

HYDROCARBON ACCUMULATION IN AN AIR BOX

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"How frequently should air boxes be defrosted and solvent washed?"

This article gives the experiences of one air plant operator, the Sun Oil Co., Marcus Hook, Penn. with defrosting and solvent washing.

The air plant went on stream in January 1957. It nominally charges 440 tons per day of air to produce 330 tons per day of pure nitrogen for use in the synthesis of ammonia. The impure product oxygen stream (110 tons/day) is put to the atmosphere. During the four general shutdowns since the plant start-up, the air box has been defrosted four times and solvent washed twice.

Air box defrost

Prior to the actual defrost operation, liquid in the plant is dumped to the atmosphere following normal procedures set up by plant operating personnel. In defrosting, eight separate circuits are monitored for flow, hydrocarbons + CO₂, and temperature (Figure 1). Circuit A—feed air inlet line through the feed air exchangers to the high pressure tower inlet line and then out of the high pressure reboiler. Circuit B—high pressure tower bottoms line through Exchangers E-1 and E-2. Circuit C—high pressure tower reflux line through Exchanger E-3, the low pressure tower reflux line and the low pressure reboiler. Circuit D—the low pressure tower feed line. Circuit E—the product oxygen line through the feed air exchangers. Circuit F—the product nitrogen line from the top of the low pressure column through Exchangers E-3, E-2, E-1, and feed air. Circuit G—Turbo outlet line. Circuit H—Turbo inlet line.

When valves for flow in circuits A through F are set, dry, CO₂-free (<1 ppm) air is cut to the air box. Total flow to the box is maintained at about 150,000 SCFH. When temperatures in the air box reach 0°F, circuits G and H are then defrosted.

Eleven monitors

The three plant infra-red analyzers are used to monitor the hydrocarbons + CO₂ at eleven separate points (Figure 1) during the defrosting operation. These analyzers catalytically oxidize all hydrocarbons to CO₂. Hence, the analyzer reading indicates hydrocarbons + CO₂ (ppm by volume) in the stream being sampled. To obtain CO₂ alone, the catalyst oxidation chamber is by-passed. (Reference 2 explains these analyzers in more detail.) The data from the analyzers, plus the orifice flow data, permit calculation of the hydrocarbons + CO₂ removed from the various pieces of equipment in the cold box.

Temperature rise

Defrosting our air box takes between 36 and 42 hours from the time air first enters the box. Figure 2 shows a typical time-temperature plot during our last general shutdown for two points in the cold box. All other points in the box follow the same general temperature rise. As expected, temperatures rise very rapidly during the first 6 to 10 hours. Similarly, this is the time when most of the hydrocarbons and CO₂ are removed. Figure 3 shows the hydrocarbon + CO₂ content in the defrost air entering the cold box and in the defrost air leaving the high pressure reboiler and low pressure reboiler. Hydrocarbons + CO₂ are removed rapidly from equipment in the front of the plant (high pressure tower) as soon as defrost begins. In equipment farther downstream (as the low pressure reboiler), removal is much slower. As the defrost nears completion, the hydrocarbon + CO₂ content (as measured by infra-red) of all the streams approaches that of the inlet defrost air.

About 95% of the total defrost air is used in circuits A, E, and F. The flow of air from the high pressure reboiler was about 30% of the defrost air versus only 1.5% for the low pressure reboiler. Hence, the difference in the amount of hydrocarbons + CO₂ removed from these two spots is much greater than Figure 3 suggests.

Removal of contaminants

A summary of the contaminants removed from the air box equipment for the four defrosts since start-up are listed in Table 1. The data show that most of the contaminants (>60% of those removed) accumulate in the high pressure tower and reboiler. To a lesser extent, the contaminants accumulate in the low pressure tower reboiler, product nitrogen line, and product oxygen line. Since the first defrost, the amount of hydrocarbons + CO₂ removed indicates a considerable decrease with each successive defrost. However, these data show a different conclusion when the accumulation is prorated on a per stream day basis and corrected to an average feed air contamination of 5 ppm (Table 2). For the period October 1958 to December 1960, the accumulation in our plant per day has remained constant. These data indicate that hydrocarbon accumulation is a direct function of on-stream time and average feed air contaminant level.

