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New Era no HBCD means back to basics

Flame Retardants used for *EPS-XEPS /XPS*

Ronald Wilmer Technical Advisor

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Agenda

- Oceanchem group LTD who we are
- What happend
- Flame retardants
- EPS/XEPS
- XPS
- Q/A

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What happend

HBCD banned in 2019 EU-2022,
ICL, Albemarle, Lanxess stopped production

Replacement chosen “the Polymeric”

Japan used the FR130 since 2014 as polymeric was not ready
Capcity increase

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KEY CRITERIA FOR SELECTING HBCD REPLACEMENT:

- *Fire Performance*
- Superior Environmental and health profile (more sustainable):
  Stable, non-toxic high molecular weight material that is inherently safer due to limited bioavailability/toxicity
- *Compatible with existing processes. Neutral for production.*
- Max 5% loading level. Cost performing.
- *Reasonable thermal Stable (TGA)*

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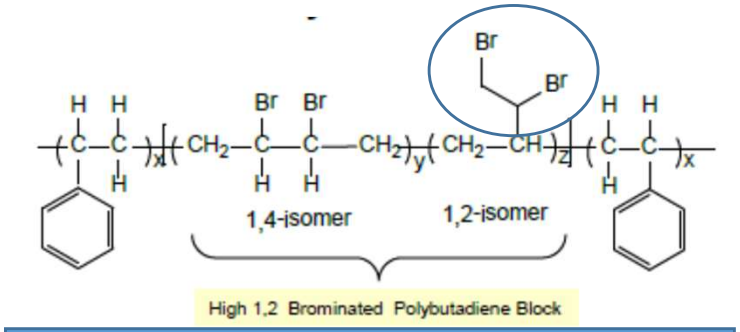
Possible Flame retardants

start point past short intro(many testings done)

1. Polymeric
   EPS,XPS,XEPS
2. FR130
   EPS,XPS,XEPS
3. BDDP
   XPS,XEPS
4. TCP
   XPS,XEPS
5. TBBPA
   XEPS
6. other

Flame retardants for EPS XEPS and XPS

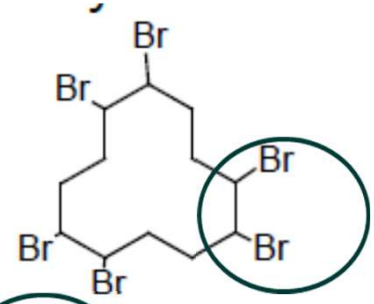


Brominated Polybutadiene-polystyrene BrPBPs

Mw 65,000-150,000

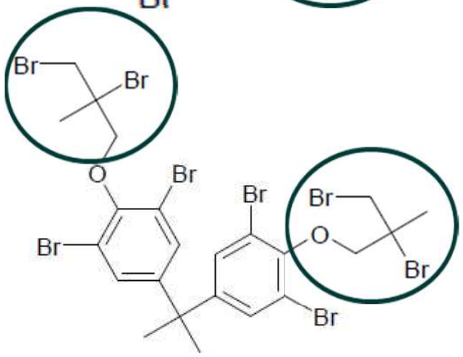
% Bromine :64

Organic Bromine compounds are very good initiators at temperatures over 280-320° C. The most effective ones are those with the bromine bonded to a secondary carbon. This means bis(2,3-dibromopropyl) group, present in HBCD and Br-polymer, are the radical initiator of this system.



