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(54) **Title:** NON-SCORCH FLAME RETARDED POLYURETHANE FOAM

(57) **Abstract:** The present invention relates to phosphorous based flame retardants useful in polyurethane foam and foams comprising the phosphorous based flame and retardants.

NON-SCORCH FLAME RETARDED POLYURETHANE FOAM

BACKGROUND AND SUMMARY

5 Discoloration of flexible polyurethane foams, commonly called scorch, is an issue to foam producers. In some markets customers will not accept foams that have internal discoloration. Scorch is thought to be caused by thermal and oxidative degradation of the polyurethane foam. Scorch is generally observed in the center of foam blocks where internal temperatures can remain high for relatively long periods of time.

10 Studies suggest that several factors can contribute to the generation of scorch in a foam block. One factor may be the presence of mineral acids HBr and HCl that formed during foam oxidation resulting in scorch. Flame retardants may be a source of these acids. It is thought that flame retardants having relatively low thermal stability could dehydrohalogenate during foam processing, generating the detrimental mineral acids. In response, flame retardant manufacturers
15 focused on aromatically bound bromine, believed to offer more thermally stable flame retardants.

Flame retardants based upon pentabromodiphenyl oxide when used in polyurethane foams have successfully reduced scorch. Recently, phosphorous based "halogen free" flame retardants have been used in greater volumes as alternatives for pentabromodiphenyl oxide.

20 Phosphate esters have been used neat or in blends as flame retardants for flexible polyurethane foam. As a component in a blend, as the concentration in the blends has increased up to and including 100%, phosphate based flame retardants, scorch emerged as an issue in polyurethane foam.

25 Further investigation revealed that these nominally phosphate flame retardants contained varying levels of phosphites. Applicants found that by reducing the phosphite content of the phosphate ester flame retardant the quality of polyurethane foam is improved, particularly with respect to scorch of the foam.

DETAILED DESCRIPTION

The invention relates to a flame retardant polyurethane foam composition and a method of making of flame retarding polyurethane foam. The composition comprises an otherwise
5 flammable polyurethane foam and a phosphate flame retardant additive that has low phosphite content and low content of impurities resulting from the decomposition of phosphites. In one embodiment, the flame retardant additive is a phosphate ester. In another embodiment, the flame retardant additive is a blend of a phosphate ester with another flame retardant additive.

Phosphites may be generated during synthesis of phosphate ester flame retardants.
10 Typical preparation of a phosphate ester uses phosphorous oxychloride (POCl_3) as a raw material. POCl_3 is reacted with phenol to prepare triphenyl phosphate, or alkyl substituted phenol to prepare alkyl-substituted triphenyl phosphate. A scheme for the preparation is disclosed in US Patent 4,093,680, incorporated by reference. POCl_3 often includes phosphorous trichloride (PCl_3) as an impurity. The presence of PCl_3 impurity in turn may lead to a phosphite
15 by-product during the synthesis of the preferred phosphate ester. Applicants found that by reducing the PCl_3 reactant concentration in the POCl_3 raw material, the phosphite content may be lowered. Perceived lower hydrolytic and thermal stability of phosphites as compared to corresponding phosphates may be related to the observed scorch in the resulting foams.

One or more of the phenyl groups of the phosphate ester may be substituted, preferably
20 with one or more linear or branched alkyl group of from 1 to 6 carbon atoms. Preferred substituents are isopropyl and isobutyl groups.

Scorch had been thought to be caused by thermal and oxidative degradation of the polyurethane foam and most likely to be observed in foams that contain labile halogens or in the case of halogen free flame retardants those that contain an elevated level of phosphite or its
25 decomposition products. Researchers in the industry have developed a quantitative test to determine the amount of scorch contained in a polyurethane foam which is disclosed in detail by M.J. Reale and B.A. Jacobs in "A Rapid Predictive Test for Urethane Foam Scorch" in the Journal of Cellular Plastics, Vol. 15(6), pages 311-314, Nov/Dec. 1979, the disclosure of which is expressly incorporated by reference herein. Stated generally, the test requires combining
30 reactants in a small box to create a foam bun. The foam bun is placed in a microwave oven for a predetermined amount of time required to generate a temperature in the center of the bun which

is intended to simulate the temperature in the center of a larger, commercial-sized bun. When the foam has cooled to room temperature a piece of foam is cut from the center of the bun and the color is measured on a HunterLab Color/Difference Meter from Hunter Associates Laboratory, Inc. in Reston, Virginia.