Unfortunately, the first two defrosts do not show this trend. However, samples of defrost air were checked for CO₂ by by-passing the catalyst oxidation

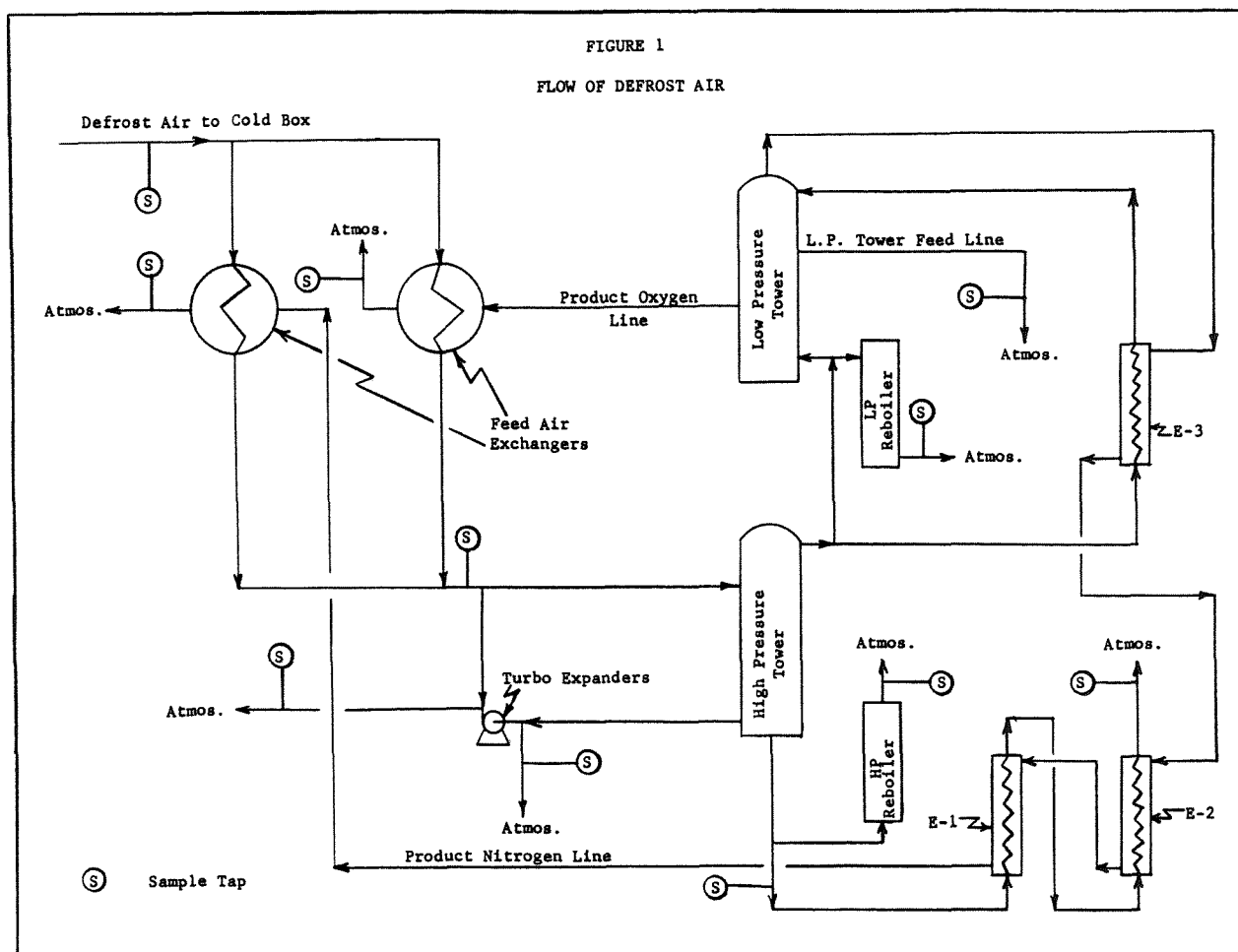


TABLE 1. LB MOLS OF HYDROCARBONS + CO₂ REMOVED AS METHANE

Date of Defrost	October	October	February	December
	1957	1958	1960	1960
Air from Feed Air Exchanger	0.00	0.000	0.042	0.000
Air from HP Tower Reboiler	0.68	0.173	0.187	0.099
Air from Product Oxygen Line	0.00	0.000	0.016	0.006
Air from Product Nitrogen Line	0.00	0.000	0.011	0.026
Air from LP Tower Reboiler	0.44	0.048	0.034	0.006
Air from Turbo Inlet Line	0.00	0.152	0.000	0.000
Air from Turbo Outlet Line	0.00	0.000	0.000	0.000
Air from E-2 Exchanger	0.00	0.000	0.001	0.000
Total	1.12	0.373	0.291	0.137

TABLE 2. RATE OF HYDROCARBON ACCUMULATION

Date of Defrost	Hydrocarbon + CO ₂ Removed, lb mols as Methane	Avg Feed Air Hydrocarbon + CO ₂ Content, ppm as Methane	Stream Days	Hydrocarbon + CO ₂ Accumulated,* lb mols/Stream Day
	October 1957	1.12	12 1/2	283
October 1958	0.37	5 1/2	360	0.00094
February 1960	0.29	7	480	0.00043
December 1960	0.14	5 3/4	270	0.00045

*Corrected to 5 ppm of Hydrocarbon + CO₂ in feed air.

