end, exo-5,8-dimethanophthalene, 1,4,5,6,7,7-hexachloro-2-formylbicyclo[2.2.1]5-heptene, 1,4,5,6,7,7-.
Re. 30,193

13 hexachloro-2-cyanobicyclo[2.2.1]-5-heptene, and hexachlorocyclopentenones.
7. A composition according to claim 4 wherein the mineral is present together with the halogen such that the weight ratio of mineral borate to halogen is between 1 and 8.
8. A composition according to claim 7 wherein said ratio is between 1 and 4.
10. A flame-stabilized composition comprising a normally flammable organic material and the fire retardant composition of claim 5.
12. A flame-stabilized composition comprising a normally flammable organic material and the flame retardant composition of claim 6, the weight ratio of mineral to halogen source being between 1 and 8 and the mineral being present in the composition in an amount between 2 and 400 parts per part of organic material.
13. A flame-stabilized composition according to claim 12 wherein the amount of mineral introduced is between 5 and 50 parts per 100 parts of organic material and the weight ratio of mineral to halogen is between 1 and 4.
14. A flame-stabilized composition according to claim 13 wherein the organic material is selected from the group consisting of polymers of alpha olefins, vinyl polymers, polyamides, polycetals, polyurethanes, polyesters, rubbers and latexes.
15. A flame-stabilized composition according to claim 14 wherein said organic material is a polymer of an alpha olefin.
16. A flame-stabilized composition according to claim 15 wherein said organic material is a polypropylene.
17. A flame-stabilized composition comprising a normally flammable organic material selected from the group consisting of polyethylene, polypropylene, polybutene-1, polysisobutylene, polviny1 chloride, polymethylmethacrylate, polyethylene methacrylate, polyacrylonitrile, polyvinylacetate, polyvinylbutyral, polystyrene, nylon 6, nylon 6/6, natural and synthetic rubbers, natural and synthetic latexes, polyisoprene, polybutadiene, polyethylene glycol, acrylic polymers, and their compositions, polyethylene compositions and polyurethanes, said composition containing a flame retardant composition which comprises a calcium or magnesium borate and a source of halide of atomic weight greater than 19, said source of halide being selected from the group consisting of a compound having the formula