% Bromine : 75

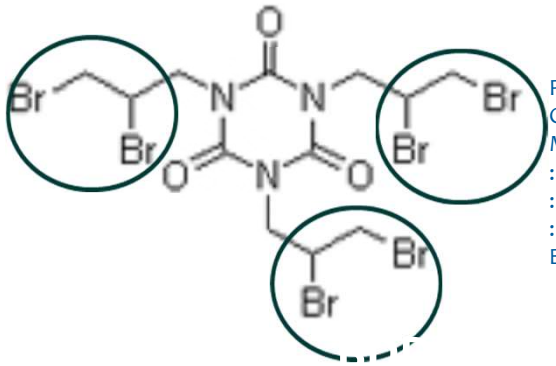
Change in use in EPS/XEPS and XPS



% Bromine : 66

EPS/XEPS

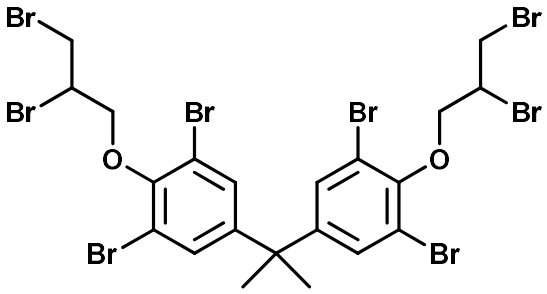
XPS



Product Name : Tris-(2, 3-dibromopropyl)isocyanurate [TBC]
Cas No. : 52434-90-9
Molecular Weight : 729
Bromine content 65

XPS

Initial decomposition point ° C.....230 min.
TGA
1% weight loss ..... 110° C
5% weight loss ..... 172° C
10% weight loss .....208° C

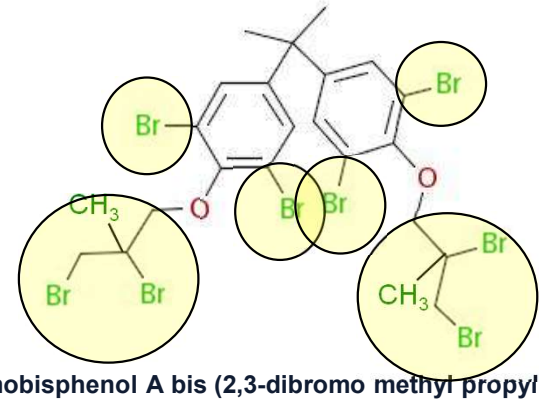


BDDP bromine content 68

XPS/XEPS

FR130 (FR130X)oceanchem

- FR130 is a brominated flame retardant formulation HBCD free with 66% Br content.
- FR130X is reach registered
- FR130X new developed is thermal stable and compatible with PS.
- Works with synergist.
- Shows 4 active points similar to HBCD.
- Aromatic Br shows little action.
- Flame retardancy is similar to HBCD



Tetrabromobisphenol A bis (2,3-dibromo methyl propyl ether), FR130X

EPS-XEPS XPS producers cost in transition

Known

- Extra costing as new FR types are more expensive and less effective but
  EPS: increase about 4%/ton produced for Polymeric FR
  XPS: Increase of more as 4% /ton produced for polymeric FR

- The most important part its a sustainable product !

- optimization is needed

Technical challenges

- Situation on process behavior for FR systems (producers, suppliers)
- Optimization of process control parameters unknown effect of impurities
- The polymeric FR is mainly for XPS developed
- FR130 is a suitable for EPS and XEPS

EPS and XEPS and Process Variations

EPS

- Different recipes from producer to producer
- Suspension process
  white EPS sensitive for impurities
  grey eps less sensitive for impurities
- Blowing agent Pentane
- Many variations: lambda, psd, densities , nucleation
- New PFR Increase costing's FR and recipe but in the future recipes will be optimized due to learning curve

Industrial aspects:

- Commodity products however each company has his **own "SECRETS"**
- Consistency of Raw materials is key issue
- "**GOOD**" might be **"BAD** " for others

XEPS :

