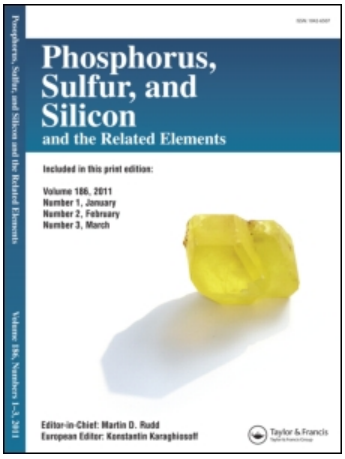

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Methyl Salicyl Phosphates–Novel Flame Retardants

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Methyl salicyl phosphates and related diphosphates are developed as flame retardants. Because of the unique structures of these molecules, they are expected to function as intrinsic fire extinguishers.

Keywords: Salicyl phosphates; flame retardants

INTRODUCTION

Flame retardancy of engineering plastics and fabric materials employing phosphorus-based flame retardants is of topical interest. Triphenyl phosphate and tricresyl phosphate were two of the earliest widely used flame retardants. Development of aromatic diphosphates such as resorcinol diphosphate[1] was a breakthrough in the evolution of aromatic and phosphorus-based flame retardants. The quest for more efficient products led to our interest in the development of salicyl phosphates (figure 1) as novel flame retardants for engineering plastics. Increased molecular weight and a corresponding decrease in volatility render them potentially safe materials. Most important, salicyl phosphates do contain carboxyl ester groups. Under fire conditions, when molecules undergo breakdown, salicyl phosphates may be expected to produce more carbon dioxide. Consequently, salicyl phosphates could function as flame retardants as well as intrinsic fire extinguisher.

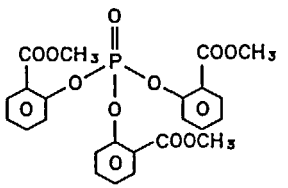

FIGURE 1 Tris(methyl salicyl) Phosphate (MSP)

Limited references[2-4] available indicate that salicylate related derivatives could be used as flame retardants. In spite of these disclosures, it was not obvious whether they employed

salicylates just as a source of phenol or as a potential intrinsic fire extinguisher as envisioned here.

Synthesis of Methyl Salicyl Phosphates (MSP)

Methyl salicyl phosphate is most conveniently prepared by reaction between methyl salicylate and phosphorus oxychloride in toluene in presence of triethylamine as a hydrogen chloride acceptor (figure 2).

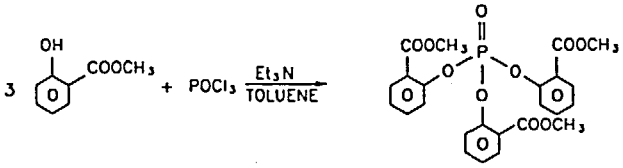

FIGURE 2 Synthesis of tris(methyl salicyl) phosphate

Methyl salicyl phosphates are also formed by a direct reaction between methyl salicylate and phosphorus oxychloride at elevated temperatures catalyzed by Lewis acids. Direct reaction, however, yields two major products: one with a molecular weight of 500 and the other with a molecular weight of 620 (figure 3). The product number I is readily identified as tris(methyl salicyl) phosphate. The product number II is identified as bis(methyl salicyl) (methyl salicylsalicyl) phosphate[5] (figure 4). The structure assignmen is based on high resolution mass spectral data.

FIGURE 3 Direct syntesis of methyl salicyl phosphates

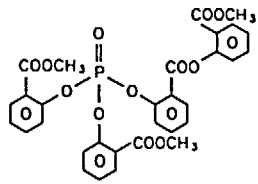

FIGURE 4 Structure of Bis(methyl salicyl) (methyl salicylsalicyl) phosphate

It is not explored whether formation of methyl salicylsalicylate takes place between two free methyl salicylate molecules (figure 5),

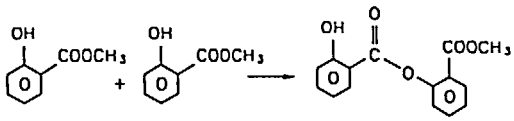

FIGURE 5 Possible formation of methyl salicylsalicylate from free methyl salicylate

