ICL Industrial PRODUCTS

FR Division

Caring for your Future-Today!

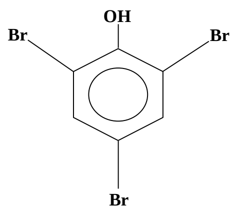
FR-613

2,4,6 Tribromophenol

Application Data Sheet as wood preservative

- FR-613 is comparable in efficacy to and in some instances even better than other wood preservatives such as chlorinated phenols.
  It is effective against certain brown molds resistant to chlorinated phenols, soft rot fungi, blue sapstain.
- Its mammalian acute toxicity is much lower than corresponding chlorophenols (oral and dermal LD_{50} >5000 and > 2000 mg/kg body weight respectively compared to 140-250 mg/kg for tetra- and pentachlorophenol).
- FR-613 is easy to formulate into stable and effective composition in oil or aqueous systems.
- The fungicidal, bactericidal and insecticidal efficiency can be synergistically enhanced by combining TBP or Na-TBP with other active ingredients, permitting the reduction of the levels of total active ingredients.

Table 1: Physical properties

Chemical structure	 2,4,6 tribromophenol
Formula	$C_6H_3OBr_3$
Molecular weight	331
Specific gravity	2.55 at 20°C
Melting point	93°C
Solubility in water	1 part in 14,000 at 15°C (72 ppm)
Solubility in other solvents	excellent solubility in acetone, diethylether benzene, toluene, alcohols, petroleum distillates etc….
Appearance and odor	white to off-white crystalline flakes with phenolic odor

Applications:
Tribromophenol and sodium tribromophenolate are used as wood preservatives to control insects, fungi and putrefying bacteria in construction lumber, plywood timbers, railroad ties, fence posts, utility poles, landscape materials and building foundation materials.
Standard application methods of pressure and vacuum impregnation, dipping, brushing and spraying are suitable.

Efficacy and comparative tests

Efficacy

TBP and Na-TBP were found effective against the following organisms:

Fungi

- Soft-rot fungi
  - Trichoderm SP. (esp. Viride, Virgantum, Harzianum, Pseudokoningii)
  - Aspergillus SP. (esp. niger v. tiger)
  - Phialophora Fastigiata
  - Penicillium SP
- Brown-rot fungi
  - Serpula Lacrymans
  - Coniophora Puteana
- Others
  - Ceratocystis SP. (Coerulescens, pilifera)
  - Aureobasidium Pullulans (blue stain)
  - Graphium SP.
  - Alternaria SP.
  - Cephalouscus Fragrans Hanawer
  - Tyromyces Palustris
  - Gliocladium Virens
  - Polystictus Versicolor – bacteria
  - Polyporous Versiporous – bacteria

Table 2: Application methods of TBP and Na-TBP

Timber product	Reason for treatment	Dosage	Application directions
Green timber	Discoloration of wood due to fungi and putrefying organisms	Na-TBP at 1.5 kg/100 liters water (1.5%).	Spray on or dip freshly sawn timber. Dosage depends on thickness of timber. Retention required about 0.05 mg/cm^2.
Structural joinery timber	For long-term control of insects	Na-TBP or TBP at 40 g/liter (4%)	Vacuum/pressure impregnation.
Timber in-situ use	For temporary protection	Na-TBP or TBP at 40 g/liter (4%)	Apply liberally with brush. Permit solution to soak into wood.

Table 3: Some antifungal efficacy data
(Values for Na TBP unless otherwise indicated)

Tested Organism Fungi	Minimum inhibitory growth concentration (%)
Aspergillus Niger	0.0025
Penicillium Citrinum	0.005
Trichderma Viride	0.025
Rhizopus Nigricans	0.05
Chaetomium globosum	0.005
Tyromyces Palustris	0.01
Polystictus versicolor	0.008 (value for TBP)
Polyporus versisporus	0.004 (value for TBP)
Cephaloascus fragrans	More effective than chlorinated phenols

Insects

Prionpulus Reticuloris – white larvae
Coptotermes Curvinathus – Subterranean termite
White ant
Tribolium Castaneum Herbest
Lyctidae SP.

