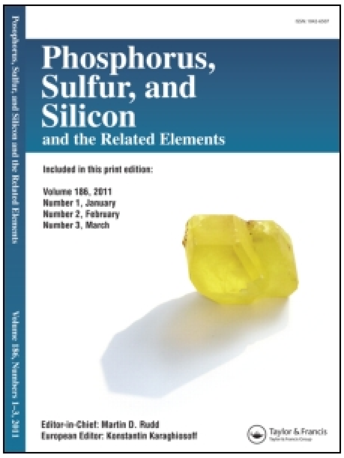
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Design of New Organophosphorus Flame Retardants

Gary Woodward; Christopher Harris; Jasvir Manku

To cite this Article Woodward, Gary , Harris, Christopher and Manku, Jasvir(1999) 'Design of New Organophosphorus Flame Retardants', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 25 — 28

To link to this Article: DOI: 10.1080/10426509908546173

URL: http://dx.doi.org/10.1080/10426509908546173

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 25-28
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Design of New Organophosphorus Flame Retardants

GARY WOODWARD, CHRISTOPHER HARRIS and JASVIR MANKU

International Technical Centre, Albright and Wilson Limited, P.O. Box 80, Trinity Street, Oldbury, Warley, West Midlands, B69 4LN, ENGLAND

Considerations for the design of new additive flame retardants are discussed. The chemistry and potential application of new developmental polymeric flame retardants is described.

Keywords: Flame retardant; Albright and Wilson; polymeric; polyurethane foams

INTRODUCTION

Flame retardants are applied in a whole range of materials such as coatings, textiles, furniture, etc. This is a mature market using materials which are commodity chemicals. Outside of 'niche' applications, it is unlikely that a new flame retardant will displace an existing product unless legislation or end customer expectation demand it. Examples of potential changes which could drive development work are the emergence of ecolabels such as the Blue Angel Mark in the German Polyurethane foam market, volatility and toxicity of volatile components, the trend towards recycling of plastic materials, chlorine content, toxic combustion products and the fate of the end flame retardant in the environment. Phosphorus based chemical Flame retardants account for about 38% of the European market[1]

This paper describes the strategy behind recent new developmental non-halogenated flame retardants at Albright and Wilson.

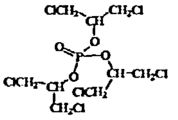
Discussion

Any new flame retardant must satisfy the following set of criteria

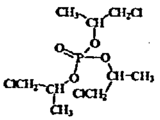
1. Preferably low volatility - often liquid, issues with leaching of the flame retardant
2. Non-halogen - environmental concerns with toxic halogen combustion products
3. Non-toxic
4. %Phosphorus- as high as possible
5. Environmental profile - both the flame retardant and the manufacture process
6. Chemical Weapons Treaty - should be exempt
7. Cost - must compete with very low cost current materials

8. *Thermal Decomposition* - must be compatible with processing temperatures of the intended application.
9. *Compatibility* - must not react unintentionally in the application or compromise physical properties.

Below are the structures of some commonly used phosphorus flame retardants. Both are manufactured from low cost raw materials and meet most of the above criteria except halogen content and in some applications they have unacceptably high volatility.

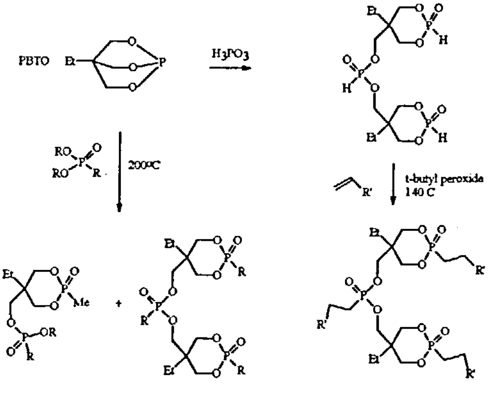


TDCP



TMCP

In the design of new flame retardants we have adopted the approach of initial selection of candidates based mainly on what process chemistry is practical, environmentally acceptable and cost effective. We began by modification of a current flame retardant process, which is operated on a multi tonne scale at Albright and Wilson to make the Antiblaze™ AB-N flame retardant range. The bicyclic intermediate PBTO is reacted at high temperature with dimethyl methyl phosphonate[2] (DMMP) to yield AB-N (R=CH_3



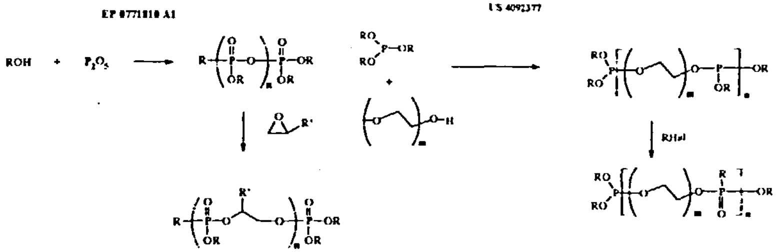
AB-N type Flame retardants

Experimental compounds

above). This process is very slow (>24h) with DMMP. Attempts to repeat this work where R=Ethyl, butyl results in longer reaction time, even with alkyl iodide catalysis, and recovery of R-P(O)$(OR)_2$ because of significant polymerisation / decomposition of PBTO.