its acids, mixed acids, bi-acids, mixed esters, bi-esters and anhydrides, wherein R can be \(H\), \(C_1\)-C1 alkyl or a halogenated derivative thereof, \(1,2,3,4\)-tetrachloro-5,5-dimethoxycyclopentadiene, \(1,2,3,4\)-tetrachlorocyclopentadiene, nonachlorobicyclo[3.2.0]-heptene-2, 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene, dechloropentacyclo[5.3.0]16,6,10,10,11,11-hexafluorocyclopentene, bis(pentachloro-2,4-cyclopentadiene-1-yl), 1,2,3,5,5,6-hexachloro-4-(4-dichlorophenyl)-cyclopentene, perchloropentacyclo[5.2.1.03,9]10,10,11,11-hexafluorocyclopentene, 2,3,4,4,5-pentachloro-2-cyclopen tone-1-one, 1,2,4-trichlorocyclopentene-3,5-dione, 2,2,3,4,6-thexachlorobicyclo[2.2.1]-5-heptadiene, 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-5-heptene-3,2-dicarboxylic acid, 1,4,5,6,7,7-hexachloro-2-bis(chloromethyl)-bicyclo[2.2.1]-5-heptene, 1,4,5,6,7,7-hexachloro-2-dichloroethoxybicyclo[2.2.1]-5-heptene, 1,4,5,6,7,7-hexachloro-2,3-bis(hydroxymethyl)-bicyclo[2.2.1]-5-heptene, undecachloropentacyclo[5.3.0]16,6,10,10,11,11-hexafluorocyclopentene, 3-decylenesulfonate, 4,5,6,7,8,9-hexachloro-3,7a-dihydro-4,7-methano-indene, 1,2,3,4,10,10-hexachloro-1,4,4a,5,5,8a-hexahydro-1,4-end, exo-5,8-dimethanophenadene, 1,4,5,6,7,7-hexachloro-2-formylbicyclo[2.2.1]-5-heptene, 1,4,5,6,7,7-hexachloro-2-cyanobicyclo[2.2.1]-5-heptene, and hexachlorocyclopentenones.
18. A composition comprising rubber and a flame-retarding agent selected from the group consisting of calcium mineral borate or a calcium metabolite and a halogen source, said halogen having an atomic weight greater than 19.
19. A composition according to claim 18, in which the calcium mineral borate or calcium metabolite is a natural mineral comprising a hydrated salt.
20. A composition according to claim 19, in which the inorganic compound is coalmanite.
21. A composition according to claim 19, in which the inorganic compound is selected from ultrade and pan灾难ite.
22. A composition according to claim 18, which contains calcium carbonate.
23. A composition according to claim 18 which is unfoamed.
24. A composition according to claim 18 which is foamed.
25. Carpet comprising a composition as claimed in claim 18 adhered to the undersurface of said carpet.
26. A composition of a normally flammable organic material selected from the group consisting of a polymer of an alpha olefin, a polyamide, a polycetate, a polyurethane, a polyester, a rubber, rubber latex and an acrylic polymer, a calcium or magnesium mineral borate or a calcium or magnesium metabolite and a halogen source, said halogen having an atomic weight greater than 19.
27. A composition according to claim 26 wherein said mineral borate is a calcium borate.
28. A composition according to claim 27 wherein said mineral borate is coalmanite.
29. A composition according to claim 26 wherein said mineral borate is a magnesium borate.
30. A composition according to claim 26 wherein the calcium mineral borate is selected from the group consisting of 2CaO.3Bu2O2.H2O; CaO.2Bu2O2.5H2O; CaO.2Bu2O2.4-H2O; CaO.3Bu2O2.3.5H2O; 2CaO.3Bu2O2.H2O; 2CaO.3Bu2O2.9H2O; 2CaO.3Bu2O2.1H2O; CaO.2Bu2O2.2H2O; Colemanite, Sassolite, Ulexite, Tertschite, Preblerite, Preble, Panderolite, Panderite, Inyoute, Meyerhoffrite, Nobleite, Gowerite, Ginorte, Caliborite, K2O. CaO.4Bu2O2.12H2O; (NH4)2CaO.4Bu2O2.12H2O and Na2O.2CaO.5Bu2O2.16H2O.
31. A composition according to claim 30 wherein the calcium borate preferably has a negligible solubility in water at 25° C.

32. A composition according to claim 30 wherein the halogen source is selected from the group consisting of halogen-containing polymers, halogen-containing rubbers, halogen-containing phenolics, halogenated aliphatic compounds and halogenated aromatic compounds.

33. A composition according to claim 30 wherein the halogen source is selected from the group consisting of halogenated acids where the halogen is on a non-carbonyl atom, said acid having between 3 and 24 carbon atoms and being saturated or unsaturated, polyethers, ketones where at least one substituent attached to the carbonyl has between 4 and 12 carbon atoms, aldehydes where the substituent attached to the carbonyl group has between 4 and 12 carbon atoms, anhydrides of halogenated acids where the halogen is on a non-carbonyl atom and the group attached to the carbonyl atom has between 3 and 24 carbon atoms, primary alcohols in which the group attached to the OH radical has between 4 and 12 carbon atoms, secondary alcohols in which at least one group attached to the carbon atom to which the OH radical is attached has between 4 and 12 carbon atoms, acid halides of C₁ to C₁₂ atoms, monosaccharides, polysaccharides, starch, cellulose, esters of said acids, thio derivatives of said acids, aldehydes, ketones and alcohols where the sulfur atom replaces the oxygen atom, aryl compounds of C₆ to C₁₈ carbon atoms, aryl ethers where the organic group attached to the oxygen contains at least 4 carbon atoms, aryl aldehydes where the organic radical attached to the oxygen atom contains between 4 and 12 carbon atoms, alkylaryl compounds where at one organic group attached to the oxygen atom has between 4 and 12 carbon atoms, arylalkenyl compounds where the alkanyl group contains between 4 and 12 carbon atoms, arylalkenyl compounds where at least one organic radical attached to the carbon bearing the hydroxy group has between 4 and 12 carbon atoms, hydroxy aryl compounds, sulfonated aryl compounds, mercapto aryl compounds, amine aryl compounds, aromatic dicarboxylic acids and their anhydrides, cyclic and heterocyclic organic chemicals having between 5 and 10 members in the ring.