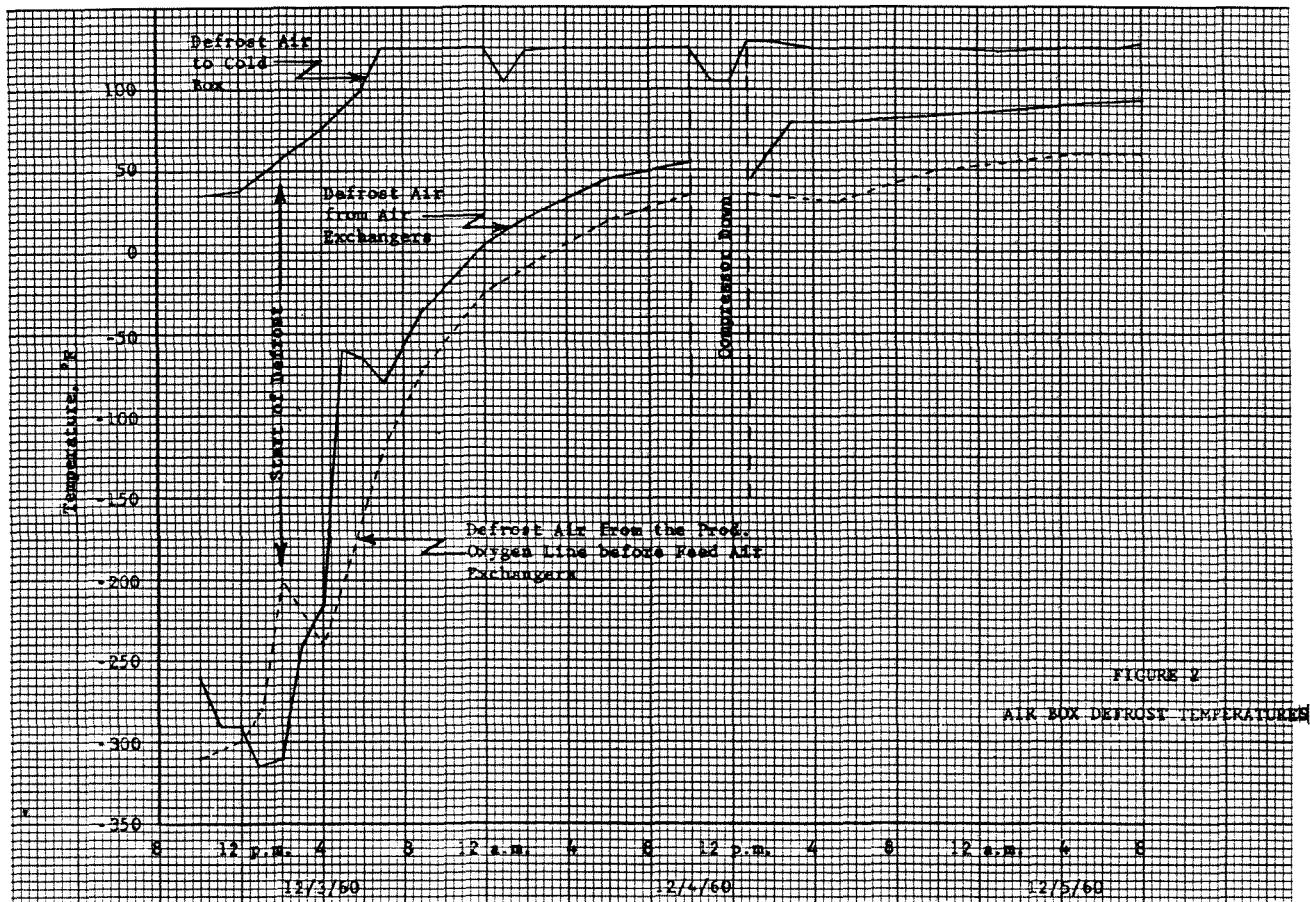


Figure 2. Air box defrost temperature.

chamber in the infra-red analyzers. Table 3 shows that during the first defrost, the air from the high pressure reboiler contained 0.63 lb mols of CO₂ (as methane). This is better than 90% of the total contaminants removed from the high pressure reboiler. Hence, it is probable that the contaminants in the low pressure reboiler also contained considerable CO₂ during this defrost. The other three defrosts showed very little total CO₂ removed. Plant data prior to the October 1957 defrost showed that the CO₂ content of the air entering the air box averaged 5-6 ppm. Since then, the CO₂ content of the feed air has run consistently below 1 ppm. Therefore, the rate of contaminant accumulation up to the first defrost should be high due to the larger quantities of CO₂ entering in the Feed Air.