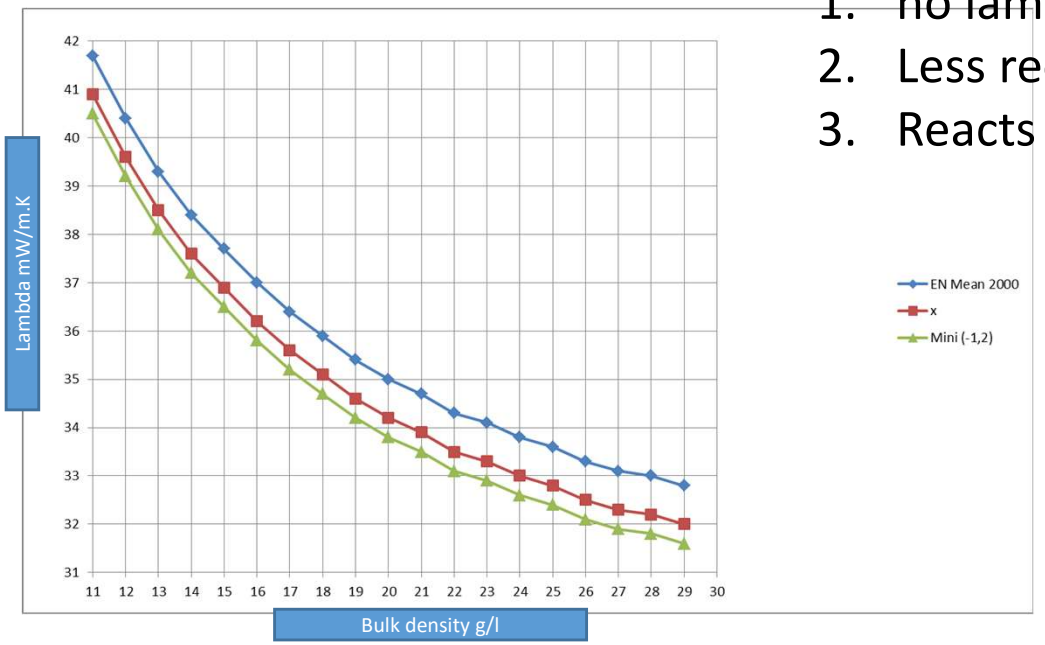
- Base polymer is polystyrene
- Master batch or inline compounding
- Blowing agent pentane
- Less sensitive as EPS but higher temp used >180 C (200 C max)

EPS	PFR	FR130X	HBCD
Dispersion SM	less	oke	oke
lamda	neg	better	ref
Nucleating agent	no	yes	yes
PSD	coarse	Some fines*	ref
Recipe changes	++	-/+	ref
Fouling	+	0	0
cost	++	+	0/+

SBI and B1 B2 test !!!!!

Example Lambda values EPS

With HBCD the lambda values are around 1.0mW/m.K below the CEN curve
With polymeric the lambda values are from -0.5 (CEN curve) to 1.5 mW/m.K up the curve with FR130X looks better as with HBCD



1. no lambda changes
2. Less recipe changes
3. Reacts almost as HBCD

Business Development New Markets

XEPS

- Base polymer is Crystal polystyrene or EPS
- Master batch or inline dosing during process
- pentane

  Should be nice if the polymeric has the same nucleating effect as in EPS
- Less sensitive as EPS but higher temp used
- Dispersion of FR (powder or compacted) or via MB route
- Compounding difference of HBCD and the polymeric FR not for the FR130

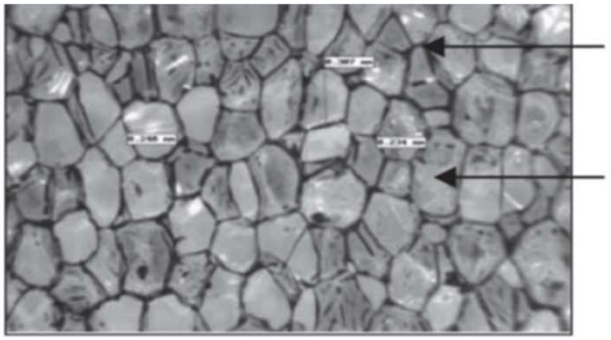
XEPS

XEPS	PFR	FR130 x (FR130)	HBCD
Dispersion	depends	oke	oke
Nucleating agent	To be changed	Similar as HBCD	ref
Cluster/ sieve issue	yes	no	no
Recepe changes	+++	-/+	ref
Efficency FR	--	+	+
cost	++	+	0

XPS

- Base polymer is Crystal polystyrene
- Master batch or inline dosing during process
- Blowing agent CO_2 and ethanol, ethanol and dimethyl ether , water, isopropanol , HFC134a etc.

