DATE: January 11, 1961

TO: J. A. Borror

FROM: J. H. Perkins

SUBJECT: Trichlorophenol Tests

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Attached are plots of the analytical data from the recent series of trichlorophenol tests. They were obtained in one-gallon runs of the process proposed for use in the new equipment at Newark. These data, along with the data from the first series of runs, show the effects of most of the major variables in the process and, I believe, provide a basis for choosing the levels of the variables in the initial operation of the new plant.

Summary

Four runs of the proposed process were made. Two runs were required for checking out the feed system, the temperature-control system, and the sampling system. Useful data were obtained from the other two (Runs 17 and 20) by taking samples every fifteen minutes and analyzing them completely.

In addition, one run each, of the old Newark process, in which all of the reactants are charged to the reactor before heating, and the process believed being used by Monsanto, in which molten tetrachlorobenzene is added gradually to a hot solution of caustic in methanol, were made. These two runs were made, along with Run 17, before the sampling and analytical techniques had been perfected, and when the analyses from Run 17 indicated that some of the volatiles may have been lost during sampling, it was decided not to analyze them.

The analytical data from Runs 17 and 20 are plotted on pages 5 and 6. Data from the first series of runs are repeated on page 7 for reference.

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Conclusions

Examination of the data leads to the following conclusions:

1) The process of gradually adding a methanol solution of caustic into molten tetrachlorobenzene (the proposed process) should be safer to operate than the old process. The addition of caustic at a controllable rate is inherently safer than adding it all at once.

2) The proposed process should produce yields, based on tetrachlorobenzene, at least equal to those obtained in the old process. Yields of 96% to 100% have been obtained in four hours' reaction time.

3) The proposed process should require less caustic than the old process. The 96% yield was obtained with a 10% excess of caustic (2.20 moles per mole tetrachlorobenzene); the 100% yield was obtained with an 18% excess. Both of these are appreciably less than the 46% excess which was standard in the old process, and which, when present all at once, probably caused condensation reactions leading to the formation of chloracnegens and corresponding loss of product.

4) Although the data of Run 20 show that dimethyl ether definitely is formed in the proposed process, it appears that methanol losses should still be quite a bit lower than were experienced in the old process. I estimate that the loss will be 1/4 to 1/2 of the 0.1 gallon per lb. trichlorophenol experienced in the old process.

5) At the budgeted production level of 95,000 lb. per month, the probable savings is $1,200 to $3,000 per month.

Recommended Initial Plant Operating Conditions

The following conditions are suggested for initial operation of the new plant:

Charge molten 1,2,4,5-tetrachlorobenzene to the reactor until about 2.4 lb. per gallon of reactor volume has been charged, and heat it to 175°C (347°F).

Make up a solution of flake caustic, 20% by weight, in methanol and hold it at 50°C (122°F), or lower.

Over a period of two hours, pump 2.04 lbs. of caustic solution per lb. of tetrachlorobenzene, into the reactor at a uniform rate (decreasing the rate if the reaction temperature cannot be held at 175°C).

Maintain the reaction temperature at 175° for three hours after the completion of caustic addition. Reactor pressure will rise during addition of caustic and then level out. Pressure has not exceeded 425 psig in our runs and will probably level out at 325-375 psig.

This procedure should be safe for use in checking out the new equipment. In later runs, the following changes may result in improvements in yield of sodium trichlorophenate versus time:

1) Decrease the caustic addition time.

2) Decrease the hold time, after caustic addition, to 2-1/2 or 2 hours.

3) Increase the reaction temperature during all or a part of the reaction. I would guess that the temperature could be increased, without the danger of forming chloracnegens, once the tetrachlorobenzene is all used up.

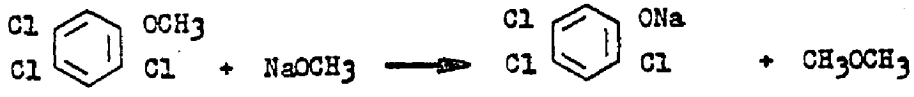
4) Adjust the concentration or the temperature of the caustic-methanol solution or the amount of water in it.

Most of these changes could also affect the formation of dimethyl ether, possibly increasing it.