5 Using the scorch measuring method developed by Reale and Jacobs, it has been observed that foams prepared with phosphate esters show unacceptable signs of scorch when the phosphite content in the phosphate ester is above 0.33 area % based on NMR integration. The phosphite content can be measured by phosphorous (^{31}P) NMR. The phosphite peak studied for the experiment was at 155 parts per million (ppm). Generally, phosphites are found in the region of
10 125-160 ppm. ^{31}P NMR measurements were conducted on a Varian 200 MHz NMR. The samples were evaluated as solutions in deuterated chloroform and referenced with phosphoric acid. The phosphite impurities were observed at 155.11 ppm as opposed to the typical phosphate resonances which appeared in area of -24ppm to -40ppm. The relative intensities of the peaks were measured based on integration of the specified peaks and then normalized by comparing to
15 a known quantity of an internal standard placed in each sample. The internal standard was phosphoric acid.

Typically flexible polyurethane foam is open-cell. Such foam is prepared from difunctional isocyanate such as toluene di-isocyanate or methylene di-isocyanate, a trifunctional polyol having molecular weight on the order of 3000, and water. Useful catalysts include an
20 amine catalyst such as triethanol amine, a tin catalyst such as stannous octanoate and a silicone surfactant such as L 620 produced by Osi Specialties. Since August 1, 2003, Osi is a unit of GE Silicones, Wilton CN 06897, USA. Blowing agents such as chlorofluoroalkanes (FreonTM), and CO_2 resulting from the reaction product of isocyanate and added water. Flame retardants are typically added to the polyurethane reaction ingredients. Flame retardant performance standards
25 typically followed for flexible polyurethane foams are the California bulletin 117 combustibility test part A and part D for household furnishings, and the United States Motor Vehicle Safety Standard-302 (MVSS-302) for motor vehicle seating and other comfort applications of flexible polyurethane foam.

Typically rigid polyurethane foam is closed-cell prepared from a high functionality polyol
30 having a molecular weight of about 500, and poly(methylene)-poly(phenyl isocyanate) having a

functionality of about 2.7. Specific flame retardants as described are added in the following examples.

Examples 1-4

Table 1 illustrates the results of a comparison in the amount of phosphite present and the level of scorch for three flame retardant foams and one non-flame retardant foam. The foam was prepared from the recipe according to Example 10.

Table 1

Flame Retardant	Area% Phosphite	Triphenyl phosphite by GC	Scorch	
			DE	YID
Example 1				
Butylated Triarylphosphate	0.42	5ppm	7.63	12.02
Example 2				
Butylated Triarylphosphate	0.33	2ppm	4.20	3.16
Example 3				
Isopropylated Triarylphosphate	0	<0.5 ppm	5.17	0.94
Example 4				
Non-Flame Retardant		<0.5 ppm	3.29	-0.09

Quantification of phosphite content by NMR is described above. Gas chromatography analysis of phosphite content was determined using an Agilent gas chromatograph model 6890N having on column injection. The column was a Restek Rtx-1MS x 0.32 mm id x 0.5 micron film. Temperatures were inlet: cool on-column with oven track, detector 250° C The oven temperature program was 40° C initial temperature for 2 minutes followed by an increase of temperature at the rate of 15° C per minute to 310° C. Temperature was held at 310° C for 10 minutes. Triphenylphosphite peak eluted at 15.7 minutes. The identity of triphenylphosphite was confirmed by comparing retention time to a known standard and by gas chromatography/mass spectrometry.

The flame retardant for Examples 1-3 is entirely of the phosphate variety indicated. YID is the yellowness index which is described in detail in "Standard Practice for Calculating Yellowness and Whiteness Indices from Instrumentally Measured Color Coordinates" ASTM Standard E

313-00 (American Society for Testing Materials) which is expressly incorporated by reference herein. DE or ΔE is a measure of the change in color of parameters L, a, and b as compared to a standard white tile as described in the ASTM Standard E 313-00. As shown in Table 1, as the level of phosphite increases the level of scorch (YID) increases.

5 Examples 5 - 8

Referring now to Table 2, shown below, isopropylated triaryl phosphate, as shown in Table 1 was determined to have no phosphite by NMR. The phosphite free isopropylated triaryl phosphate was then blended 50/50 with a tetrabromobenzoate. Triphenylphosphite was spiked into formulations of polyurethane foam prepared from the recipe of Example 10 to determine the effect of the phosphite. The flame retardant was stored at 45° C for 12 hours prior to use to ensure that decomposition products of the phosphite were present. The data again shows that as the phosphite level increases the amount of scorch (YID) increases as well.