34. A composition according to claim 30 wherein said halogen source is selected from the group consisting of a compound having the formula...
UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : Re 30,193
DATED : January 15, 1980
INVENTOR(S) : James D. O'Shaughnessy

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

<table>
<thead>
<tr>
<th>Column</th>
<th>Line</th>
<th>Correction</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2</td>
<td>After &quot;chlorine&quot; insert --,--.</td>
</tr>
<tr>
<td>4</td>
<td>46</td>
<td>&quot;0^4, 6&quot; should be --0^4, 10--.</td>
</tr>
<tr>
<td>6</td>
<td>33</td>
<td>&quot;Supex&quot; should be --Sipex--.</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>&quot;Pholite&quot; should be --Pliolite--.</td>
</tr>
<tr>
<td>7</td>
<td>8</td>
<td>&quot;K_2CO_1&quot; should be --K_2CO_3--</td>
</tr>
<tr>
<td>7</td>
<td>14</td>
<td>&quot;Spartalil&quot; should be --Spartafil--.</td>
</tr>
<tr>
<td>7</td>
<td>17</td>
<td>&quot;Sb_2O_1&quot; should be --Sb_2O_3--</td>
</tr>
<tr>
<td>7</td>
<td>18</td>
<td>&quot;NH_1O_1H&quot; should be --NH_4OH--.</td>
</tr>
<tr>
<td>7</td>
<td>19</td>
<td>&quot;Afquad&quot; should be --Arquad--.</td>
</tr>
<tr>
<td>7</td>
<td>19</td>
<td>&quot;g&quot; should be --9--.</td>
</tr>
</tbody>
</table>
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

<table>
<thead>
<tr>
<th>Column</th>
<th>Line</th>
<th>Correction</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>32</td>
<td>&quot;BR6399&quot; should be --FR6399--</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>In the table under Example V, line 3, &quot;CHEX&quot; should be --CITEX--.</td>
</tr>
<tr>
<td>9</td>
<td>63</td>
<td>(below the table) insert the following: --(x)=&lt;sup&gt;(vinyl chloride-vinylidene chloride copolymer)&lt;/sup&gt;--.</td>
</tr>
<tr>
<td>10</td>
<td>42</td>
<td>&quot;3/8&quot; should be --1/8--.</td>
</tr>
<tr>
<td>10</td>
<td>53</td>
<td>&quot;Epsin&quot; should be --Epsyn--; &quot;BPDM&quot; should be --EPDM--.</td>
</tr>
<tr>
<td>10</td>
<td>57</td>
<td>&quot;Xn0&quot; should be --Zn0--.</td>
</tr>
</tbody>
</table>
**UNITED STATES PATENT AND TRADEMARK OFFICE**

**CERTIFICATE OF CORRECTION**

<table>
<thead>
<tr>
<th>Column</th>
<th>Line</th>
<th>Correction</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>59</td>
<td>&quot;Inpure 1 W (Ti O₁)&quot; should be --TiPure LW (TiO₂)--.</td>
</tr>
<tr>
<td>10</td>
<td>61</td>
<td>&quot;Benzothrazyl&quot; should be --Benzothiazyl--.</td>
</tr>
<tr>
<td>11</td>
<td>47</td>
<td>&quot;12H₃O and&quot; should be --12H₂O and--.</td>
</tr>
</tbody>
</table>

Signed and Sealed this First Day of July 1980

[SEAL]

Attest:

SIDNEY A. DIAMOND

Attesting Officer
Commissioner of Patents and Trademarks