Hydrocarbon retention

During the defrosting operation, samples of defrost air were analyzed by mass spectrometer to determine hydrocarbon type and quantity. The analyses showed varying amounts of C₁ through C₆+ hydrocarbons. Due to insufficient samples and wide variation between defrosts, no conclusions could be made from the data.

Using Tables 1 and 3, hydrocarbon retention in the air plant was calculated (Table 4). The last two defrosts show that about 0.3% of the hydrocarbons charged to our air plant are retained in the air box equipment. This accumulation is equivalent to about 3 lbs per year of hydrocarbon (as methane) which is only 10% of the hydro-

TABLE 3. LB MOLS OF CO₂ REMOVED AS METHANE

Date of Defrost	October 1957	October 1958	February 1960	December 1960
Air from Feed Air Exchanger	N.M.	0	0	0
Air from HP Tower Reboiler	0.63	0.014	0.023	0.002
Air from Product Oxygen Line	N.M.	0	Tr	0
Air from Product Nitrogen Line	N.M.	0	Tr	0
Air from LP Tower Reboiler	N.M.	0.002	0.012	Tr
Air from Turbo Inlet Line	N.M.	0	Tr	0
Air from Turbo Outlet Line	N.M.	0	Tr	0
Air from E-2 Exchanger	N.M.	0	Tr	0
Total	0.63+	0.016	0.035	0.002

