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Analytical Chemistry
Special Study 71-2
Job No. 13480

MCS 1016 - AN ENVIRONMENTALLY COMPATIBLE AROCLOR

INTRODUCTION

The objective of this report is to bring together all the information, so far generated by Monsanto, et al, that supports the contention that an environmentally compatible Aroclor can be manufactured. The product would be designed for use in areas where its industrial properties are unique enough to merit close control of the amount of material allowed to escape into the ecosystem.

SUMMARY

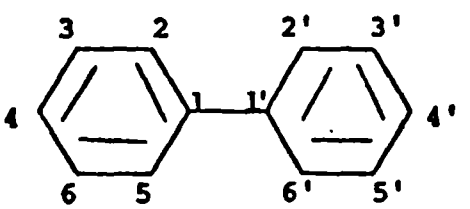
The information present in this special study report demonstrates that, from an environmental viewpoint, MCS 1016 is at least 10 times better than the current product Aroclor 1242 and in turn 75 times better than Aroclor 1254.

The above conclusion is based on the rather simplified assumption that the major environmental hazard associated with polychlorinated biphenyls (PCB's) is their ability to resist metabolic and non-metabolic degradation. The resistance of the PCB's combined with their high lipid solubility in turn leads to their undesirable biological build up toward the end of the exposed food chain.

RESULTS AND DISCUSSION

Polychlorinated biphenyl products are produced by direct chlorination of biphenyl which means that there exists in all PCB products at some level every conceivable isomer. The biphenyl ring structure (Figure I) can have theoretically 0-10 chlorine atoms substituted on it in any of the positions designated by the numbers on the ring. Assuming that the phenyl rings can rotate freely about the 1,1'-bond whatever the number and positions of chlorine substituents it can be calculated that there are 210 possible isomers. The distribution of these isomers according to the number of chlorines per biphenyl molecule is shown in Table I, column 1.

Figure I



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TABLE I

Homolog No. of Cl Per Biphenyl Molecule	Dist. of Theoretical PCB Isomers	Dist. of Most Probable PCB Isomers	Dist. of Most Probable PCB Isomers Found in Nature	Dist. of Most Probable PCB Isomers Co-Oxidized by C_2	Dist. of Identifiable PCB Isomers Absent in Tissue Extracts
0	1	1	-	1	1
1	3	3	-	3	3
2	12	6	-	5	9
3	24	18	-	11	4
4	42	21	-	4	-
5	46	36	36	5	-
6	42	21	21	1	-
7	24	18	18	-	-
8	12	6	6	-	-
9	3	3	-	-	-
10	1	1	-	-	-
Total:	210	130	81	30	17

The number of possible isomers can be reduced from 210 to 130 by further assuming that the most probable structures are those where the number of chlorine atoms on the two rings differ by not more than one. The distribution of the most probable structures are shown in Table I, column 2. Of these 130 most probable isomers, the ones of further interest are those that have 5-8 chlorine atoms per biphenyl molecule. The reason for this lies in the fact that PCB's containing 5-8 chlorine atoms are the most refractory toward degradation as witnessed by what has and is being found in "weathered" biological materials. This leaves a total of 81 isomers that are the cause of the undesirable biological build up phenomenon. The isomers of concern are listed in Table I, column 3.

With this information in hand, it is instructive to discuss the homolog distribution of Aroclor 1254, Aroclor 1242 and the replacement fluid MCS-1016. This distribution is shown in Table II.

Some simple arithmetic with the numbers in Table II shows that ~75% of Aroclor 1254, ~10% of Aroclor 1242 and only ~1% of MCS 1016 are the refractory PCB isomers that are responsible for the biological build up.

CONCLUSION

"MCS 1016 can decrease the level of refractory PCB isomers currently being released to the environment from use of Aroclor 1242 and Aroclor 1254 by factors of 10X and 75X, respectively."

To further verify the above conclusion, a number of research programs have been instituted which include studies of bacterial degradation of the products in question by natural and accumulated bacteria as well as some work involving rat metabolism.