Table 4: Insecticidal efficacy

Filter Paper Substrate	
Test organism	**Kill rate at specified time and concentration**
White ant	100% after 24 hours, 0.05% Na-TBP and 0.1% TBP
Triboleum Castaneum Herbest	90-95% after 1 week, 2% Na-TBP and TBP
Lyctidae	80% after 4 weeks, 3% Na-TBP

Comparative efficacy

Laboratory experiments for comparison to Chlordane.

TBP and Na-TBP exhibit better insecticidal activity than chlordane against the White ant and comparable activity againt Triboleum Castaneum Herbest. Chlordane at 100 times the concentration of Na-TBP is required for equivalent efficacy against White ants.

Table 5.

Ingredient	Mortality percentage among insects			
	Insect	Hours post treatment		
		24h	120h	168h
0.1% Chlordane	White ant	0%	70%	100%
0.1% TBP	"	100%	---	---
0.1% Na-TBP	"	100%	---	---
0.01% Na TBP	"	77%	100%	---
1.0% Chlordane	Tribolium	2%	77%	88%
1.0% TBP	Castaneum Herbest	3%	67%	90%

Laboratory experiments for comparison to CCA, Creosote.

Wood species: 1) Crytomeria japonica - Sapwood
2) Picea jezovensis – Heart wood

Fungi: Serpula Lacrymans – Brown-rot
Tyromyces palustris

Table 6

Effective value**			
Material	**Const.**	**S. lacrymans**	**T. palustris**
CCA	1.6%	100%	100%
Creosote	--	86%	60%
TBP *	1%	100%	100%

*TBP contains 48% chlordane
**Effective value = 100x(weight loss % of original wood – weight loss % of treated wood) / weight loss % of original wood

Laboratory Experiments for comparison to Na TCP

Wood species: Douglas Fir
Hemfir (Western hemlock and Amabilis Fir)
All woods are soft woods

Fungi: Mold and staining fungi

1. Aureobasidium pullulans
2. Ceratocystis pilifera
3. Cephalouscus fragrans
4. Trichoderma pseudokoningii (soft-rot)
5. Penicillium (soft-rot)
6. Aspergillus niger (soft-rot)
7. Phialophora fastigiata (soft-rot)
8. Gliocladium virens

Table 7

Material	**Conc. %**	**Period (weeks)**	**Hemfir**			**Douglas Fir**		
			m*	**s***	**d***	**m**	**s**	**d**
Na TCP	2.0	4	2	0	0	1	0	0
		16	1	1	0	2	1	2
TBP	2.0	4	0	0	1	1	2	1
		16	1	1	0	4	2	2

Rating: sum of the rating for fungal growth divided by 400 (the theoretical maximum sum of rating on 80 pieces and multiplied by 10).

*m = mold; s = stain; d=decay

Actual and simulated field tests

Four-month closed pile field tests on several specimens of planed Canadian timber and simulated three-year field tests on pine show that TBP and Na-TBP are as effective as chlordane and tetrachlorophenol (TCP) in wood preservation.

Table 8

Efficacy					
Ingredient	**Treatment method**	**% reduction in fungal growth vs. no treatment**			**% damage by white ants 12 months post-treatment**
		Mold	**Stain**	**Decay**	
1% Chlordane	Pressure	---	---	---	0
1% TBP	Pressure	---	---	---	0
1% Na-TBP	Pressure	---	---	---	0
No treatment	Pressure	---	---	---	100
1.2% Na-TBP	Dipping	91	93	95	---
1.5% Na-TCP	Dipping	97	87	96	

Synergy

Insecticidal efficacy is synergistically enhanced when TBP and Na-TBP are combined with other active ingredients, permitting reduced levels of wood preservative.

Insects:

Table 9

Mortality percentage among white ants			
Ingredient	**Hours post-treatment**		
	6	**12**	**24**
A: 1.0% Chlordane	0	30	42
B: 0.05% Na-TBP	0	47	100
C: A+B	57	80	100

Other organisms

Polystictus versicolor - bacteria

Polyporus versisporus - bacteria

Table 10

Ingredient	Minimum growth inhibitory const (ppm)	
	P. Versicolor	P. Versisporus
TBP	80	40
EIBP * + TBP (1:1)	10	20

*EBIP - 3-Ethoxycarbonyl-oxy-1-bromo-1,2-iodo-1-propene

Wood penetration

The excellent wood penetration properties of water soluble Na-TBP can be further increased by proper formulation with borax buffers which also exhibit antibacterial and antifungal properties.