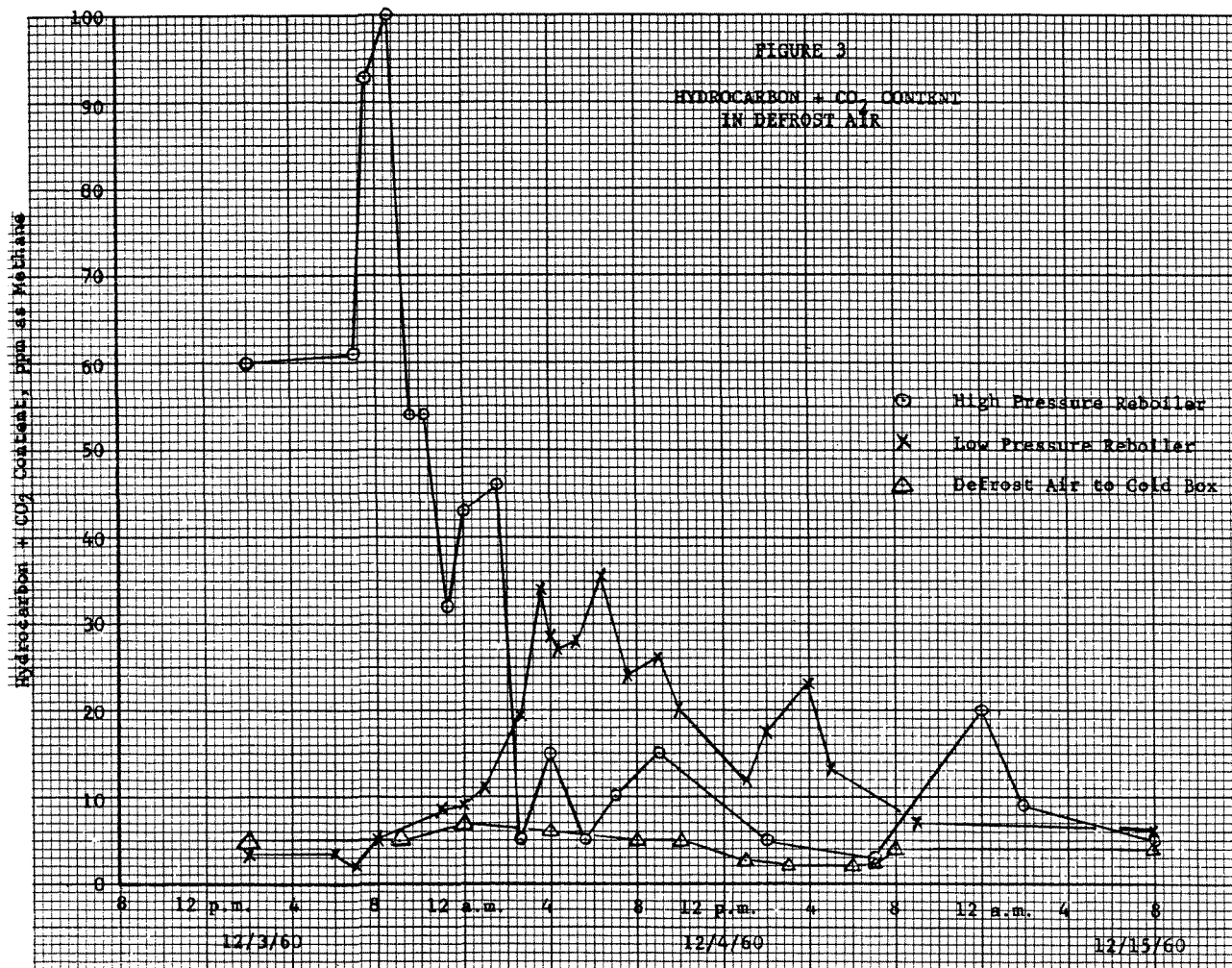


Figure 3. Hydrocarbon + CO₂ content in defrost air.

carbons which caused our 1956 air plant explosion. When the air plant is operating, the maximum contaminant levels in the low pressure reboiler before dumping the plant are 0.5 ppm for acetylene and 500 ppm for total hydrocarbons. These concentration limits are approximately 10% of their solubility limit in liquid oxygen. On the basis of these safe operating limits and the amount of hydrocarbons which accumulate during operation, we at Sun Oil will continue to defrost our air box yearly.

Solvent washing

Solvent washing is an expensive and time consuming operation. Expensive, since it usually requires the purchase of an expensive solvent and the services of

an experienced cleaning firm. Time consuming, since it takes about 3 1/2 days to solvent wash a plant our size when we could be on stream making ammonia. If the decision has been made to solvent wash the air box, this operation will follow immediately after defrosting. The following equipment is washed (Figure 1): Feed air Exchangers; high Pressure Tower; high Pressure Reboiler; low Pressure Tower; low Pressure Reboiler; Exchangers E-1 and E-2.

Air box was solvent washed with a chlorinated solvent during the October general shutdowns of 1957 and 1958. It has not been done since; however, it is being seriously considered this year (1961). A chlorinated solvent was selected as the wash solvent primarily because it is not flammable or explosive and it is an excellent

TABLE 4. HYDROCARBON RETENTION

Plant Operating Period	Total Air Charged During Run lb mols $\times 10^{-6}$	Avg Hydrocarbon in Feed Air, ppm	Hydrocarbons Charged to Air Plant, lb mols	Hydrocarbons Removed During Defrost, lb mols	Hydrocarbons Retained, %
Jan. 1957-Oct. 1957	8.1	7	56.7	0.49-	0.86-
Oct. 1957-Oct. 1958	10.2	5 1/2	52.5	0.36	0.69
Oct. 1958-Feb. 1960	13.7	7	95.9	0.26	0.27
Feb. 1960-Dec. 1960	7.7	5 3/4	44.3	0.13	0.29

degreaser. The solvent, when purchased, should be oil free.

Removal of oil

During the October 1957 wash, about 14 pounds of oil were removed from the cold box. A maximum of 1.2 lbs of oil (most probably less) were removed downstream of the feed air product exchangers (see Figure 1). At the next shutdown, October 1958, only 1 1/2 pounds of oil were removed from the cold box; all of this came from the feed air exchangers. The large reduction in oil removed was attributed to:

1. Installation of a new oil separator before the air box;
2. Lower oil consumption at the feed air compressors;
3. No upsets on condensate-oil separators spilling into the air box as had occurred in 1957.

As a result, about three years have elapsed since the last solvent wash. The above data strongly indicate that oil will not penetrate into a cold box very far. However, normal startup problems and operating problems during the first year of a new plant usually result in oil accumulation in air box equipment. Experience indicates that solvent washing a new plant after the first year's operation is good practice. Solvent washing after the first year should only be done yearly if it is known that a large volume of oil has entered the box or if there is an unknown obstruction in the box which is suspected to be oil.

Washing recommendations

If solvent washing must be done, it is recommended that the washing take place from the back of the plant to the front. Clean the plant in the following order (see Figure 1):

1. Wash the low pressure towers and reboilers with fresh solvent;
2. Wash the high pressure tower and reboiler using the same solvent;
3. Wash the feed air exchangers using the same solvent and then discard it;
4. Wash the feed air exchangers again using fresh solvent.

