Monsanto

A-3

CONFIDENTIAL

FROM (NAME, LOCATION) R. W. Weiss - Research Center

DATE : June 23, 1969

cc: Q. E. Thompson
L. R. Stark
J. F. Herber/JDS

SUBJECT :

REFERENCE :

File Brominated Aroclor

TO : W. R. Richard

Production of bromine containing Aroclors is investigated to make fluids that are easier biodegradable than present Aroclors. It is accepted that for most physical properties one equivalent bromine will substitute for two equivalents of chlorine. Initial fire testing (AIT and Hot Manifold) support this reasoning. Capability of bromine containing Aroclors as electrical fluids has yet to be assessed, samples of Aroclor 1242 equivalents were submitted to R. H. Munch for evaluation.

Bromine modified Aroclors can be produced by the following alternate routes:

I Bromination of biphenyl (all Br-Aroclors).

II Bromination of Aroclors (Bromo-Aroclors).

III Co-halogenation of biphenyl (Bromo-Aroclors).

The first two alternates have been used in the laboratory to prepare test samples. Neither is considered for economical production of modified Aroclors.

The manufacturing solution would be production of Bromo-Aroclors by co-halogenation. Biphenyl will be chlorinated to below the desired chlorine level first and the halogenation will be finished by admission of chlorine and bromine in the right ratio to obtain the desired product. This route has not yet been demonstrated in the lab; however, the process is reported for manufacturing of bromobenzenes.

The attached cost calculation (A) is calculated for the theoretical case that all Aroclors with higher chlorine content than 1242 will be discontinued and Aroclor 1254 equivalent is made by bromination of Aroclor 1242. The following cases (B-D) are based on the same volume.

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Conclusions: Production of Bromo-Aroclors is feasible in currently existing plant facilities. The increase in total manufacturing cost for incorporating one equivalent bromine in Aroclors 1254 and 1248 is ¢ 4.34 and 4.78 per lb., respectively. Corresponding figures for one half equivalent bromine in Aroclors 1248 and 1242 are ¢ 2.26 and 2.8, respectively. This increase in price does not favor addition of Bromo-Aroclors to our current product line. However, it does not exclude Arobroms as possible substitutes if the higher Aroclors have to be discontinued.

Manufacturing costs are calculated on the following assumptions:

Batch co-halogenation carried out in existing Aroclor facilities,

No change in charge, catalyst and time cycles except for reduction of the chlorine charge,

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Bromine will be charged from tank car directly to new vaporizer

Cost of new equipment: vaporizer plus metering device for bromine (at ± 10% accuracy) at $50,000 amounts to ¢ 0.05 per lb product at 10 M lb production, and will be neglected.

The assumptions allow the use of current process cost figures by computing a price weight ratio for the amount of chlorine substituted for with bromine. The bromine/chlorine weight ratio will be reduced by 1/4 since every bromine substitutes for 2 chlorines and no bromine loss as hydroboronic acid will occur (cf. equation I for Aroclor 1254 and eq. II for brominated Aroclor 1254 equivalent/# $\frac{\text{equivalent Br } 80}{\text{equivalent Cl } 35.5} \times 1/2 \times 1/2 =$

$\frac{1}{1.78}$ = weight ratio.

One lb. of bromine at ¢16 per lb. will substitute for 1.78 lb of chlorine at ¢2 per lb. The increment "replaced" chlorine (equation I vs. II) will be multiplied by $\frac{16}{2} \times \frac{1}{1.78} = 4.5$ to arrive at the additional raw material cost for bromine. A small allowance will be made for the amount of chlorine necessary to oxidize HBr.

A. Production of Aroclor equivalent 1254 (cf. Equation II) by bromination of Aroclor 1242

$$Ph_2 + 5\ Cl_2 \longrightarrow C_{12}H_5Cl_5 + 5\ HCl \qquad (I)$$

$$\not{2}\ C_{12}H_7Cl_3 + Br\not{2} + Cl\not{2} \longrightarrow \not{2}\ C_{12}H_6BrCl_3 + HCl \qquad (II)$$

	Aroclor 1254 c/lb.		Aroclor equiv. 1254 c/lb.
Raw Matl. Cost	5.06		
Increment Cl	2.9		
Increment others	2.16		2.16
Remaining Cl 3/5	1.74		1.74
Replaced Cl 2/5	1.16	x 4.5	5.21
Oxidizing Cl 2/5 x 1/4	--		0.29
Raw Matl. Cost	5.06		9.40
Conversion Cost	1.79		1.79
Total Manuf. Cost	6.85		11.19

Increased cost for substitution of two chlorine by one bromine in Aroclor 1254 4.34 c/lb.

