INTER-OFFICE CORRESPONDENCE

Diamond Alkali Company

January 9, 1967

TO: Mr. F. G. Steward - Newark

FROM: Mr. J. J. Lunardi - Newark

SUBJECT: INTERIM REPORT OF EXPERIMENTAL WORK FOR TCP PURIFICATION

I. INTRODUCTION

It had been thought for a long time that the chloracne problem was related to TCP production. The Dow Chemical Company executed exhaustive studies which led to the easing of this problem in their production facilities. When they had achieved a measure of success, they disseminated their information to others (Diamond among the group), who were known to have chloracne problems. Dow's contributions include: identification of the compounds causing chloracne, and analytical procedures used to determine their trace concentrations in product streams.

The chloracnegens were identified as follows: 2,3,7,8-Tetrachloro-dibenzo-p-dioxin (2,3,7,8-TCDB-p-D), 2,3,7,9-TCDB-p-D, 2,3,7-Trichloro-9-methoxy-DB-p-D, and 2,2',4,4',5,-Pentachloro-5'-methoxy-diphenyloxide; where the 2,3,7,8-isomer was identified as the most active in producing chloracne.

The details of the analytical procedures used to quantitatively identify these impurities are described in separate reports by Mr. W. A. Goodloe. It will suffice to mention here that the impurities are extracted from TCP solutions by chloroform or benzene, and the concentrations in the extract determined by flame ionization chromatography.

The goal of our investigation is, of course, to eliminate or reduce incidence of chloracne, and specifically, to reduce the concentrations of the chloracnegens to 1 ppm or less in our product stream. This could be accomplished in several ways, perhaps the most effective of which would be to eliminate their production or modify their structure so as to render them harmless. This would require alteration of the TCP condensation reaction. Another method which utilized the techniques of engineering rather than of chemical kinetics is to remove the traces of chloracnegens from our process streams after they have been produced. These are the techniques discussed in the remainder of this report.

II. FILTRATION

Laboratory investigation had shown that when the sodium TCP solutions were diluted to 10% strength by weight, several of the impurities were precipitated. The most predominant impurity is 2,4,5-trichloroanisole; so this is steam-stripped and saved for recycle before dilution. In the Laboratory, the 2,3,7,8-isomer was quantitatively removed by dilution to 10% TCP, and filtering in a büchner filter with filter-aid, so the following Plant-scale tests were performed.

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Using a 5000-gallon tank (132), several batches of 10% TCP solution (by weight), were made up and filtered either to one of the storage tanks or to the TCP recovery area of the Plant. Filtration was first attempted through a Fuji-flo type cartridge with Hy-flo filter aid, with poor results. Several filtrations were made using a Purolator P-92 filter with cellulose impregnated paper elements rated at 2, 5, and 10-micron particle retention size. In all cases, the filter plugged too rapidly to be considered useful as is for Plant operation, but valuable information was obtained. One test incorporated two filters in series: a P-32 (double element) with 25-micron retention elements, and a P-92 filter containing a 5-micron retention element. Apparently the 25-micron elements passed nearly all of the solids leading to more rapid plugging of the 5-micron element than was expected. The results of this sample analysis from the above tests were mixed; some yielding useful data, and others merely producing meaningless numbers. Useless numbers were generated by either poorly mixed batches of TCP solution, samples contaminated with either trichloroanisole or NaCl, or totally plugged filters (as was the case with the 2-micron attempt).

The information that was meaningful follows:

When Run	% TCP	Filter Medium	p-Dioxin (ppm) Before	p-Dioxin (ppm) After	TCAnisole Before	TCAnisole After	% p-D Removed	% Anisole Removed	Comments
May	10.4	Precoat	43	23	.235%	.216%	46.5	8.1	
July	11.6	10 μ	48	8	.332	.332	83.5	0	
Aug.	10.2	5 μ	26.5	1	.25	.19	97	24	Anisole & related compounds were isolated for identification.
Nov.	10.1	10 μ	33	5.6	.20	.20	83	0-Within exp. accuracy	
	10.1	10 μ	30*	13*			56.5		
				25 μ / 5 μ					
Nov.	10.1	25/5 μ	51	40 / 3.6	.16	.16	93	0-Within exp. accuracy	2nd p-D sample (2 hrs.) yielded higher concentrations.
	10.1	25/5 μ	33*	26* / 9.5*			71		
	10.1	25/5 μ	6.5*	6.5* / 4.0*			23		

* Indicates less active isomers in producing chloracne.
All concentrations of impurities are based on 100% TCP.