Table 2

Flame Retardant	Wt % Phosphite	Scorch	
		DE	YID
Example 5			
Benzoate/Phosphate Foam	0.5	6.32	10.54
Example 6			
Benzoate/Phosphate Foam	0.1	3.90	6.31
Example 7			
Benzoate/Phosphate Foam	0	3.53	1.82
Example 8			
Non-Flame Retardant Foam		3.29	-0.09

15 Example 9-11

In one embodiment of the present invention, the flame retardant additive is comprised of one or more compounds from group A which may be blended with compounds from group B, and the compounds from group A may contribute between 1-100% of the blend. The blend of A and B will have an unusually low content of phosphite and or its decomposition products of less than 0.33 area % by NMR.

Group A

The flame retardant additives in Group A are comprised of one of an alkyl, aryl, or alkaryl phosphate that is optionally halogenated and prepared from a POCl_3 source that has unusually low PCl_3 content. Group A includes one or more phosphorous based flame retardants having at least about 5 wt.% phosphorus. Compounds having less than about 5 wt.% phosphorus may also be useful, but it is believed that excessively high amounts of such compounds would be needed to provide the necessary level of flame retardancy. Included in the description of suitable phosphorus sources is the class phosphates. These may contain various alkyl, aryl or alkyl aryl groups as long as the size of the groups does not dilute the phosphorus content below about 5 wt.%. The component from Group A may be monomeric, dimeric, or oligomeric and may contribute between 1-100% of the blend.

Group A also includes phosphorus-containing additives including phosphates having either one or two phosphorus atoms per molecule. Examples include tris(1,3-dichloro-2-propyl) phosphate, tris(1-chloro-2-propyl) phosphate, tris chloroethyl phosphate, tricresyl phosphate, trixylyl phosphate, butylated triphenyl phosphate, isopropylated triphenyl phosphate, triphenyl phosphate, triethyl phosphate, tris(2-ethylhexyl) phosphate, isodecyl diphenyl phosphate, cresyl diphenyl phosphate, tri-n-butyl phosphate, tri-iso-butyl phosphate, tributoxyethyl phosphate, resorcinol bis(diphenyl phosphate), bisphenol A bis(diphenyl phosphate), and 2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane-4-methanol, 1-oxide.

Group B

The flame retardant additives in Group B are comprised of halogenated flame retardants containing greater than (>) 30% halogen. Compounds having less than about 30 wt.% halogen may also be useful, but it is believed that excessively high amounts of such compounds would be needed to provide the necessary level of flame retardancy. Included in the description of suitable halogen containing flame retardants are compounds containing various halogenated alkyl, aryl or alkyl aryl groups as long as the size of the groups does not dilute the halogen content below about 30 wt.%. The components of Group B may be monomeric, dimeric, or oligomeric and may contribute between 0-99% of the blend. Examples of halogen-containing additives include brominated aromatic benzoates and phthalates.

Typical laboratory hand mix flexible polyurethane foam was prepared using the formulations listed below in Table 3. Lab preparation yielded flexible polyurethane foams with densities as described in the following tables. The flame retardant used in the prepared foams and load level is shown in Tables 3-4 for the different foam densities. The scorch data for the 24 kg/m³ foam is shown in Table 5. The flame retardant component of the polyurethane foam is as indicated: a butylated triaryl phosphate or a blend equal parts by weight of 2-ethylhexyl-3, 4, 5, 6-tetrabromobenzoate mixed with an isopropylated triaryl phosphate. All components are expressed in parts by weight per hundred of polyol (php). The foams meet the California bulletin 117 combustibility test part A and part D, and the requirements of the MVSS 302 standard for foam in automotive applications as shown in Table 4.

Table 3

	Example 9	Example 10	Example 11
Foam Density	19 Kg/m ³	24 Kg/m ³	29 Kg/m ³
Polyether Polyol (56.6 OH index)	100	100	100
Water	6.2	4.4	3.3
Flame Retardant Additive	See Table 4	See Table 4	See Table 4
Amine Catalyst	0.48	0.5	0.5
Silicone Surfactant	1	1	1
Tin Catalyst	0.26	0.26	0.26
Toluene di-isocyanate	75.9	56.7	45.1

Table 4

Minimum Flame Retardant Loading to Pass MVSS-302 and Cal 117 standards

Example / Foam Density	Flame Retardant Additive expressed as php							
	Butylated Triarylphosphate ¹ (0.42 area % phosphite)		Butylated Triarylphosphate ² (0.33 area % phosphite)		Benzoate/Phosphate ³ (0.1 wt % phosphite)		Benzoate/Phosphate ⁴ (0 wt % phosphite)	
	MVSS- 302	Cal 117	MVSS- 302	Cal 117	MVSS- 302	Cal 117	MVSS-302	Cal 117
Example 9								
19 Kg/m ³ Density	32	37	--	--	23	21	23	21
Example 10								
24 Kg/m ³ Density	18	28	18	23	14	15	14	15
Example 11								
29 Kg/m ³ Density	7	10	16	16	4	9	4	9

¹ Phosphite content of Example 1.