  Should be nice if the polymeric has the same nucleating effect as in EPS
- Less sensitive as EPS but higher temp used >220deg C (250deg C max)
- Dispersion of FR (powder or compacted) or via MB route
- Compounding difference of HBCD and the polymeric FR not for the FR130



- **Requirements**
  thermally stable
  min dosage
  Master batch (easy operation)
  No side effects (Color , corrosion)
  Effective at Combustion Temp

- **Constraints**
  Aromatic bromine is more stable than aliphatic but less effective
  Aliphatic is effective but less stable
  Blowing agent used as the polymeric reacts different as with HBCD
  Polymeric FR makes clusters due to high molecular weight and long aliphatic chains

- **Industrial compromise**
  Aliphatic as stable as possible
  usage of Stabilizers internal or external
  also needed a different stabilization pack for Generated Br, Polymeric FR and PS

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- Replacement for HBCD
- Polymeric Flame Retardant is environmentally friendly but …..
- Fire Performance HBCD→FR130X→PFR
- Superior Environmental and health profile (more sustainable): PFR equal to FR130X
- Polymeric FR Stable, non-toxic high molecular weight material that is inherently safer due to limited bioavailability/toxicity
- FR needs to be compatible with base polymer systems
- Overall Cost – a “drop-in” replacement that utilizes existing manufacturing facilities
- Dispersion of the flame retardant in EPS/XEPS and XPS is important

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XPS

Product	PFR	BDDP	FR130X	TBC
Fire test DIN 4102 B2	1,3-2,6%	1,5-3%	1-2%	1,5-3%
Molecular Weight, g/mol	Br-Polymeric Over 30000	Low molecular weight	Low molecular weight	Low molecular weight
Br, %	65%	68%	66%	65%
Compatibility with PS	Very good dispersion	Very good dispersion	Very good dispersion	Very good dispersion

Many patents on other Fr systems have been checked !!!

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	HBCD + synergist + HS	Br-POLYMER + synergist + HS	BDDP + synergist + HS	FR130 + synergist +HS
Fire test DIN 4102 B2	1-2 %	1,3-2,6%	1,5-3%	1-2%
Classification & Labelling	Face out 2015. "SVHC" molecule	Not classified	Not classified	Not classified
Molecular Weight, g/mol	Low molecular weight	Br-Polymeric Over 30000	Low molecular weight	Low molecular weight
Br, % **Active Bromine, %**	75% 75%	65% 55%	68% 40%	66% 66%
Compatibility with PS	Good dispersion.	BrSBS makes clusters due to high molecular weight rubber.	Very good dispersion	Very good dispersion
Thermal Stability	5% @ 240° C Needs stab. For free and for PS and for PS Resists 15 minutes @ 210°C	5% @ 248°C Needs stab. for free Br and for Br-polymer and for PS Resists 10 minutes @ 210°C	Extremely thermal stable Resists more than 20 minutes @ 250°C	Resists less than 5 minutes @ 210°C New type higher
Compacting behaviour	Poor, 5% fines	Very good, less than 2% fines	Good, less than 2% fines	No experience

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+ and – From 2-5	HBCD + synergist + HS	Br-POLYMER + synergist + HS	BDDP + synergist + HS	FR130X+ synergist +HS
FLAME RETARDANCY	5	4	3	5
COST PERFORMANCE	5	2	4	3
THERMAL STABILITY	4	3	5	5 new type
PROCESS, COMPATIBILITY	4	4	5	4
AVAILABILITY	0	4	5	5
HYSTORY OF THE PRODUCT	5	2	5	3