It can be generally seen that a 5-micron filter element removes 95% (average) of the most active chloracnegen (2,3,7,8-isomer); and that a 10-micron element removes 83% of the same isomer. Removal of the less active impurities is unsatisfactory.

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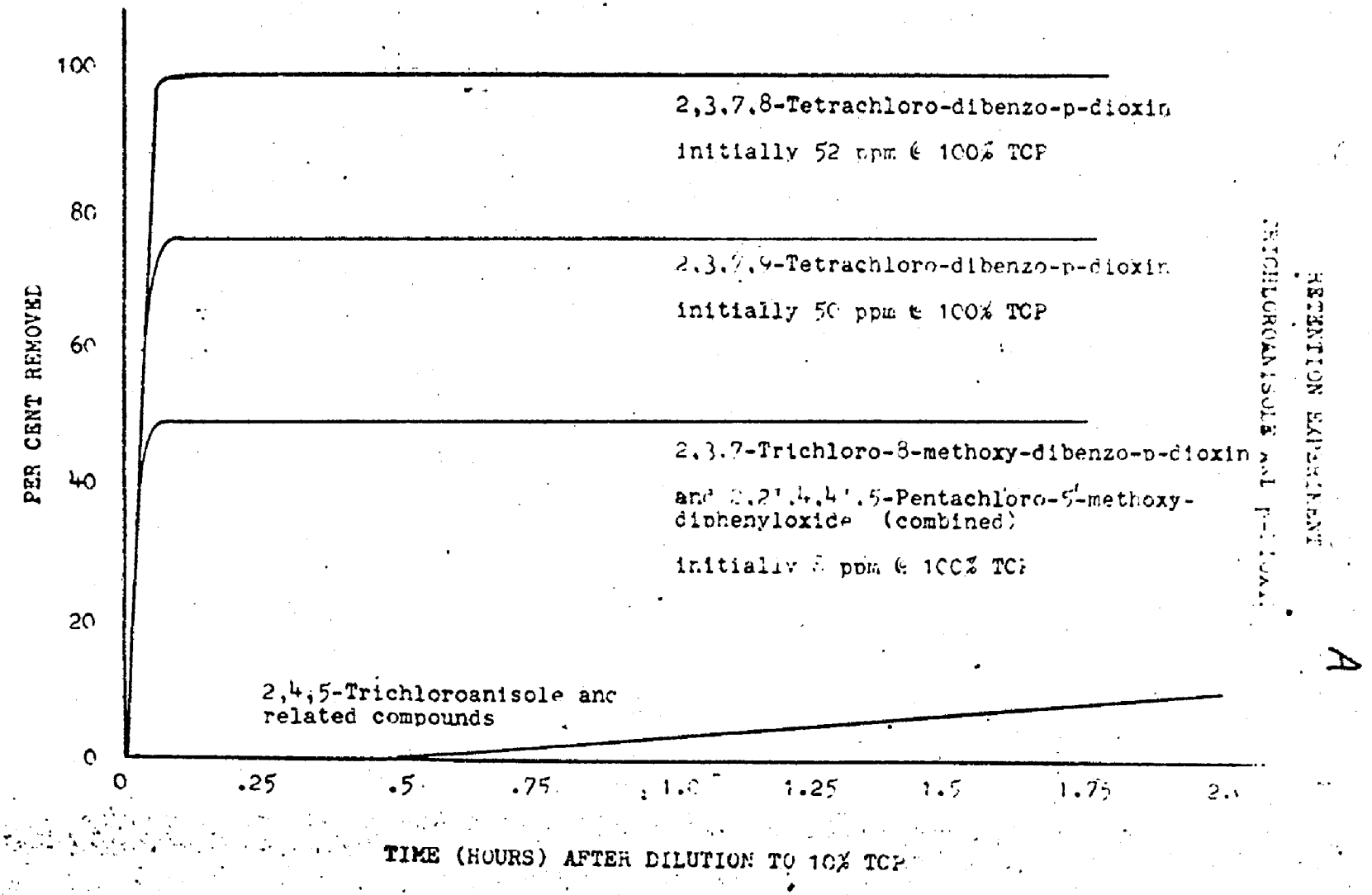
The major problem encountered during the above filtrations was plugging of the filter. In all cases, except when the 25 and 5-micron filters were used in series, the apparatus plugged within an hour, rarely passing more than 200 gallons of material. Approximately 350 gallons were filtered through the double filter apparatus. It is not known which of the materials is responsible for the rapid plugging. Investigation of the filter elements shows that the flow obstruction is due to a thin slimy film. Recovery, isolation, and identification of the slime components obtained from one of the filter runs was attempted. The chromatogram indicates that the film is rich in anisole-related rather than p-dioxin related impurities. A sample of the predominant impurity has been sent to Research, and has been identified as 2,4-dichloro-1,5-dimethoxy benzene.

