



FEATURED PRODUCT

PIP (3:1) and TIPPP

Phenol isopropylated phosphate, otherwise known as PIP (3:1) is used as a flame retardant, plasticiser, and additive in electronics and automobiles, among another applications. PIP (3:1) is produced by isopropylation of trisphenyl phosphate. Trisisopropylated trisphenyl phosphate is referred to as TIPPP (Trisisopropyltrisphenyl phosphate).

The compound was banned for processing and distribution by the US Environmental Agency (EPA) in January 2021. Despite its persistent, bio accumulative and toxic (PBT) properties, the EPA will not enforce the ban of PIP (3:1) until October 31, 2024.¹⁻³ The justification was «to ensure that supply chains are not disrupted for key consumer and commercial goods». This followed concerns raised by importers, distributors, and retailers that it may take several years to fill the gap.



What is PIP (3:1)?



Commercial PIP (3:1) is a complex industrial mixture. Its analysis is challenging as the composition may vary from producer to producer, and from batch to batch.

EPA refers to PIP (3:1) as propylated, phenol, phosphate with CAS 68937-41-7.² This is in line with Chemical Abstract Services (CAS) definition of CAS number 68937-41-7 as «unspecified propylated phenol phosphate». The structure and the composition are not given and no

alternative names are referenced. ECHA, also refers to PIP (3:1) as propylated phenol phosphate with CAS 68937-41-7, however they give the structure as a mixture of four compounds with increasing number of isopropyl groups from zero to three.⁴ The PIP (3:1) mixture is further described by the UK Environmental agency.⁵

Chiron have analysed two technical products, one of which was called 'propylated trisphenyl phosphate' by the producer. The other was called diisopropyltrisphenyl phosphate. The products were analysed in detail and also separated into fractions. The composition of the two products were similar.

Chiron isolated by prep LC four fractions (1-4 below) of the technical mixture with an increasing number of isopropylated groups from zero to three. The original mixture also contained some minor amounts of isomers with four isopropyl groups according to GC-MS analysis:

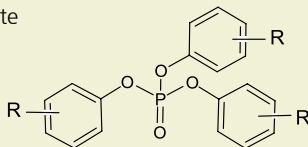
Fraction (% in original mixture)	Mass	Chiron Catalogue. No.	Name	Number of isomers detected
1 (23.2)	326	2138.18	Triphenyl phosphate	1
2 (29.6)	368	12833.21	Monoisopropyltrisphenyl phosphate, m/z 368	3
3 (38.9)	410	12832.24	Diisopropyltrisphenyl phosphate, m/z 410	6
4 (6.1)	452	12832.27	Trisopropyltrisphenyl phosphate, m/z 452	5
5 (2.2)	494	N/A	Tetraisopropyltrisphenyl phosphate, m/z 494	3

Fraction 2 (12833.21) consists of 2.4 % diphenyl-3-isopropylphenyl phosphate (coeluting with reference standard 11445.21), and the two other isomers 2- and 4-isopropylphenyl in 28.4 and 69.3 %, but it is unclear which was which.

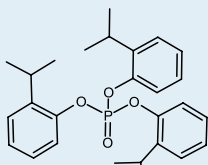
Fraction 3 (12834.24) was a mixture of three major components (16, 20 and 49%). Based on the results from fraction 2 above they are likely combinations of 2- and 4-isopropylphenyl isomers, e.g. di(4-isopropylphenyl)phenyl phosphate, 2-isopropylphenyl-4-isopropylphenylphenyl phosphate and 2,4-diisopropylphenyldiphenyldiphenyl phosphate.

Fraction 4 (12831.27), Tris(isopropyl)trisphenyl phosphate has the generic structure shown here:

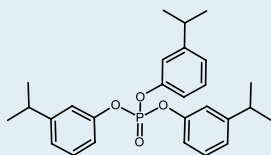
$R = H$ or $CH(CH_3)_2$. It can be one or several $CH(CH_3)_2$ groups in each ring, but only totally three in the molecule



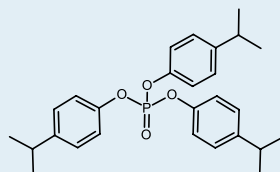
Furthermore, we synthesised three different congener reference standards; tris(2-isopropylphenyl) phosphate (11234.27), tris(3-isopropylphenyl) phosphate (11441.27) and tris(4-isopropylphenyl) phosphate (11136.27) of this generic structure, but none of these corresponded to compounds in the technical fraction 12831.27.