Xps	PFR	FR130X	HBCD
Dispersion	depends	oke	oke
Nucleating agent	To be changed	Similar as HBCD	ref
Recepe changes	+++	-/+	ref
Blowing agent	effect	oke	oke
Efficency FR	--	+	+
cost	++	+	0

Contact Us

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M: +32 476850297
E: rgb.wilmer@oceanchem-group.com

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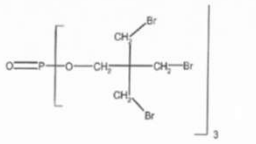
Thank You!

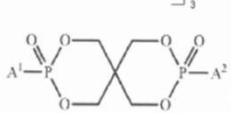
The Leading Supplier of ***Flame Retardant*** *from* ***China***

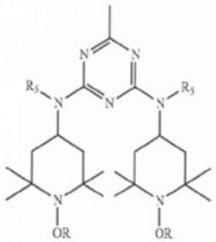
www.oceanchem-group.com

Patents/synergist

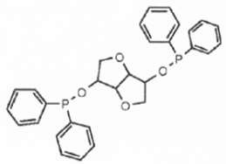
- Elemenater Schwefel
- Roter Phosphor
- Phosphate
- Bromierte Phosphate
- Triazine



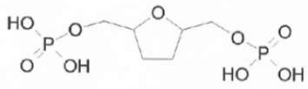




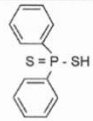
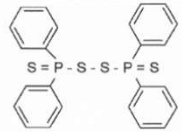
- Aluminiumtrihydroxid (ATH)
- Sn und Sn-legierungen
- Aluminuium Dibromsaliciate

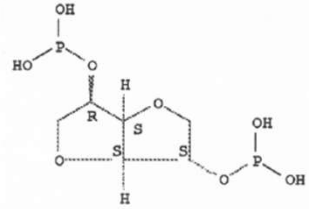


1,4:3,6-Dianhydro-hexitol-2,5-bis(P,P-diphenylphosphinit) (D2)

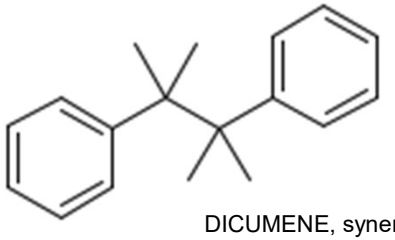


(D1) 2,5-Anhydro-3,4-dideoxy-hexitol- bis(dihydrogen phosphat)

	Diphenyldithiophosphinsäure
	Bis(diphenylphosphinthioyl)disulfid
	1,1,2,2-Tetraphenyldiphosphindisulfid
$O=P(O\text{-}Ph)_3$	Triphenylphosphat



1,4:3,6-Dianhydro-bis(dihydrogen phosphit)-hexitol (D11)



DICUMENE, synergist

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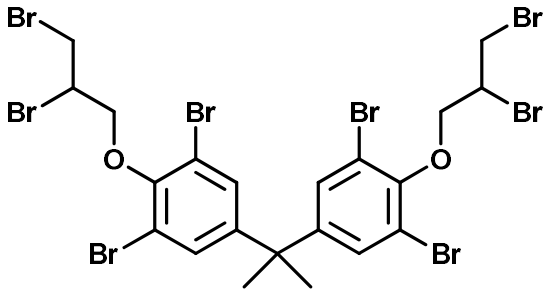
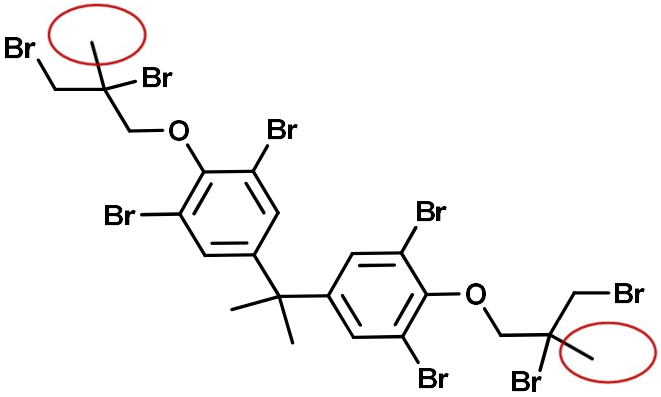
G'sal™ **FR-130X**