Chemistry

In a system like this, which is heterogeneous part of the time and homogeneous the rest, the chemistry is probably not so simple as it appears in the equations below. Nevertheless, the data suggest to me that these reactions are involved. Sodium methylate (or methoxide ion) must be involved in the conversion of tetrachlorobenzene to trichloroanisole.

Sodium methylate (or methoxide ion) must also be partly responsible for the conversion of trichloroanisole to sodium trichlorophenate, because dimethyl ether is found in the system.



However, since the amount of dimethyl ether found in Run 20, where we are fairly confident that dimethyl ether was not lost, is not equivalent to the amount of sodium trichlorophenate formed, it is probable that sodium hydroxide also is involved in converting trichloroanisole to sodium trichlorophenate. It regenerates methanol rather than producing dimethyl ether.

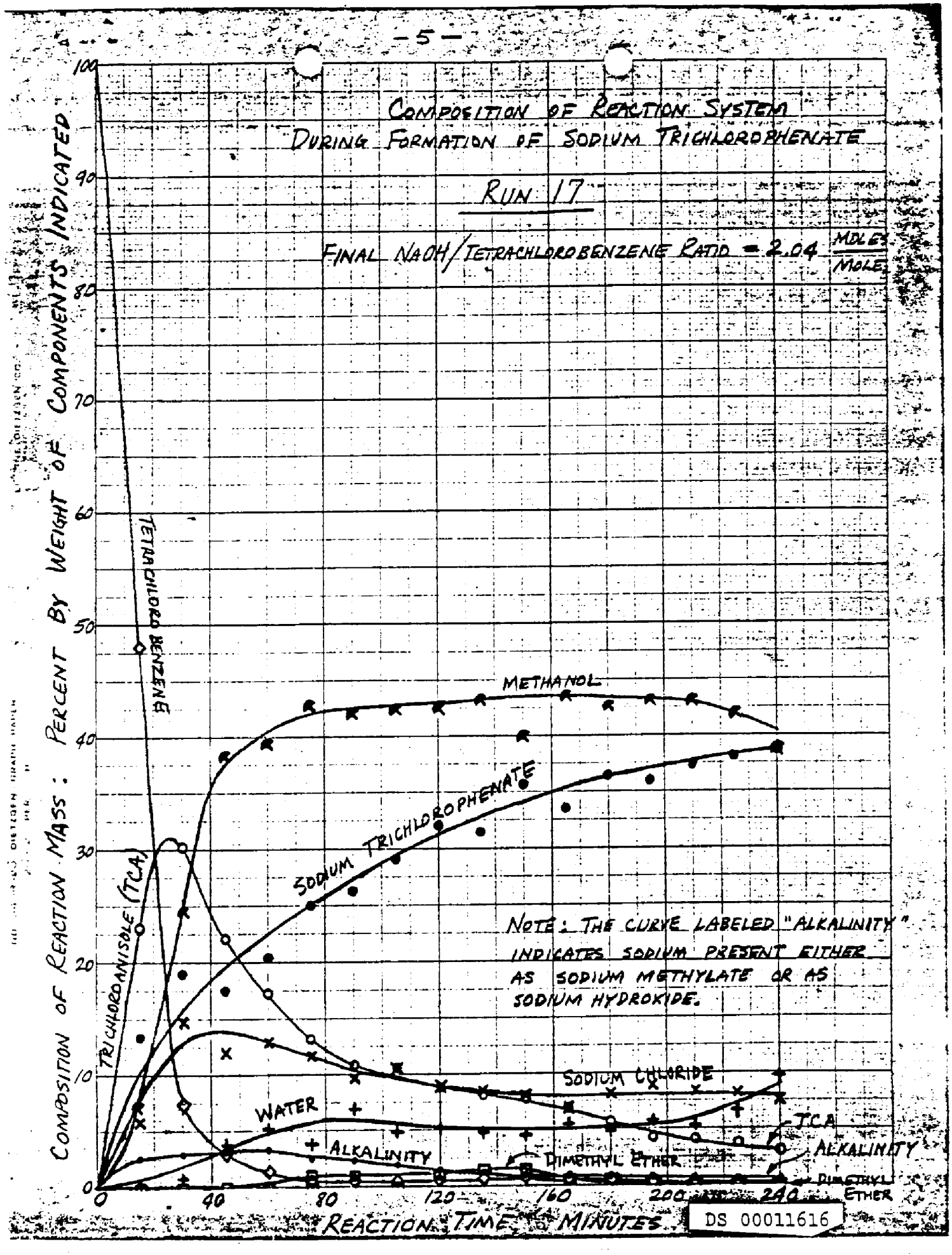
Comparison of the data for Runs 17 and 20 shows that, regardless of whether the sodium is present in the system as sodium hydroxide or as sodium methylate, the caustic-to-tetrachlorobenzene ratio has a considerable effect on the time required to convert all of the trichloroanisole to sodium trichlorophenate. In Run 17, the caustic/tetrachlorobenzene ratio was only 2.04 moles per mole, and the conversion was much slower than in Run 20, where the ratio was 2.37. The conversion in Run 20 was so rapid, in fact, that it appears that the reaction was essentially complete after about three hours. (Keep in mind, in comparing Runs 17 and 20, that in Run 17 the indicated concentrations of all of the non-volatile components are probably too high, due to the loss of volatiles from the samples.)