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TABLE II
HOMOLOG DISTRIBUTION OF AROCLOR PRODUCTS

Homolog No. of Cl Per Biphenyl Molecule	Aroclor* 1254	Aroclor** 1242	MCS** 1016	Aroclor* 1221
0	0.05	0.01	0.02	19.00
1	0.06	0.70	1.00	54.10
2	0.32	15.50	19.70	20.40
3	0.78	49.40	57.30	3.90
4	22.99	24.80	21.20	2.30
5	47.38	8.70	0.80	0.25
6	19.75	0.85	0.05	-
7	4.62	-	-	-
8		-	-	-
9	3.96	-	-	-
10		-	-	-

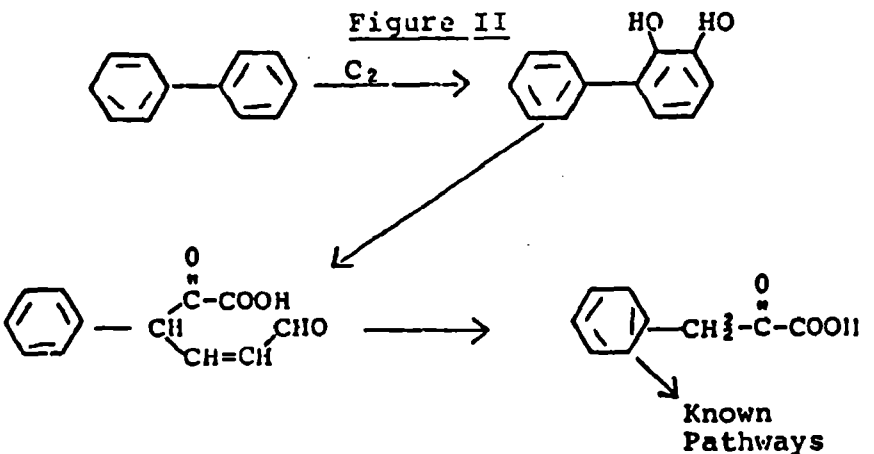
* Spectroscopy Special Study
**Memo, E. M. Emery to R. E. Keller, 1-22-71.

Accumulated Bacterial Degradation[1]

It has been demonstrated in the laboratory that a number of single PCB isomers and simple binary mixtures can be co-oxidized in the presence of biphenyl by a biphenyl degrading organism, C_2. The metabolic oxidation of biphenyl by C_2 is believed to occur as shown in Figure II.

The technique employed in these studies is a standardized shake flask procedure described in detail in the referenced report. The results of these studies have suggested that the structure of the

Figure II



[1] MCL Review report, "Biodegradability of Polychlorinated Biphenyls", J. H. Mainprize, Reference No. MP10103.

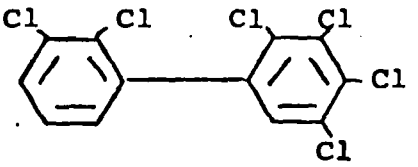
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most highly chlorinated PCB that will undergo at least primary degradation by C_2 is:

Figure III



Furthermore, all other C_2 degradable PCB's can be arrived at by progressively removing chlorine atoms from the structure in Figure III. This means that of the 130 most probable PCB isomers, 30 alone can be co-oxidized by this single culture, C_2. The distribution of these isomers is shown in Table I, column 4.

Long term exposure of MCS 1016 and Aroclor 1242 to C_2 has indicated that the order of degradability is MCS 1016>MCS 717*>MCS 762*> Aroclor 1242.

Conclusion

"The dominant isomers present in MCS 1016 can undergo at least primary bacterial degradation."

Natural Bacterial Degradation

Two techniques which are believed to more closely simulate actual environmental situations are also currently under investigation, Semi-Continuous Activated Sludge Testing (SCAS) and river die-away (RDA) exposures.

The decay of Aroclor 1221, Aroclor 1242 and Aroclor 1254 exposed to the natural biological population of river water was briefly studied in the following manner.

A five gallon supply of natural water was obtained from the Meramec River, and after allowing the sediment to settle for two days, the water was decanted into another container, remixed, and 200 ml aliquots placed in the appropriate number of 16 oz. wide mouth bottles. The bottles were then spiked with 250 ppb of Aroclor 1221, Aroclor 1242, and Aroclor 1254 by injecting 0.5 ul of a 10% (w/v) solution in ethanol and 4 ppm of LAS reference #2 (Dodecene-1) added as an internal standard. After swirling to mix, the bottles were then loosely covered with foil and placed in a cardboard box. Duplicate distilled water controls were prepared with no LAS as were river water and distilled water controls containing LAS but no Aroclor.