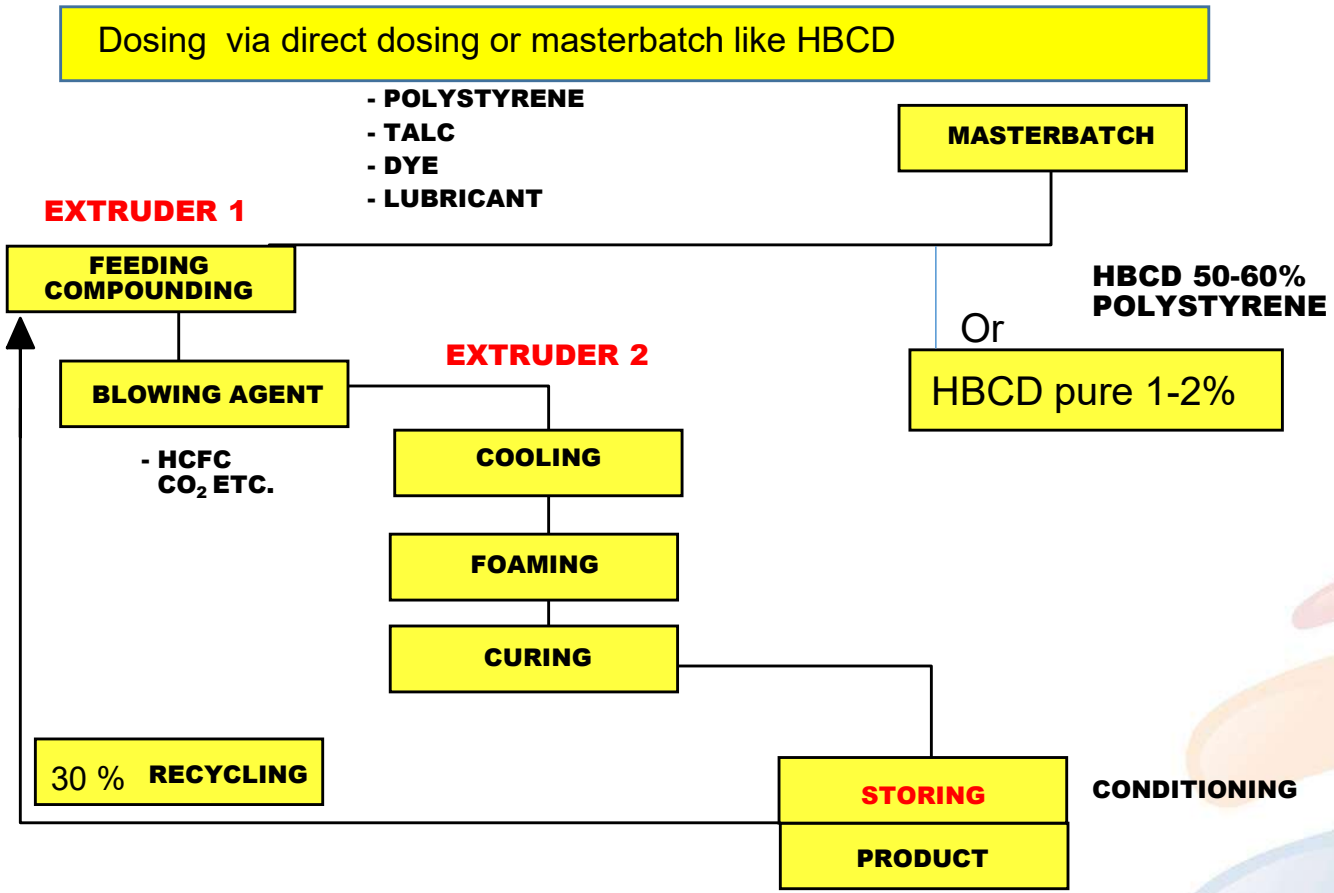


BDDP	
Cas No.	: 21850-44-25
Equivalent	: Chemtura PE-68; Albermarle Saytex HP-800; ICL FR-720

FR-130X	
Cas No.	: 97416-84-7

TECH ITEM		Quality Standard
Appearance	/	White Powder.
Purity	%	95 min.
Melting Point	°C	100 min.
Volatile	%	0.30 max.
Whiteness	%	90 min.
Bromine Content	%	65.0 min.

Flowchart XPS



Replacement and Synerchist

- HBCD till 2019 and 2022 china
- Polymeric FR = only lanxess ICL and Sunris with licence
- PE 68 = FR720 = C21H20Br8O2; mol. wt. = 943.9
- SR130=FR130= others via traders =C23H24Br8O2
- TBC (Tris (2,3-dibromopropyl) isocyanurate = C12H15Br6N3O3
- Synerchisten:
- Brominated epoxies
- Epoxy
- other

- Cooperated with Japanese Partner - Dai-ichi Kogyo Seiyaku Co.,Ltd. developed FR-130. Based on the technology of our Brominated Flame Retardant: BDDP

- **Good Flame Retardancy Performances**

- Suitable HBCD replacement without formulations changes
  Ensure the end foam cells structure and size will remain unchanged.

- **Health-Safety-Environmental aspects**
  Not Persistent,Bio accumulative and Toxic(PBT) subtance.
  Not adversely affect human health.
  Not a mutagen,reproductive toxin nor a probable carcinogen(CMR)

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G'sal™ R-130X

- REACH Situation

Substance Name	EC No.	Cas No.	Tonnage Band	Reference Number
1,1'-(isopropylidene)bis[3,5-dibromo-4-(2,3-dibromo-2-methylpropoxy)benzene]	306-832-3	97416-84-7	1000-10000 tonnes/year	01-2120086211-65-0001

REACH :
OR: NETSUN EU B.V.
We have Full Registration and can guarantee the sales in EU region.