Another more puzzling filtration problem is that the p-dioxin concentrations increase in the filtrate with time. It has been observed and reported that samples taken downstream from the filter after two hours of operation contained more p-dioxin than the samples taken earlier in the run. Specifically, when using the double filter, samples taken downstream one-half hour after the start contained only 7% of the initial p-dioxin (2,3,7,8-isomer); and after two hours of constant filtration, contained 30% of the initial p-dioxin. The reason for this phenomenon is unknown; however, a possible explanation is that perhaps the cellulose-paper element swells or distorts after exposure to TCP, and allows larger than specification particles to pass. The element was not broken.

Future filter test plans include use of two filters in series with 10 and 5-micron elements, respectively. With the 10-micron filter having approximately three times the capacity of the 5-micron filter, tests of longer duration can be run, yielding data relevant to the problem of loss of filter efficiency with time.

Laboratory experiments were performed to provide information pertinent to the proposed TCP filtration plant operation. The following pages contain graphs showing: (a) time necessary to precipitate impurities from TCP solution after dilution to 10%, and (b) specific gravity vs. concentration of TCP at different NaCl levels. The chart (a) shows that the proposed in-line mixer immediately followed by the filter is feasible. Chart (b) shows that measuring specific gravity is a likely means of controlling the dilution to 10%.



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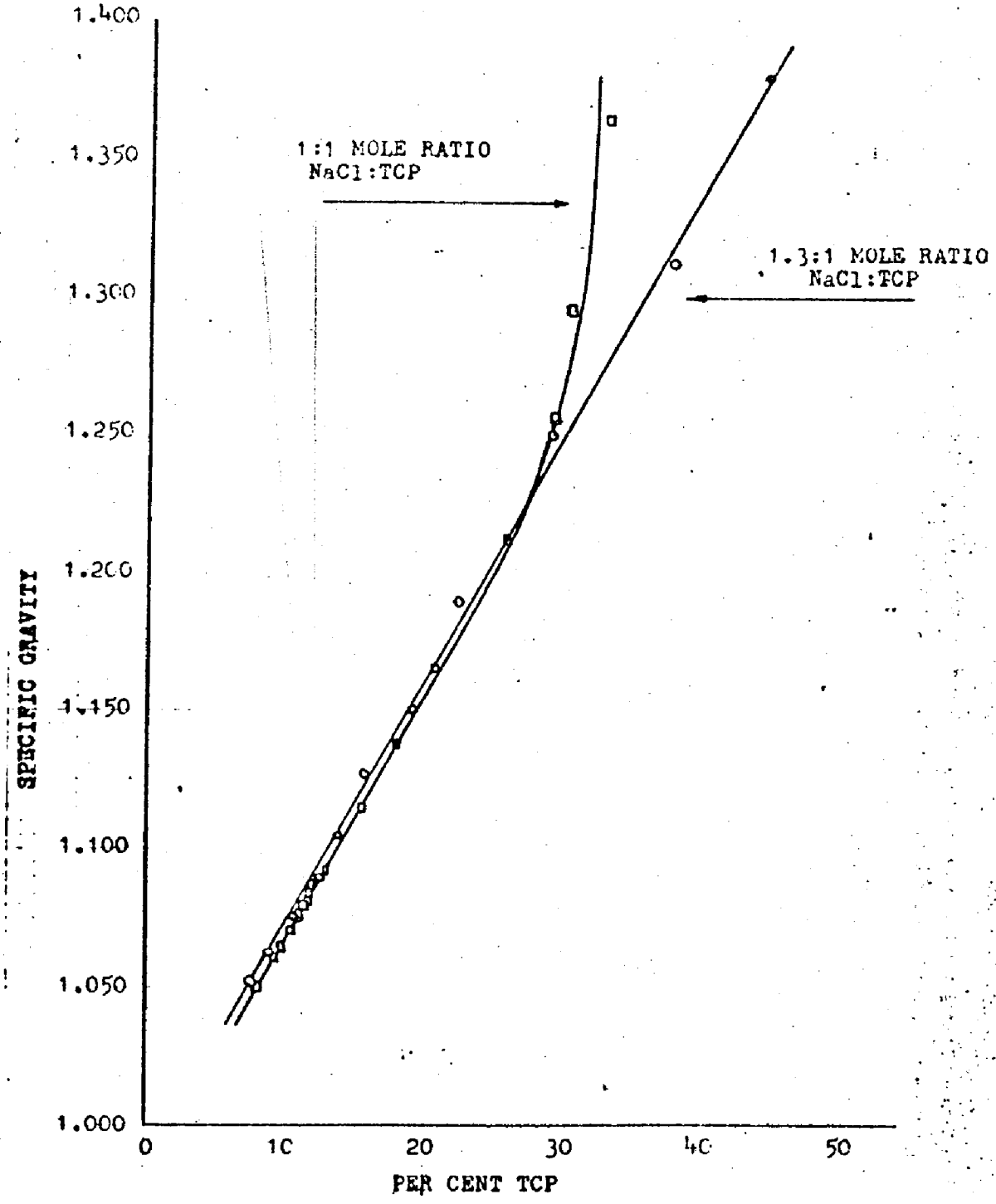
SPECIFIC GRAVITY VS TCP CONCENTRATION B