Or, between a free methyl salicylate molecule and an activated methyl salicyl residue of the phosphate ester(figure 6):

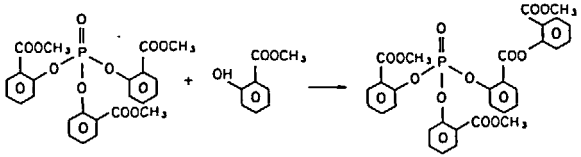

FIGURE 6 Possible formation of methyl salicylsalicylate from activated salicylate moiety

Synthesis of Methyl Salicyl Diphosphates

In addition to MSP, three additional methyl salicyl diphosphates were also synthesized: BISPHENOL A TETRAKIS(METHYL SALICYL) DIPHOSPHATE, **BASP**, RESORCINOL TETRAKIS(METHYL SALICYL) DIPHOSPHATE, **RSSP**, HYDROQUINONE TETRAKIS(METHYL SALICYL) DIPHOSPHATE, **HQSP**

Typical mass losses in the TGA analyses (in air) of methyl salicyl phosphates are given in table I. TGA confirms that methyl salicyl diphosphates are stabler molecules and that after decomposition, they yield reasonable amounts of "char".

TABLE I Representative TGA data for Methyl Salicyl Phosphates.

% Mass Loss	MSP	BA-SP	RS-SP	HQ-SP
5 %	255 °C	290 °C	180 °C	215 °C
10 %	260 °C	305 °C	290 °C	295 °C
50 %	290 °C	350 °C	310 °C	325 °C

Organic Chemistry of Methyl Salicyl Phosphates

Salicyl phosphates have two reaction centers: -P-O-R and –COO-R ester linkages. Can the carboxyl ester function of salicyl phosphates undergo simple organic chemistry in preference to the phosphate ester linkage? For example, reactions with lithium aluminum hydride (figure 7), with Grignard reagents (figure 8) and with a diol in a trans esterification reaction (figure 9):

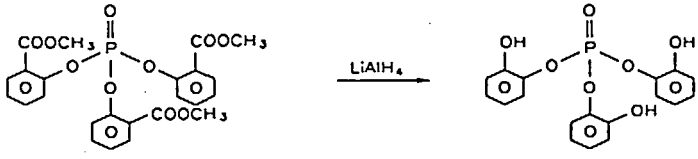

FIGURE 7 Potential reaction of MSP with $LiAlH_4$

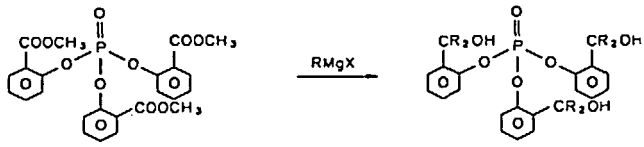

Figure 8 Potential reaction of MSP with Grignard reagents

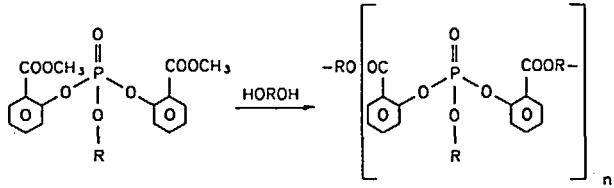

FIGURE 9 Potential trans-esterification reaction of MSP with a diol.

Formulation of Salicyl Phosphates in Engineering Plastics

Salicyl phosphates were formulated in three engineering plastics – PC/ABS, PPO and PBT - to evaluate the flame retardant properties. The test results produced V-2 or V-1 rating only (table II). None of the test results produced V-0 rating. It is expected that the additives will be reformulated and reevaluated shortly.

TABLE II Flame test results of formulated plastics

	MSP		BA-SP	
	1/8"	1/16"	1/8"	1/16"
PC/ABS	V-2	V-2	V-2	V-2
PPO	V-1	V-2	V-1	V-2
PBT	V-2	V-2	-	-

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