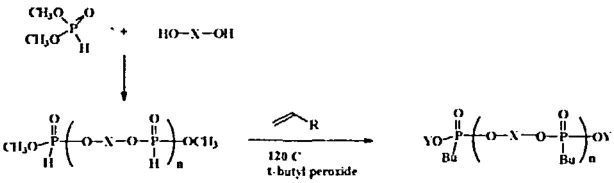
In this paper we report a method that has been developed and patented[3] where PBTO is reacted with acids, e.g. phosphorous acid, to yield the phosphite above. This phosphite can then be reacted with gaseous or liquid olefins to obtain the flame retardant analogues that are not available by the Arbuzov route. The chemical properties of these materials can be selected by variation of the olefin. Polymeric analogues are also possible by the use of acetylene or a alpha-omega diene.

Polymeric flame retardants would be expected to have the advantage of low volatility. Clearly such polymeric materials can potentially be crosslinked resulting in high viscosity. Polymeric flame retardant candidates are not unique - see EP0771810(1997 to Hoechst) for a phosphate polymeric material and US4092377(1978 to Stauffer). The first is a linear phosphate polymer and the second phosphonate is practically / economically limited to lower alkyl phosphontes that would not be chemical weapons



exempt and the route also allows for cross linking of the polymer.

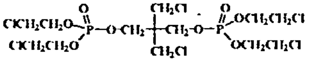
In another project the methodology of reacting a polymeric phosphite with an olefin has allowed the development of a series of new linear polymeric phosphonates at Albright and Wilson[4].



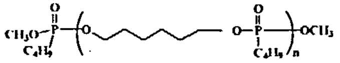
Dimethyl phosphite is reacted with an alpha omega diol to yield a polymeric phosphite which is further reacted with olefin to obtain the desired polymeric phosphonate material. Electrospray mass spectral data has been used to demonstrate the polymeric nature of the material. A degree of polymerisation(n) of up to approx. 10 has been obtained. Clearly this system is quite flexible, the chemical properties of resultant flame retardants can be tailored to suit the application by choice of olefin and molecular weight.

Application Results: Several analogues of this polymeric phosphonate and the PBTO derived phosphonate are being evaluated in various polymer systems. These are the subject of current patent applications.

The table below demonstrates the use of such a novel low volatility non chlorine polymeric flame retardant in a flexible polyurethane foam formulation vs. a current industry chlorinated organophosphorus standard.



FR-1



FR-2 (n=6)

		FR-1	FR-2
SHELL CARADOL SC46-02	PARTS	100	100
WATER	PARTS	4.15	4.15
OSI NIAX A1	"	0.04	0.04
AIR PRODS. DABCO 33LV	"	0.12	0.12
GOLDSCHMIDT BF2370	"	1.3	1.3
AIR PRODUCTS DABCO79	"	0.25	0.25
TOLUENE DIISOCYANATE	INDEX	110	110
CHLORINATED FR-1	PARTS	13	
POLYMERIC FR-2	"		11
REACTIVITY PROFILE			
CREAM TIME	seconds	20	15
RISE TIME	"	107	100
DENSITY	(Kg/m^3)	25.34	23.91
AIR POROSITY	(L/min)	82	55
%P AT 104°C/ 24h	(%)	100	100
FEDERAL MOTOR VEHICLE PERFORMANCE		self extinguishing	self extinguishing
UNAGED SPECIMENS			
AGED @ 140°C / 16h	"	"	"
FOGGING PERFORMANCE TO DIN 75201 PART B IN 30 DENSITY POLYETHER FOAM	(mg / 10mm foam)	1.7	0.8

References

[1] For a recent popular review of the flame retardant market see 'In the line of fire' Catherine Martin, Chemistry in Britain No. 6 June 1998

[2] US 3,789,091 (1974) to Mobil Oil Corp

[3] GB9516794. 6 (1995) to Albright and Wilson

[4] GB9623584. 1 (1996) to Albright and Wilson