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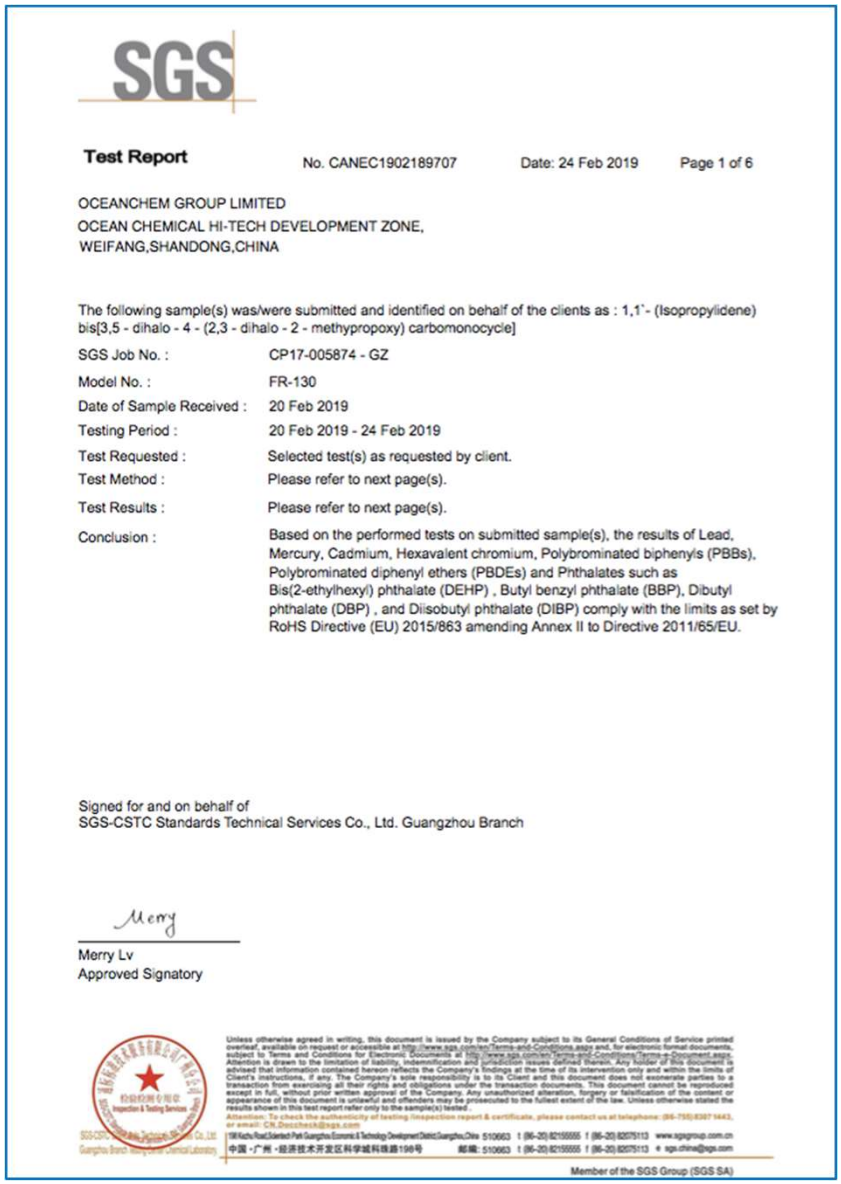
G'sal™ FR-130X

- SGS comply to RoHS directive



SGS

Test Report No. CANEC1902189707 Date: 24 Feb 2019 Page 1 of 6

OCEANCHEM GROUP LIMITED
OCEAN CHEMICAL HI-TECH DEVELOPMENT ZONE,
WEIFANG,SHANDONG,CHINA

The following sample(s) was/were submitted and identified on behalf of the clients as : 1,1`- (Isopropylidene) bis[3,5 - dihalo - 4 - (2,3 - dihalo - 2 - methypropoxy) carbomonocycle]

SGS Job No. :	CP17-005874 - GZ
Model No. :	FR-130
Date of Sample Received :	20 Feb 2019
Testing Period :	20 Feb 2019 - 24 Feb 2019
Test Requested :	Selected test(s) as requested by client.
Test Method :	Please refer to next page(s).
Test Results :	Please refer to next page(s).
Conclusion :	Based on the performed tests on submitted sample(s), the results of Lead, Mercury, Cadmium, Hexavalent chromium, Polybrominated biphenyls (PBBs), Polybrominated diphenyl ethers (PBDEs) and Phthalates such as Bis(2-ethylhexyl) phthalate (DEHP) , Butyl benzyl phthalate (BBP), Dibutyl phthalate (DBP) , and Diisobutyl phthalate (DIBP) comply with the limits as set by RoHS Directive (EU) 2015/863 amending Annex II to Directive 2011/65/EU.

Signed for and on behalf of
SGS-CSTC Standards Technical Services Co., Ltd. Guangzhou Branch

Merry

Merry Lv
Approved Signatory

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中国·广州·经济技术开发区科学城科珠路198号 邮编: 510663 t (86-20) 82155555 f (86-20) 82075113 e sgs.china@sgs.com
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We can issue the SGS Certificate for each lot as customer's requirement.