Analytical Method

The analytical scheme developed during this work and used in Run 20 gives complete information about the composition of the reaction system, except that it does not distinguish between sodium hydroxide and sodium methylate. (There apparently is no method known which will.) Because the method is expected to be useful in the plant for investigating the effects of process changes, it is being reported in detail by C. D. Hildebrecht.

J. H. Perkins

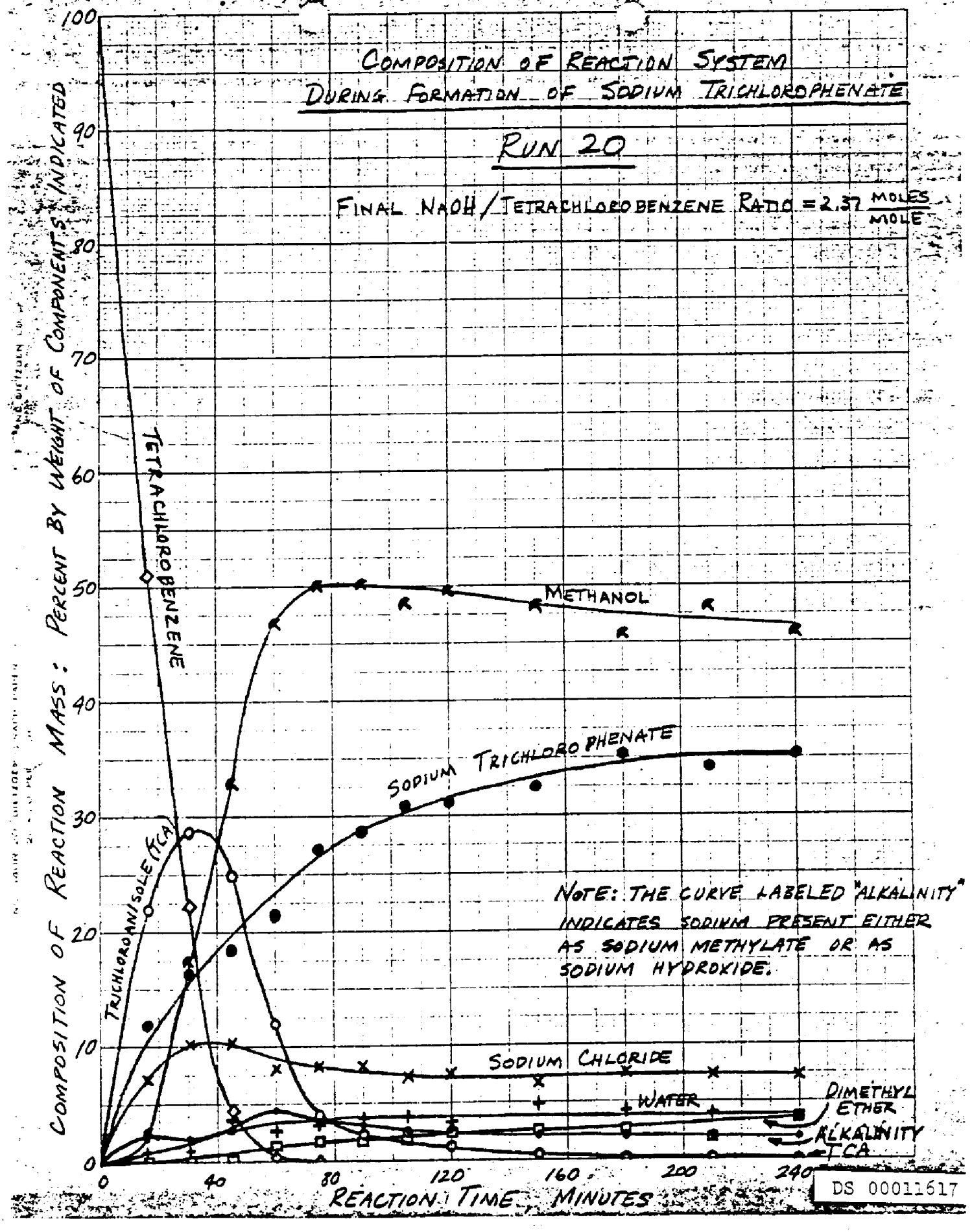
JHP:tmm



COMPOSITION OF REACTION SYSTEM DURING FORMATION OF SODIUM TRICHLOROPHENATE

RUN 20

FINAL NaOH / TETRACHLOROBENZENE RATIO = 2.37 MOLES / MOLE



Trichlorophenol Tests
First Series

% NaCl	Run No.	Tetrachlorobenzene Charged, Grams	Methanol Charged, Grams	Sodium Hydroxide Charged, Grams	% Excess NaOH Charged	Total Charge, Grams	Material Recovered, Grams	% Recovered	Feed Time, Hours	Hold Time, Hours	Reaction Temp., °C.	Color of Product	Approx % Solids in Product	% NaOH in Product	Trichloroanisole (water insolubles)	Trichlorophenol (found)	% Trichlorophenol (theory)	% Conversion to Trichlorophenol	Maximum Pressures, p.s.i.g.