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NO. 340-10 DIETZGEN GRAPH PAPER
10 X 10 PER INCH

III. ADSORPTION WITH ACTIVATED CARBON

Five one-liter samples of TCP salt solution at concentrations of 10, 12.5, 15, 17.5, and 20 per cent TCP, by weight), were agitated for one-half hour with 1% by weight activated carbon (Nuchar C-190), then filtered through #1 filter papers in a buchner and extracted with benzene. The results of this initial test were favorable:

Initial concentrations: (100% Basis)	
2,3,7,8-isomer	- 52 ppm
2,3,7,9-isomer	- 50 ppm
2,3,7-TC-8-MeO and 2,2',4,4'-5PC-5-MeO isomers	- 8 ppm

All of these impurities were quantitatively removed at the above (5) concentrations, by treatment with activated carbon.

Trichloroanisole and its related compounds were affected as follows:

	Initially	After Treatment at % TCP			
		10%	12.5%	15%	17.5%	20%
2,4,5-Trichloroanisole	.064%	Less than 100 ppm				
Unknown #1	.035%	Less than 100 ppm	100 ppm			100 ppm
Unknown #2	.152%	Less than 100 ppm	1000 ppm			1600 ppm

It is seen from these initial experiments with activated carbon that this should be pursued further, and in detail. Tests are now being performed in the Lab to both duplicate the above and to find how much of the various materials are adsorbed per unit of carbon. Laboratory tests using a bed rather than a batch treatment will be duplicated in the Plant using more concentrated material than had been used for filtrations, and larger granules of carbon than had been used in the Lab. It is anticipated that this line of experimentation will result in a better method of TCP purification than filtration alone.

IV. FUTURE CONSIDERATIONS

Disposal of the wastes obtained from TCP purification is the major future problem to be considered. If adsorption with activated carbon proves to be the best method, the waste disposal problem will be intensified due to larger volumes of contaminated material than would be obtained through filtration. This portion of the chloracne problem merits a great deal of consideration.

The rate at which the proposed tests will be performed will be somewhat accelerated in order to make specification data available to meet the deadlines for the Plant.

J. J. Lusardi
J. J. LUSARDI

JJL/nc

cc: F. R. Kennedy
E. Bak
W. A. Goodloe

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