During the first solvent wash (October 1957), the reverse of the above procedure was used. As a result, contaminated solvent from the feed air exchangers was used to wash the rest of the plant. This undoubtedly resulted in leaving some oil from the feed air exchangers in the rest of the plant which had to be removed by the second wash. However, at the October 1958 washing, the above procedure was used satisfactorily. As a result, solvent usage was cut down by better than 10%.

Solvent loss

During both solvent washes, about 25% of the solvent used was lost in spite of extra precautions. The losses were attributed to leaks, spillage, evaporation, and solvent left in the air box during the wash. During the drying out process, some of the unrecovered solvent was blown out of the box as a mist and was evaporated.

REFERENCES

1. "A survey of operating practices in 63 Air and Ammonia Plants," CEP Technical Manual, 1961, published by A.I.Ch.E.
2. Continuous Monitoring of Hydrocarbon Contaminants in a Low Temperature Air Separation Plant, Chem. Eng. Prog., February 1959, pages 54-58.

DISCUSSION

HART—Dow Chemical: We have solvent-washed once and it was a messy situation. What precautions do you take as far as the toxicity of the solvent to the personnel is concerned?

SCHILLY—Sun Oil: We insure that all of the operators are well familiar with the toxicity of the material and all attempts are made to make sure that they do not handle it and, if they have to, they will normally follow and use the proper safety equipment.

HART: Was the odor level quite strong in the building?

HEPP—Sun Oil: Our air box is outside. It isn't enclosed so any leakage, spillage or evaporation disappears fairly rapidly. The area is roped off and "keep away-toxic" signs are installed, and we only allow a limited number of people in the area. We have fresh air masks available if some major catastrophe happens and the usual portable face masks are available. I think we had to use them on some occasions. As you say, the solvent is quite messy, very hard to contain.

HART: What did you use to determine for positive that you had all of the solvent out? Your nose, for odor, or an analysis.

SCHILLY: We were mostly just using our nose, but only following a very long period of drying out when we were sure the concentrations were at a very low value. Practically, you don't know that it is all out. After about six months or stream, we went to take a pressure survey,

opened up one of those seldom-used pressure taps, and carbon tetrachloride rolled out.

WELLS—Calumet Nitrogen Products: Did you ever have any problems with plugging due to incomplete removal of the solvent wash?

SCHILLY: I don't know of any.

WALKER—Cyanamid of Canada: What is the purity of your nitrogen?

SCHILLY: Essentially 100 percent pure.

WALKER: You don't use deoxidation then?

SCHILLY: We do oxidize the small remaining oxygen before the nitrogen enters our synthesis section.

WALKER: And what is the criterion for shutting down the box for defrost? How do you decide exactly when to shut it down?

SCHILLY: Based in the data presented here, we plan to follow the yearly shutdown for normal clean-up and air box defrost.

TIXHON: Did you ever consider the possibility of washing with a caustic solution? If not, why?

SCHILLY: We have not considered it, but I would imagine the problem of removing a large volume of water

from your plant would be a problem. We have had, not specifically in this part of the plant, but in the other one, problems of moisture getting in, which have caused pressure drop problems due to icing.

TIXHON: This was common practice in Europe where I used to work and we used caustic, except in the case when we had aluminum equipment. We washed with one caustic solution and we kept washing until it was clear, and we never had any trouble.

HEPP: With regard to how we decided to shutdown for defrost, I want to reiterate the final paragraph in this paper of Mr. Schilly's. We originally started out with a one-year defrost because this seemed to be industry practice and, as a result of these studies, we have decided that in about a year, three-tenths of a percent of the incoming hydrocarbons are retained in the air box, which amounts to three pounds per year of hydrocarbons retained in a box. This is ten percent of what it took to blow the plant up originally. Therefore, we feel that we are following the same type of safety margin if we stick to a ten percent accumulation of hydrocarbons as we were following when we said ten percent of solubility limits in the reboiler was permissible. Also, in the low pressure tower reboiler circuit, if you compute the pounds of hydrocarbons available with maximum allowed concentrations of hydrocarbons, they turn out to be two or three pounds of hydrocarbons. Thus we will normally accept two or three pounds of hydrocarbons in our plant during normal operation in our reboiler circuit. In terms of parts per million, this is 500 in our case. So again, we think that we are being consistent in saying that we will also permit three pounds of hydrocarbons spread throughout the rest of the plant but when it reaches that level, then we are going to defrost which, in our case, turns out to be a year.