*Chlorinated biphenyl test materials intermediate in chlorine content with respect to MCS 1016 and Aroclor 1242.

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One bottle from each set was then analyzed on a weekly basis. The analysis consisted of extracting the bottle and contents with three 50 ml portions of hexane, diluting or concentrating the combined extracts to the appropriate volume and measuring the residual Aroclor by electron capture gas chromatography. Additionally, the LAS was monitored by methylene blue chloroform extraction method.

Neither Aroclor 1242 nor Aroclor 1254 disappeared at a measurable rate under the conditions of this experiment. However, the results of the EC/GC analysis for Aroclor 1221 are shown in Table III. Figure IV is a normalized composite of the EC chromatograms for the Aroclor 1221 river water and distilled water exposures. Figure V is just a plot of the disappearance rate. LAS disappearance was normal in all cases.

TABLE III

	ppb Aroclor 1221			
Weeks ⟶	0	1	3	5
Aroclor 1221				
River Water	246	121	77	28
Distilled Water	269	167	152	101

Although MCS 1016 was not available at the time this study was carried out the results are pertinent since MCS 1016 is intermediate in chlorine content with respect to Aroclor 1221 and Aroclor 1242. The homolog distribution of Aroclor 1221 is shown in Table II, column 4.

Conclusion

"The RDA disappearance rate of MCS 1016 should fall somewhere between those observed for Aroclor 1221 and Aroclor 1242."

Semi-Continuous Activated Sludge Tests

The details of the SCAS test procedure are outlined in Physical Chemistry Method 70-16. Briefly, the test consists of observing the disappearance rate of the material in question exposed to a bacterial sludge being feed a synthetic sewage mixture and aerated. Some samples of the results obtained via this test are shown in Table III to give the reader a feeling for the disappearnace rates which have been observed for similar non-chlorinated aromatic materials. To date, the results from tests with MCS 1043*, MCS 1016, Aroclor 1242 and Aroclor 1254 have allowed the following conclusions[2] to be drawn:

- Significant evidence of biodegradability was found for MCS 1043. Significance level used - 95%.

[2] "Analysis of Biodegradation Data", Statistics Special Study 70-22, J. D. Hinchen.

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-MCS 1016 and Aroclor 1242 showed evidence of biodegradation but neither was significant at 95%.

-Aroclor 1254 showed no evidence of biodegradation.

TABLE IV

Test Material	Exposure Level	Disappearance Rate (24 Hrs.)
Linear Alkyl Benzene Sulfonate (Dodecene-1)	20 Mg	>99%
Biphenyl	5 Mg	>95%
Isopropylated Biphenyl Mixture	10 Mg	79%
Hydrogenated Terphenyls	10 Mg	49%

Determination of PCB Residues in Rats Fed Aroclor 1242, Aroclor 1254, and Aroclor 1260[3]

The rat tissue samples were analyzed after extraction by electron capture gas chromatography as outlined in Analytical Chemistry Method 70-1. Upon completion of the electron capture work all tissue extracts, for each Aroclor fed, were combined and concentrated. The concentrates were then further purified via liquid chromatography and subjected to high resolution gas chromatography on a support coated open tubular (S.C.O.T.) column to identify as many of the unaffected isomers and homologs as possible.

The results of this study demonstrated that the residual PCB levels in all rat tissues (fat, kidney, muscle, and liver) decrease significantly as the degree of chlorination and the dietary exposure level of the material fed decreased.

Additionally, it was observed that the amount of isomeric alteration increased as the degree of chlorination decreased resulting in the fact that major PCB isomers retained by the rats fed Aroclor 1242 were those predominantly present in Aroclor 1254 and Aroclor 1260.

The distribution of the PCB isomers that were not retained in the composite tissue extracts are shown in Table II, column 5. Most important to note is that the 4,4'-dichloro and the 2,6-dichloro biphenyl isomers, which cannot be theoretically co-oxidized by the C_2 bacteria, were metabolized and/or excreted by rats.