11234.27

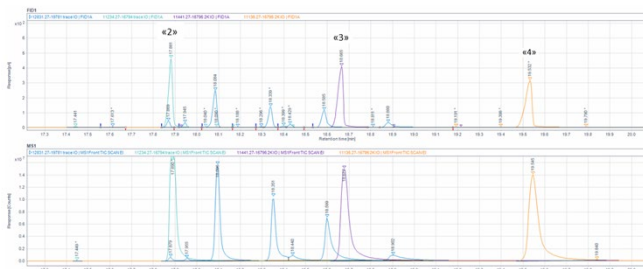


11441.27



11136.27

The technical mixtures were analysed by Gas Chromatography with Flame Ionisation Detection and Mass Spectrometry (GC-FID/MS) and were compared with the individual congener reference standards. An overlaid chromatogram is shown below. The analysis of the tris(isopropyl) fraction from Chiron is also published by Shimadzu.⁶



The chromatogram is the GC-FID data, the bottom the GC-MS data of the tris(isopropyl)trisphenyl fraction (12832.27 Tris(isopropyl)trisphenyl phosphate, m/z 452)

The darker blue peaks in the chromatograms originate from the technical mixture

Light blue: "2" Tris(2-isopropylphenyl) phosphate (11234.27)

Purple: "3" Tris(3-isopropylphenyl) phosphate (11441.27)

Yellow: "4" Tris(4-isopropylphenyl) phosphate (11136.27)



We can state that the technical mixture of PIP (3:1) is a complex mixture of trisphenyl phosphate with zero to four isopropyl groups attached. The majority of the mono is a mixture of the 2- and 4-isopropylphenyl isomers, the di- and tris- consists of several undefined isomers, likely mainly with a combination of 2- and 4-isopropyl and 2,4-diisopropyl isomer. Without doubt we can conclude that the tris does not

contain tris(2-isopropylphenyl) phosphate (11234.27), tris(3-isopropylphenyl) phosphate (11441.27) or tris(4-isopropylphenyl) phosphate (11136.27) in any major proportions. Rather, it is likely to contain a mixture of isomers with different substitution patterns in the rings, with from zero to 2-isopropyl groups in one ring and up to two isopropyl groups in one of the other phenyl rings.

Available Standards:

Chiron No.	Name	Synonym	CAS
8777.27	Isopropylated trisphenyl phosphate (techn. 5% TIPPP)	TIPPP techn.; PIP (3:1)	68937-41-7
12831.27	Tris(isopropyl)trisphenyl phosphate, ion m/z 452	TIPPP: PIP (3:1)	68937-41-7
12832.24	Diisopropyltrisphenyl phosphate, ion m/z 410	DIPPP	28109-00-4
12833.21	Monoisopropyltrisphenyl phosphate, TIPPP ion m/z 368	MonolPPP	28108-99-8
11234.27	Tris(2-isopropylphenyl) phosphate	2-TIPPP	64532-95-2
11441.27	Tris(3-isopropylphenyl) phosphate	3-TIPPP	72668-27-0
11136.27	Tris(4-isopropylphenyl) phosphate	4-TIPPP	2502-15-0
11442.27	Tris(4-isopropylphenyl) phosphate-d33	4-TIPPP-d33	N/A
11445.21	Diphenyl-3-isopropylphenyl phosphate	3-DPIPP (3-IPDP)	69515-46-4
11839.21	Diphenylisopropylphenyl phosphate, techn. isomer mix	DPIPP techn.	28108-99-8

References

1. US EPA: Current and Future Actions on PBT Rules | US EPA
2. US EPA: EPA Proposes Further Extension of Compliance Date for PIP (3:1)-Containing Articles | US EPA
3. US EPA: https://www.epa.gov/sites/default/files/2017-08/documents/pip3-1_-_use_information_8-10-17.pdf
4. Substance Information - ECHA (europa.eu): <https://echa.europa.eu/substance-information/-/Substanceinfo/100.066.404>
5. UK Environmental Agency: https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/290854/scho0809bqug-e-e.pdf
6. Shimadzu Corporation, 01-00191-EN Analysis of PIP(3:1) in Plastic by Py/TD-GCMS (shimadzu.com)





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