ROCKWOOD: I am not as familiar as I should be with your 1956 explosion. I am curious as to whether you began solvent washing primarily to remove hydrocarbons which entered in the air feed as vapor, or hydrocarbons which might have entered as the result of oil contamination either through your inlet air compressor or the expander. It seemed from your plots that you got relatively good removal of your air-borne hydrocarbons by the warming process. Upon what do you base the further need of solvent washing?

HEPP: As it has been mentioned, solvent washing is extremely messy. Therefore, we haven't solvent-washed our plant in over three years. Now, the last time we washed, we only removed one and one-half pounds of oil and we know that during the preceding period, that one year's period, we had very good operation and there were no large amounts of oil consumed by the compressors nor were there any spillages going into the box itself. I would say that if we solvent wash the plant this year, it is mainly because we are going to have considerably more time this shutdown. Since it has been three years and it is possible that more oil could be getting into the box than we are aware of, we feel that we will do solvent washing. Solvent washing, in our opinion, is mainly to remove those heavy hydrocarbons which will not normally volatilize during the defrost operation. That is the difference between the two operations.

EDWARDS—Columbia-Geneva Steel: We have German Linde equipment and have worked quite closely with them on several problems. They have made a recommendation concerning the use of solvents for washing. They have recommended that we use only carbon tet and not any solvent that contains hydrogen atoms. Perhaps you would like to make a comment on that. The gentle-

men that spoke here previously suggested the use of caustic solution for washing. We have had a little experience along this line, not in our air boxes, but in our hydrogen box. The primary objection that we have to using caustic soda is that we get a removal of tin from the copper. The tin is put on for protection against acetylides. We have rather detailed studies of this as to the amount of tin removed, and it is an appreciable amount. Of course, the amount that is removed is reduced by limiting the concentration of the caustic soda. We have gone now to the neighborhood of one percent and also by keeping the temperature low.

HEPP: I know that carbon tet, of the solvents used for degreasing, is an extremely toxic one. I think a lot of the people are switching to the less-toxic trichloroethylene.

JENKINS: We have a centrifugal compressor. I can see no need after the original carbon tet wash to wash again. Is this generally accepted in the industry on a centrifugal compressor where there is no oil?

HEPP: I think solvent washing is only if you have oil. If we had centrifugals, we would not solvent wash or even consider it.

JENKINS: When we originally built the plant, we solvent washed with carbon tet and dumped the carbon tet on the ground. It worked into the electrical leads and we are still replacing electric leads throughout the plant.

In our hydrogen purification box, we went to perchloroethylene to clean our oil filters on our nitrogen liquefaction circuit, and immediately found that the perchloroethylene went on into our ethylene vaporizer at -150°F where it blocked and ruptured our tubes. Apparently perchloroethylene forms a harder ice which makes rupture more likely than carbon tet.

HEPP: Do you solvent wash your oil filter?

JENKINS: Yes, in order to eliminate the last traces of oil from our oil filter shell when we change desiccant. We have a desiccant bed and the bed, of course, must be replaced. Then before we put the filter back together, we solvent wash the shell. This is the only way we can keep oil out of the system.

HEPP: You are changing your desiccant but are just cleaning your shell.

JENKINS: That is all.

SHANER: I think a little bit of history of the solvent washing is in order. We no longer solvent clean any of our equipment after it has been put in operation. Approximately twenty years ago, we used to solvent wash our liquid oxygen units. This, however, has been discontinued. We found it unnecessary. At that time, we cleaned it with a solution of caustic, commonly known as "Metso." More recently, we have switched our construction entirely to aluminum and naturally caustic would not go with that. At the same time, we switched to aluminum construction, we changed our cleaning procedures and have used inhibited trichloroethylene exclusively for cleaning the equipment prior to the start-up of the plant. Now because of our cycle which incorporates a fair amount of silica gel in our system, we find it unnecessary to clean the cold box after it is put into operation. Another point, we completely prohibit the use of carbon tet in our plants as this is entirely too toxic for our use.

LAMOND—Canadian Industries: We recently washed the scrubber column and selected exchangers in our hydrogen cold box. We selected trichloroethylene as

the solvent. We discarded carbon tet as being too toxic. In fact, we have a company policy on that. Perchloroethylene, we discarded because of the low volatility. It would be difficult to remove it by deriming after the washing. The operator supervising the washing, wore a vapor mask. Just a dust mask with vapor filters in it. We used a detection apparatus as the plant was drying out to check the concentration of trichloroethylene. One thing I should point out when you are washing a plant: be sure to open and blow all of the sample lines and gauge lines. We removed some twelve pounds of oil from our nitrogen scrubbing unit by washing after a major deriming.