Table 11

Treatment		
Specimen depth (mm)	2% Na-TBP	2% Na-TBP + 1.25% Borax Buffer
0-1	3006	2885
7-8	861	1582
14-15	120	721

Toxicological properties for TBP

See MSDS available at http://www.iclfr.co

TBP - Na

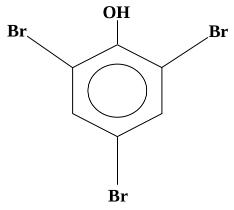
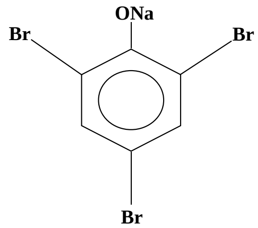
TBP is water insoluble. For in use in water systems, it is converted into its sodium salt, Na-TBP.
Hereunder is a description of the preparation of Na-TBP formulations:

1. Lab scale – using NaOH
2. Aqueous solution – using NaOH
3. Solid formulations – using Na_2CO_3

All the kinds of formulations of TBP and TBP itself are sensitive to light. Therefore the materials should be kept in dark and sealed packaging.

Lab scale (see Figure 1).

Chemical equation:

	+NaOH	⇒		+ H_2O
M.W. 331	40		353	18

1. Mix at 45° C with an agitator.
   TBP - 265 g (TBP assay : 99.1%)
   H_20 - 567 g
   $Na_2S_20_4$ - 4 g (0.4% w.t.)

2. Add 54 mg of 50% NaOH.

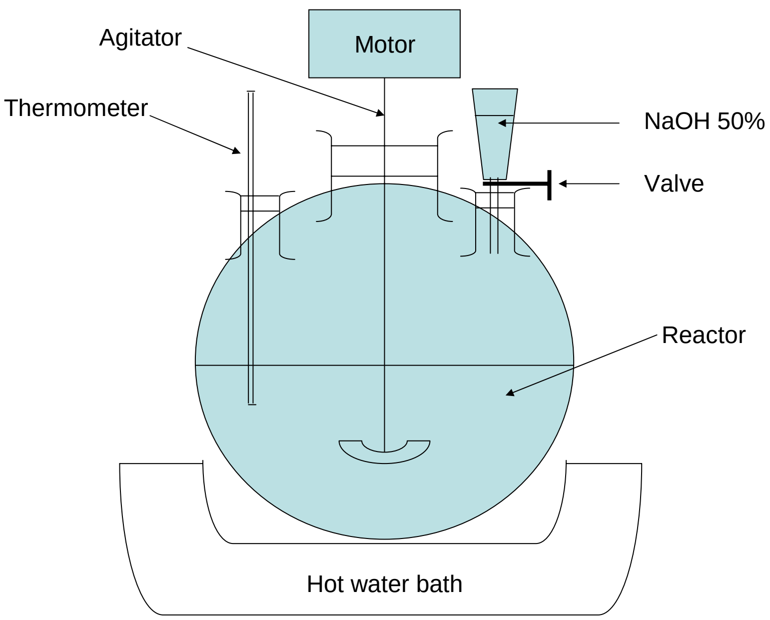
Concentration of commercially available Caustic Soda solution at low price is 50%. Since the reaction is endothermic, add the NaOH solution drop-wise, keeping the reaction temperature at 45°C.

3. The solution obtained (1000 g) contains:

TBP-Na	:	280 g	conc. 28%
H_20	:	699 g	
$Na_2S_2O_4$	:	4 g	

4. Adjust pH to 11.0 with small amounts of NaOH solution.

Figure 1: Lab scale reactor



Aqueous solution (Figure 2)

Theoretically the reaction takes place with the stoichiometric molecular ratio of TBP/NaOH = 1/1.
Practice, however, has shown that better results can be obtained with a molecular ratio of TBP/NaOH = 1 / 1.05.
The basic reactants are:
NaOH – 50% solution (diluted to 20%).
TBP – technical