² Phosphite content of Example 2.

³ Phosphite content of Example 6.

⁴ Phosphite content of Example 7.

Table 5

Scorch Data: 24 Kg/m³ Foam of the recipe of Example 10

Flame Retardant Additive	YID	ΔE	Phosphite content
Butylated Triarylphosphate ⁵ (0.42 area % phosphite)	12.20	7.63	0.42 (5 ppm triphenyl phosphite)
Butylated Triarylphosphate ⁶ (0.33 area % phosphite)	3.16	4.20	0.33 (2 ppm triphenyl phosphite)
Benzoate/Phosphate ⁷ (0.1 wt % phosphite)	6.31	3.90	0.1 (<0.5 ppm triphenyl phosphite)
Benzoate/Phosphate (0 wt % phosphite) ⁸	1.82	3.53	0
Non-Flame Retardant Foam	-0.09	3.29	0

As shown in Table 5, scorch increases with as the phosphite content increases in flame
 5 retardant additives used in flexible polyurethane foams. Foams having a YID of 2.5 or less have
 generally been found to be acceptable to consumers in the industry. Accordingly, flame
 retardant additives containing less than 0.33 % area based on NMR integration can be use to
 produce flame retardant flexible polyurethane foams with acceptable levels of scorch.

Examples 12 - 19

10 Examples 12 – 19 were prepared from the flexible polyurethane foam according to
 Example 10. The polyurethane foam incorporated constant loading of flame retardant having a
 varying amount of phosphite. The flame retardant comprises 7.5php (parts per hundred parts
 polyol) tetrabromobenzoate and 7.5 php isopropylated triaryl phosphate ester. Phosphite levels
 were achieved by adding known phosphite content to phosphite free flame retardant.

15

⁵ Phosphite content of Example 1.

⁶ Phosphite content of Example 2.

⁷ Phosphite content of Example 6.

⁸ Phosphite content of Example 7.

Table 6

Example	Phosphite	Flame Retardant	DE	YID 1925
12	2% by wt	15php	4.76	7.89
13	1%	15php	4.15	6.03
14	0.20%	15php	4.03	6.37
15	0.10%	15php	4.25	6.38
16	0.05%	15php	5.34	6.4
17	0.02%	15php	4.93	5.04
18	0.01%	15php	4.65	1.74
19	0%	15 php	3.92	0.75

The yellowing index shows a material reduction at 0.02% phosphite (200 ppm) content in the
5 flame retardant, with a significant reduction at 100 ppm.

WHAT IS CLAIMED:

1. A flame retardant composition comprising:
a phenyl phosphate ester having less than 0.33 area % phosphite based on NMR integration.
- 5 2. The phosphate ester of claim 1 wherein the one or more phenyl groups is alkyl substituted.
3. The phosphate ester of claim 2 wherein the alkyl substituent is linear or branched and has from 1 to 6 carbon atoms.
- 10 4. The phosphate ester of claim 3 wherein the alkyl substituent is isopropyl or isobutyl.
5. A polyurethane foam reaction mixture comprising the phosphate ester of claim 1.
- 15 6. A polyurethane foam comprising the phosphate ester of claim 1.
7. A polyurethane foam reaction mixture comprising the phosphate ester of claim 4.
8. A polyurethane foam comprising the phosphate ester of claim 4.
- 20 9. A polyurethane foam of claim 6 wherein the foam comprises open cells.
10. A polyurethane foam of claim 6 wherein the foam comprises closed cells.
- 25 11. A flame retardant composition comprising a phenyl phosphate ester comprising less than 300 ppm phosphite.
12. The phenyl phosphate ester of claim 11 wherein one or more of the phenyl groups is alkyl substituted.
- 30 13. The phosphate ester of claim 12 wherein the alkyl substituent is linear or branched and has from 1 to 6 carbon atoms.

14. The phosphate ester of claim 13 wherein the alkyl substituent is isopropyl or isobutyl.
15. A polyurethane foam reaction mixture comprising the phosphate ester of claim 12.
- 5 16. A polyurethane foam comprising the phosphate ester of claim 12.
17. A polyurethane foam reaction mixture comprising the phosphate ester of claim 14.
- 10 18. A polyurethane foam comprising the phosphate ester of claim 14.
19. A polyurethane foam of claim 18 wherein the foam comprises open cells.
20. A polyurethane foam of claim 18 wherein the foam comprises closed cells.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2005/043471

A. CLASSIFICATION OF SUBJECT MATTER
C08K5/523 C08J9/00 C07F9/12 C07F9/02

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 C08J C07F

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 practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.

See patent family annex.

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INTERNATIONAL SEARCH REPORT

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