FUNK—German Linde: Essentially, there are carbon tet, perchloroethylene and trichloroethylene solvents in use. We are still in favor of using carbon tet in spite of the toxicity because we found that trichloroethylene can be explosive under certain conditions. Of course, in spite of the lower toxicity, it is a problem to discard this trichloroethylene. The other choice is perchloroethylene which is, as commented before, too heavy. It is not volatile enough. Therefore, we still suggest carbon tet as the ideal solvent. It is not preferred from the point of toxicity, but it still is first choice.

WEIGERS—American Cyanamid: I am very interested in the accumulation of hydrocarbons in your plant, particularly with the occasional comments that we have heard of running plants for an extended period of time and relying on a heavy liquid withdrawal to prevent the accumulation of hydrocarbons. I was wondering, Mr. Schilly, whether you could comment on what sort of purge procedures you use in your plant? How much do you purge, how frequently and perhaps from what portion of your process?

SCHILLY: We have continuous blowdown from the low pressure tower reboiler. It averages about one percent of the feed air. Now this is smaller than most people run on a vapor plant. We feel that we can get away with less blowdown, even though we are in a higher contaminated area, because we have continuous hydrocarbon monitoring of the reboiler and also of the feed air. We also have two air intakes which permits us to be selective about the air that we pull in. As a result hydrocarbon concentrations are kept pretty much in line. The analyzers also help us anticipate our withdrawal needs from watching our feed air. I think the industry average is something like two percent. People running vapor plants usually average two percent liquid blowdown; we are only a percent. We think that a percent difference is what pays for hydrocarbon analyzers on the reboilers.

WEIGERS: Did I understand you correctly that you found the heaviest hydrocarbon contamination in your high pressure reboiler upstream of your blowdown point?

HEPP: Yes, this is right. We must remember this is the circuit that ends with the reboiler. This circuit includes the feed exchangers, the high pressure tower and the reboiler, so we must not think that all the hydrocar-

bons are located necessarily right in the reboiler. Undoubtedly, they are on the trays of the tower, etc.

MASON: If you don't want to sniff these chlorinated hydrocarbons to find them, there are Freon detectors which will detect very, very small quantities. As a matter of a fact, this high sensitivity may result in some difficulty because the units will detect such minute quantities, but the use of one of these Freon detectors would entirely eliminate any need for sniffing.

BOLLEN—Dow Chemicals of Canada: During the early days of the operation of our nitrogen scrub unit we had a problem with oil contamination in the high pressure nitrogen going into the cold box. The oil build-up in lines and exchangers in the nitrogen cycle made it necessary to shut down about every 2 1/2 to 3 months to clean out the oil. This was done by carrying out a derime on the nitrogen cycle only while still maintaining temperatures in other sections of the cold box as near their operating levels as possible. The derime operation on the nitrogen cycle was followed by a solvent wash and as long as the solvent was kept moving through the lines and was carefully drained and dried there was no difficulty. However, on one occasion, through misoperations during the drying operation, a small amount of solvent was allowed to drain down to a low section of the line where, due to proximity of other lines and exchangers which were still at low temperature, it froze solid. I can attest to the fact that it is quite a difficult job to free such a restriction. First of all the plug-up has to be located and then something has to be done to thaw it out. In this case it involved removing panels and insulation from the bottom section of the cold box to enable us to get a source of heat close enough to the affected line to thaw the frozen solvent. All in all it took about 3 days before we finally got the cold box in condition to start up again.

SEFTON—Ontario Research Foundation: What is the average hydrocarbon level of the liquid in the reboiler?

HEPP: About 150 ppm in our plant.

SEFTON: When you shut down for these yearly derimes and analyse the derime gas, do you know whether there is any liquid hold-up in the plant after you have drained? Can you drain all of the liquid? What I am getting at here is that perhaps some of these hydrocarbons which you detected in the derime gas were actually in the liquid.

HEPP: No. Because with the entire liquid in the plant, we only have an inventory of three pounds at 500 ppm. At 150 ppm in our total liquid, we would have about one pound of hydrocarbons in the total liquid. Now we can get most of it out. Certainly, we get about 95 percent of it out. That would put us down to possibly a tenth of a pound being retained in the liquid so the fact that we find three pounds in defrost, it must have been hung up in the trays, walls, etc. In other words, I don't think a significant portion of the three pounds that we get on defrost can be left through insufficient draining.

GIBSON—Atlantic Refining: We have successfully used commercial hexane to solvent wash our low temperature purification system (hydrogen cold box).