[3] "Determination of Polychlorinated Biphenyl Residues in Rats From 30 Day Aroclor Feeding Studies", Analytical Chemistry Special Study 70-17, E. S. Tucker.

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Although the action of living organisms on polychlorinated biphenyls represents an important route for their disappearance from the environment, it is by no means the only degradation pathway available. Many other factors in the environment such as interaction with light, air, water, soil, dust, and heat which have not been investigated may also contribute to the nonmetabolic decomposition of the materials in question.

db

Monsanto Company
Organic Chemicals Division
Applied Sciences Section
St. Louis, Missouri

2/71 - E. S. Tucker

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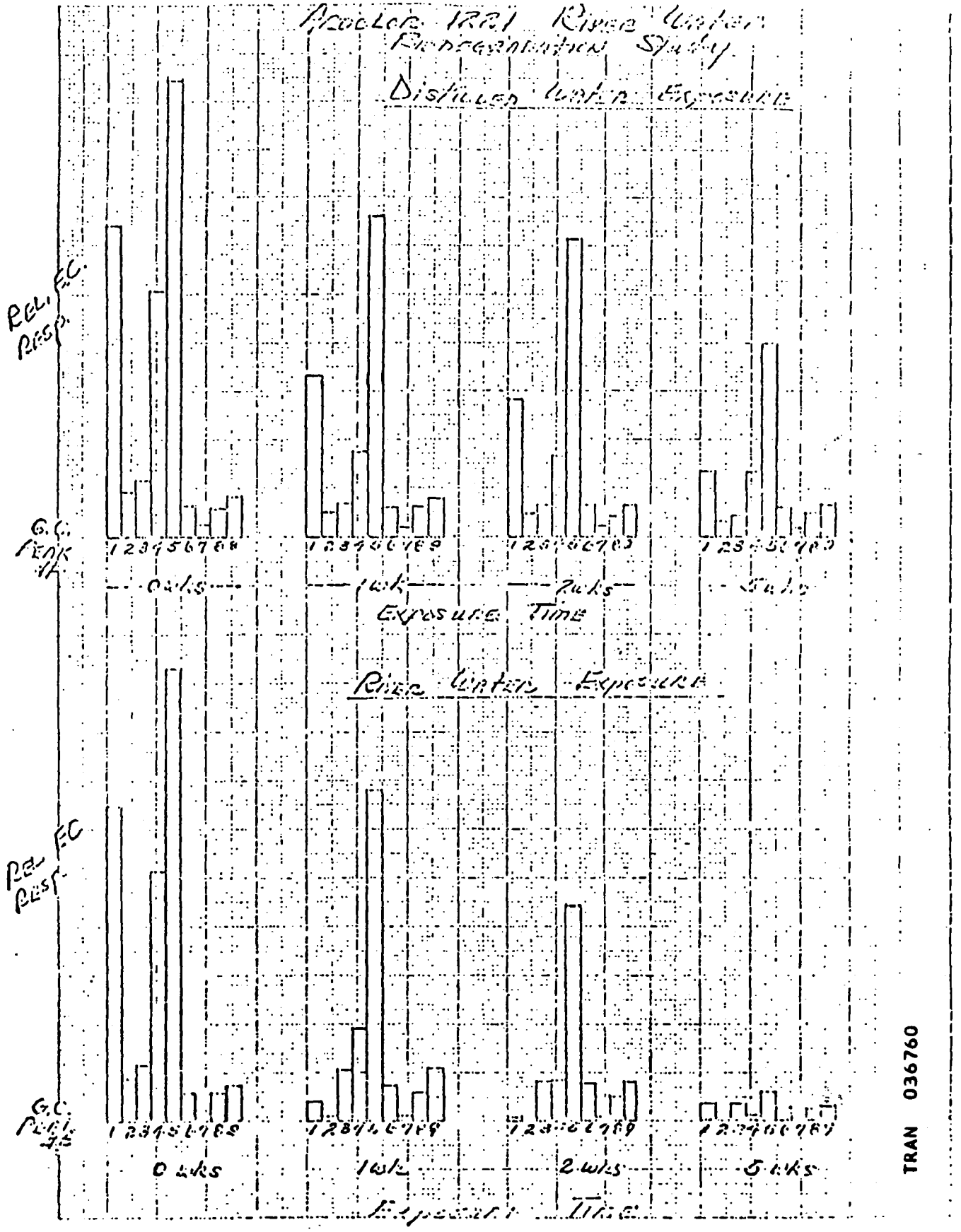