10.5	1	1080	1760	440	10	3280	2798	85.3	2	2	140-72			2.7	7.2	25.5	35.3	72.2	340
6.7	2	"	"	"	"	"	3150	96.4	5	½	165-68			1.4	7.3	23.2	31.4	73.9	225
9.4	3	"	"	"	"	"	3100	94.5	2	1	164-65			1.8	3.8	28.5	31.9	89.3	305
9.8	4	"	"	"	"	"	3110	94.6	3	1	165			1.6	6.4	23.7	31.8	74.5	360
8.6	5	"	2000	500	25	3580	3371	94.0	5	1	164-66	DK	12	3.1	3.0	28.1	31.2	90.0	565
7.3	6	"	"	"	"	"	3330	93.0	3	1	163-64	MED	12	2.6	5.9	26.2	29.3	85.7	[illegible]
7.1	7	"	"	"	"	"	3228	90.0	4	1	163-64	MED-LT	28	4.1	6.1	25.5	30.6	83.3	280
8.9	8	"	1760	440	10	3280	3167	96.7	2	2	157-62	LT	60	2.3	8.4	25.8	31.2	82.7	[illegible]
9.3	9	"	"	"	"	"	3225	98.2	2	3	163-64	MED-DK	17	1.2	4.8	28.3	30.5	92.7	[illegible]
9.2	10	"	"	"	"	"	3131	95.4	2	1	174-75	"	17	1.5	3.9	28.4	31.5	90.2	[illegible]
10.8	11	"	"	"	"	"	2701	82.4	2	2	170-88	DK	25	1.5	2.8	35.1	36.5	96.0	[illegible]
9.0	12	"	"	"	"	"	3220	98.3	1	2	164-67	MED	34	1.5	6.2	27.6	30.7	89.9	[illegible]
9.7	13	"	"	"	"	"	3198	97.5	3/4	3	173-79	DK	25	0.6	3.7	29.9	30.9	96.8	[illegible]