B. Production of Aroclor equivalent 1242 (cf. equation IV) by bromination of Aroclor 1232.*

$$Ph_2 + 3\ Cl_2 \longrightarrow C_{12}H_7Cl_3 + 3\ HCl \qquad (III)$$

$$2\ C_{12}H_8Cl_2 + 1/2Br_2 + 1/4Cl_2 \longrightarrow 2\ C_{12}H_{7.5}Br_{0.5}Cl_2 + 1/2\ HCl \qquad (IV)$$

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	Aroclor 1242 (c/lb)		Aroclor equivalent 1242 (c/lb)
Raw Matl. Cost	5.06		--
Chlorine increment	2.25		
Increment others	2.81		2.81
Remaining Cl 2/3	1.50		1.50
Replaced Cl 1/3	0.75	x 4.5	3.37
Oxidizing Cl 1/3 x 1/4	--		.18
Raw Matl. Cost	5.06		7.86
Conversion Cost	1.79		1.79
Total Mfg. Cost	6.85		9.65

Increased manufacturing cost for production of modified Aroclor 1242 by bromination of Aroclor 1232 2.80 c/lb

*Note. The co-halogenation of biphenyl to the 1242 stage with 0.5 equivalents bromine will probably require an isomerization step with anhydrous $AlCl_3$ as catalyst. This will amount to a cost increase of 0.03¢/lb or less. No other costs are foreseen if the time cycle will not increase.

C. Production of Aroclor equivalent 1248 (cf. equation) by bromination of Aroclor 1242.

$$Ph_2 + 4\ Cl_2 \longrightarrow C_{12}H_6Cl_4 + 4\ HCl \qquad (V)$$

$$2\ C_{12}H_7Cl_3 + 1/2\ Br_2 + 1/2\ Cl_2 \longrightarrow 2\ C_{12}H_{6.5}Br_{0.5}Cl_3 + 1/2\ HCl \qquad (VI)$$

	Aroclor 1248 (c/lb)		Aroclor equivalent 1248 (c/lb)
Raw Matl. Cost	5.06		--
Increment Cl	2.57		--
Increment others	2.49		2.49
Remaining Cl 3/4	1.87		1.87
Replaced Cl 1/4	0.62	x 4.5	2.80
Oxidizing Cl 1/4 x 1/4	--		0.16
Raw Matl. Cost	5.06		7.32
Conversion Cost	1.79		1.79
Manufacturing Cost	6.85		9.11

Increased cost for manufacturing of modified Aroclor 1248 by bromination of Aroclor 1242: 2.26 c/lb

D. Production of Aroclor equivalent 1248 (cf. equation VIII) by bromination of Aroclor 1232.*

$$Ph_2 + 4\ Cl_2 \longrightarrow C_{12}H_6Cl_4 + 4\ HCl \qquad (VII)$$

$$2\ C_{12}H_8Cl_2 + Br_2 + 1/2\ Cl_2 \longrightarrow 2\ C_{12}H_7BrCl_2 + HCl \qquad (VIII)$$

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	Aroclor 1248 c/lb		Aroclor equivalent 1248 c/lb
Raw Matl. Cost	5.06		--
Increment Cl	2.57		
Increment others	2.49		2.49
Remaining Cl 1/2	1.275		1.28
Replaced Cl 1/2	1.275	x 4.5	5.75
Oxidizing Cl 1/2 x 1/4	--		.32
Raw Matl. Cost	5.06		9.84
Conversion Cost	1.79		1.79
Total Manufacturing Cost	6.85		11.63

Increased manufacturing cost for production of modified Aroclor 1248 by bromination of Aroclor 1232: 4.78 c/lb.

*Note: The co-halogenation of biphenyl to the 1248 stage under plant conditions will require an isomerization step with anhydrous $AlCl_3$ as catalyst. This will amount to a cost increase of ¢0.03/lb or less. No other costs are foreseen if the time cycle will not be increased.

R. W. Weiss

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