FIGURE IV

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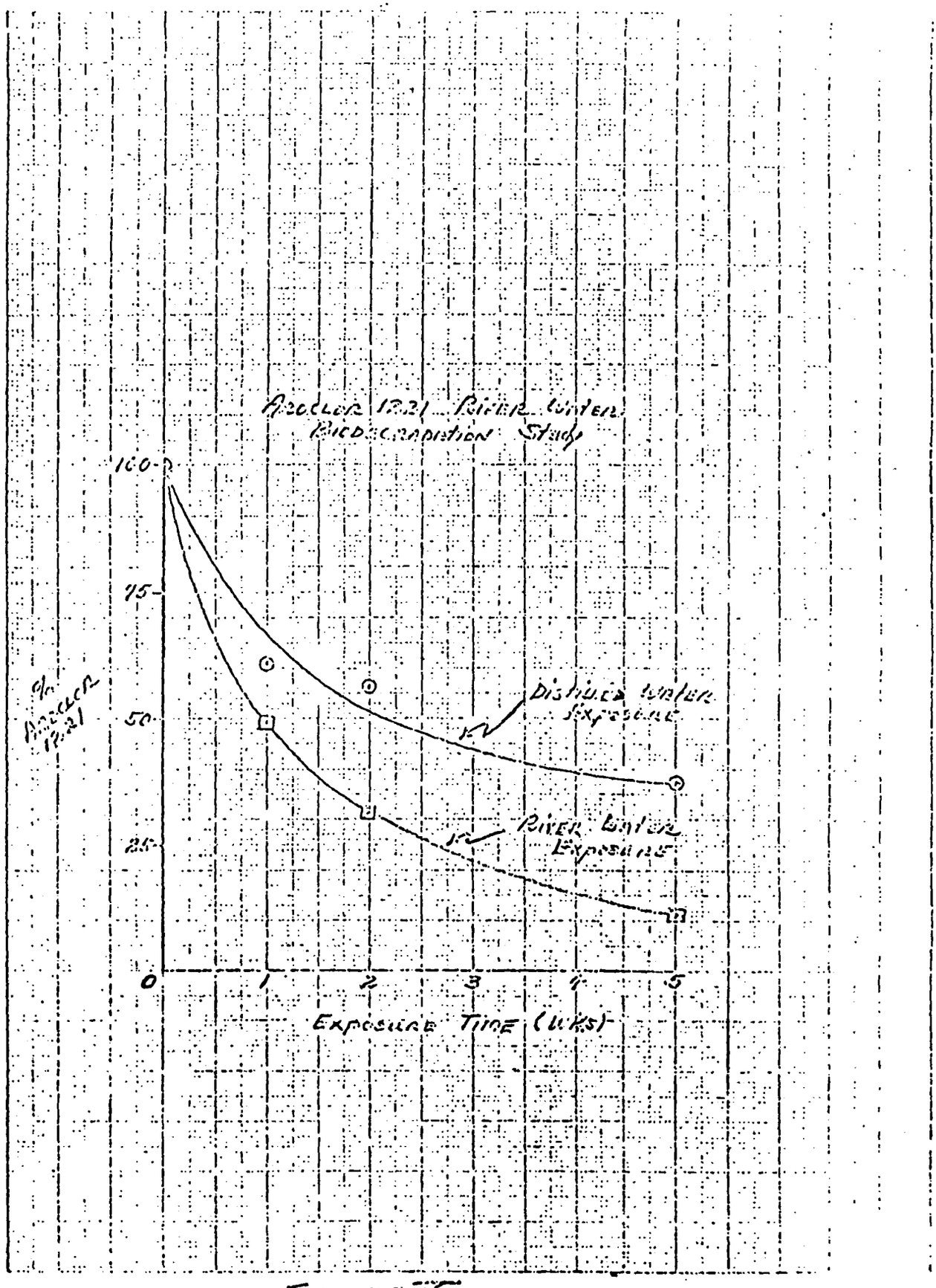


FIGURE II

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