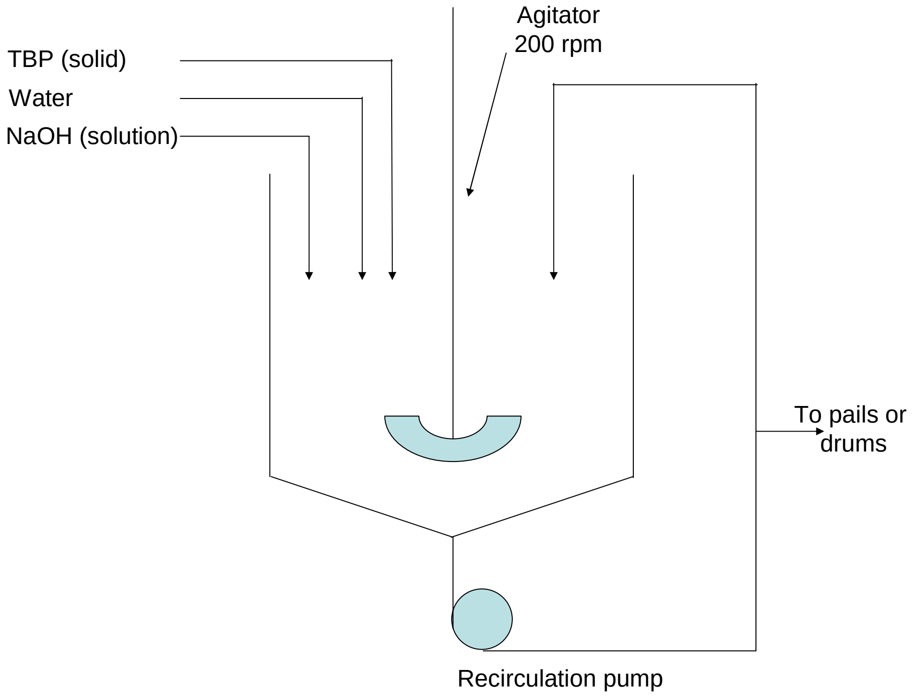
The solid TBP, in powder or flakes, should be slowly added to the NaOH solution, with continuous slow stirring action, around 200 rpm, propeller type or paddle agitator.
The endurance of the reaction depends on the particle size of the TBP. The reaction is slightly exothermic and the temperature of the reacting system goes to the 40-50^{0}C range.
The reaction is over when pH = 11.
Lower NaOH concentration, therefore lower pH, will produce darker Na-TBP.
Higher pH than 11 will affect the color of the treated wood, making it darker.

In case the pH rises higher than 11, small quantities of TBP can be added in order to lower it back to 11.
In case the pH continues to be higher than 11, although the reaction may be stoichiometrically over, small quantities of emulsifiers may have to be added, generally a combination of anonic and non-ionic emulsifiers.
This can only be determined by trial and error in the laboratory.
The result of the above procedure is a 1000 kg – 40% solution of Na-TBP, when reactants used:

TBP	-	381 kg (TBP assay 99.1%)
NaOH 50%	-	92 kg
$Na_2S_2O_4$	-	4 mg
Water	-	523 kg

Note: during the whole process, a complete absence of iron is absolutely necessary. Therefore, it is recommended not to use steel or stainless steel reactors, agitators, etc.
The reactor should be glass-lined or made out of steel lined with epoxy, resin, glass fiber, etc.
This procedure is to avoid the iron ions to take the place of the sodium ions, with the consequent formation of Fe-TBP.
After the reaction is completed, recirculation should be started.
The recirculation pump and piping can be made out of steel, since the Na-TBP has already been formed.

Figure 2: Industrial Reactor.



Solid formulation

The solid formulation is a mixture of TBP, Soda-Ash, $Na_2S_2O_4$, when dissolved in water. Na-TBP will form at a concentration depending on the quantity of water added.

TBP as flakes, Soda-Ash as granular and $Na_2S_2O_4$ as powder in their regular appearance will not give a homogenous mixture if they are simply mixed. Therefore the materials have to be ground first. The materials are mixed homogenously through the grinding process, then the mixture is sifted through a 20 mesh sieve in order to obtain a fine powder. The grain size affects the rate of dissolution.

To obtain 1000 kg of Na-TBP, use:

TBP	-	650 kg
Na_2CO_2	-	346 kg
$Na_2S_2O_4$	-	4 kg

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