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TECHNICAL COMMAND INFORMAL REPORT

PRELIMINARY OBSERVATIONS ON THE NEUTRALIZATION OF CRUDE GB WITH GASEOUS AMMONIA

F. W. Hoffmann
J. Garbus

2 February 1950

CHEMICAL DIVISION
TECHNICAL COMMAND

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PRELIMINARY OBSERVATIONS ON THE NEUTRALIZATION OF CRUDE GB WITH GASEOUS AMMONIA.

I. INTRODUCTION.

The work described in this report was undertaken in order to determine whether treatment of crude plant GB with gaseous ammonia can be used advantageously to lower the acidity of the product before or after final distillation, and whether the ammonium salts formed can be removed by filtration without difficulty.

II. EXPERIMENTAL.

A. The material available for the laboratory runs was a degassed crude (14A) obtained from the process laboratory; it contained 3.97% of hydrolyzable chlorine and had an acidity of 138 mg. of H/100 g. The hydrolyzable chlorine accounts for only 112 mg. of H, when calculated as HCl, whereas, it would correspond to an acidity of 168 mg. of H when present entirely as methyldichlorophosphine oxide. The large amount of ammonium salts obtained in all runs with GB-14A appears to indicate that the acidity of the crude is largely due to unreacted dichloride and some dissolved HCl.

B. In all runs listed in Table 1 (except in runs No. 8 & 9 where 200 g. of crude GB-14A was used) the neutralizations were carried out with 100 g. samples in a 250 ml. round-bottom flask fitted with thermometer, gas inlet tube, calcium chloride tube, and syphoning tube reaching to the bottom of the reactor. To the syphon tube was attached, by means of a rubber stopper, a 50 ml. sintered glass filter ("medium") with attached suction flask. The crude was neutralized by bubbling a moderate stream of gaseous ammonia into the liquid until it began to pass the flask unreacted, which could easily be detected with wet indicator paper. The rate of flow of the ammonia fluctuated, due to intermittent clogging of the inlet tube, and change in density of the liquid as precipitate was formed. This prevented an accurate measure of the total amount of ammonia passed into the reactor. During the course of the neutralization a considerable amount of heat was evolved which made it necessary to cool the reactor for runs with undiluted GB-14A carried out at temperatures at 40° or below. The neutralized GB was sucked

either immediately or after standing for a certain period of time directly from the reactor through the filter.

The runs with GB-14A are listed in the table below together with the reaction temperatures and properties of the precipitate.

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Table 1

AMMONIA NEUTRALIZATION OF GB

No.	Material	Reaction Temperature	Property of Precipitate	Remarks
1	GB-14A	Below 40°	Microcrystalline	Easily filterable after standing for 18 hrs.
2	GB-14A	0-10°	Milky, viscous sludge	Could not be filtered after standing for 18 hrs.
3	GB-14A	40-65°-Without cooling	Exceedingly fine precipitate;does not settle out	Very difficult to filtrate after 18 hrs.
4	GB-14A and 5% NaF	40°	Gummy precipitate;caked into hard mass after standing for 1 week	Easily filterable after standing for 1 week
5	GB-14A	20-65°-Without cooling	Exceedingly fine precipitate;does not settle out	Very difficult to filter after standing for 18 hrs.
6	GB-14A and 50 ml. of benzene	40-50°-Without cooling	Viscous sludge, rapidly settling out	Separated by decanting after 1 hr.
7	GB-14A and 50 ml. of petroleum ether	42°-Without cooling	Gummy precipitate; crystalline after 4 hrs.	Easily filterable after standing for 18 hrs.
8	GB-14A	35-40°-With cooling	Copious crystalline precipitate	Very difficult to filter after standing for 18 hrs.
9	GB-14A	35-40°-With cooling	Copious crystalline precipitate.Reaction mixture appeared to be almost completely solidified.	No attempt of filtration.
10	Distilled GB	30° Without cooling	Small amount of flocculent white precipitate	Difficult to filter after 1 hr. through "medium" filter
11	Distilled GB	30° Without cooling	Small amount of flocculent white precipitate	Immediate filtration;very easily filterable through asbestos mat
12	Distilled GB	30° Without cooling	Small amount of flocculent material;crystallized after standing for 3 days	Easily filterable through asbestos mat

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In runs 1 to 9, inclusive, the dark amber-colored crude yielded a yellowish precipitate of ammonium salts and a filtrate considerably lighter in color than the crude. An analysis of the filtrate from run No. 1 showed an acidity of only 4 mg. of H/100 g. and a content of hydrolyzable chlorine of 0.40%. A distillation analysis of run 8 yielded 91% of distillate at the temperature of GB and approximately 6% of residue. The recovery of GB was poor in all runs with GB-14A (generally not above 60%) due to the copious quantity of ammonium salts which retained considerable amounts of liquid.

In all runs with GB-14A immediate filtration of the precipitate through a "medium" glass filter was impossible, since the pores of the filter became clogged. Generally, at a temperature below 35°, the precipitate obtained was gummy, decreasing in viscosity with lowering of the reaction temperature. At a temperature of 40° to 65°, the ammonium salt was obtained as a microcrystalline solid which settled out very slowly. Easy filtration of the precipitate was never possible unless the reaction mixture was allowed to stand for at least 18 hours in order to increase the grain size of the precipitate. Addition of 5% of dry powdered sodium fluoride to the crude (run No. 4) did not improve the quality of the precipitate. Change in density of the liquid by addition of 50 ml. of benzene (run No. 6), or low boiling petroleum ether (run No. 7), yielded a rapidly settling, gummy precipitate above 35° where undiluted material gave a microcrystalline solid. Separation could easily be accomplished by decanting after standing for 1 hour or filtration after a longer period of time.

Further runs with GB-14A were discontinued, since the crude material appeared to decompose on standing over a period of a few weeks and the amount of precipitate became more abundant in the later runs (No. 8 and 9). The only other material available for similar runs was a process laboratory sample of GB with an acidity of 15 mg. H/100 g. Three runs (listed in the table as No. 10 to 12) were carried out in the described manner affording a small amount of a white flocculent material. Immediate filtration through a "medium" glass filter was difficult, but could easily be accomplished by protection of the sintered glass plate with an asbestos mat of approximately 1 mm. thickness. The clear filtrate was lighter in color than the original material and showed an acidity of only 1 mg. H/100 g. It contained, however, some ammonium salt in solution which crystallizes after standing overnight on the walls of the container. After standing for 3 days the flocculent precipitate of a neutralized run crystallized completely and the liquid could be filtered through an asbestos mat with extreme ease.

III. CONCLUSIONS.

Since neither of the available samples of GB corresponded to crude plant GB, no definite directions can be given for neutralization of the crude plant product with gaseous ammonia. It is suggested that samples of plant runs be submitted to Chemical Division, as they become available, for determination of optimum conditions for the neutralization with ammonia.

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Preliminary Observations on the Neutralization of Crude GB With Gaseous Ammonia.

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