

Interoffice Communication

To P.L. Fetzer
 From H.L. Hackett
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 Subject Progress Report, January 1972

Oxygenates in Tars

Ethyl Corporation has recently suspended purchase of our tars because of high oxygenate levels. Oxygenated compounds having OH, C=O, or COOH groups lead to trichloroacetyl chloride in their perchloroethylene product. They have observed trichloroacetyl chloride levels up to 3000 ppm when using CONOCO tars as part of their feed stock. They consider 250 ppm as the maximum permissible level of this difficult-to-remove contaminant.

Qualitative infra-red analyses of our tars showed appreciable OH and C=O absorption. No OH or C=O absorption was found in a sample of Ethyl Corporation's tars. Tars from Shell in Deer Park, Texas (Stauffer's Licensee) had somewhat higher OH but lower C=O absorption than ours. I.R. analyses of several of our plant streams were obtained. Qualitative results are tabulated below with the absorption levels found in the EDC tar still bottoms ranked as "high".

	<u>OH</u>	<u>C=O</u>
EDC TS Bottoms(1-5-72)	High	High
VC TS Bottoms(1-5-72)	Nil	Low
EDC TS Overhead(1-6-72)	High	Low
C-203 Vinyl Tower Bottoms(1-6-72)	Nil	Nil
S-309 Oxy EDC(1-6-72)	High	Low
Heavy Ends Feed(1-28-72)	Trace	Trace
Heavy Ends Bottoms(1-6-72)	High	Med
EDC TS Pumpout(5-11-72)	High	High
EDC TS Pumpout(7-71, during test)	Very High	Med
EDC TS Pumpout(9-14-71)	High	High

Several treatment schemes have been attempted for removal of oxygenates from EDC TS Bottoms with poor to moderate success.

1. Bauxite Treatment: The first bed volume of EDC TS Bottoms showed greatly reduced OH and C=O but the bauxite rapidly became loaded.

2. Extraction With 2% Caustic: One-minute extraction of EDC TS Bottoms with an equal volume of 2% sodium hydroxide solutions at room temperature cut the carbonyl absorption to less than half. The two phases did not split readily and the OH band was covered up by water even though an attempt was made to dry the sample.

3. Treatment With Concentrated Sulfuric Acid: One volume of 98% sulfuric acid was stirred vigorously with 10 volumes of EDC TS Bottoms for 30 minutes at room temperature. The treated tars (8.4 volumes) were separated by decantation from the black viscous sludge. The treated tars were washed with 2% sodium hydroxide (no emulsion problem) and then with water. A small portion was dried over anhydrous sodium sulfate. The carbonyl absorption was reduced to less than 40% and the alcoholic OH was almost gone. There was OH absorption due to water at nearly the original alcoholic OH level. Water is also detrimental to Ethyl's process and therefore, must be removed if used in any treatment scheme.

Tretolite AP5518 is added to C-103 heavy ends column to reduce fouling. This material has significant carbonyl absorption and was calculated to be present in our tars at a level of 3282 ppm. Laboratory distillation of C-103 feed (no additive and very little OH and C=O absorption) with 99% overhead gave a bottoms spectra very similar to the EDC Tar Still Bottoms. It is concluded that the additive can only be a minor contributor to the oxygenates in our tars.

Emulsion in T-102 Caustic Wash

Several attempts were made to "break" this emulsion which is very troublesome although it has not resulted in EDC loss. Filtration through a bed of filter-aid readily gave two clear liquid phases with very little cuff between them. A sand bed filter gave almost the same results although the two layers were hazy with a small cuff between them. There was a thin layer of dark brown "tar" left on the top of both beds. Both readily re-emulsified on shaking.

The following specific gravity measurements were made on the layers in T-102 caustic wash vessel when the emulsion was especially bad. Chloride analyses were obtained to check the level of dissolved sodium chloride.

	<u>Specific Gravity at Room Temp</u>	<u>Chloride Meq/Ml</u>
<u>1100 Hrs. 1-14-72</u>		
P-102 Caustic Wash Pump, Aqueous phase	1.054	.31
T-102 Caustic Wash Vessel, Emulsion	1.20	
P-102 Caustic Wash Pump, EDC Phase	1.247	
<u>1330 Hrs. 1-14-72</u>		
P-102 Aqueous Phase	1.050	.34
T-102 Emulsion	1.17	
P-102 EDC Phase	1.242	

Heating the emulsion even to the boiling point of EDC was not effective in breaking the emulsion.

A sample of the emulsion has been submitted to R&D, Ponca City, for identification of the agent(s) responsible. Their results are expected soon.

Solids from the Vinyl Distillation Column

Large black chunks of solid washed from the vinyl column in December were submitted to the laboratory. These chunks did not dissolve or break apart in refluxing EDC or boiling water. Addition of caustic to the water also failed to disperse them. No alternatives to manual cleaning has been found for removal of this type of material from the vinyl column.

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