

* SAFETY ROUNDTABLE

the operators report on **SAFETY** in air and ammonia plants

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Another CEP exclusive. Chemical engineers come together for the informal and practical discussion of safety problems in operating air and ammonia plants. Here is the actual transcript of the recent "off-the-cuff" sessions at Salt Lake City. This is Part 1. Parts 2 & 3 will appear soon in CEP.



N.H. Walton, who headed the Symposium, is general foreman in the Acid and Ammonia Group at Atlantic Refining's Philadelphia plant.

CHAIRMAN WALTON (Atlantic Refining Co., Philadelphia, Pa.): Welcome to the second annual Air and Ammonia Plant Safety Symposium of A.I.Ch.E. As you know, this is a continuation of the session held in Baltimore, which resulted from a discussion at the Boston meeting a year before that.

Air Intake

Our first topic is Air Intake. One of the principal items of interest along this line has been the development by Mine Safety Appliances of a so-called catalytic filter. Mr. R. B. Evans of that company is going to introduce the topic.

EVANS (M.S.A. Pittsburgh, Pa.): I will report briefly on catalytic oxidation as a means to remove hydrocarbons from compressor outlet air in air separation plants. In recent years, catalytic oxidation or "filtering" in this field has been closely associated with the word "Hopcalite." This is a trademarked name for any MSA catalyst containing manganese dioxide and cupric oxide. These catalysts are important for hydrocarbon oxidation because they operate at low temperatures. For example, butene is completely removed at a temperature as low as 235°, acetylene at 325°, propylene at 335°, ethylene at 375°, butane at 470° and propane at 500°. These are minimum stream temperatures for 100% oxidation for a contact time of only 0.2 second. The operating temperature can be reduced if the contact time is increased, but it is necessary to balance economy, pressure drop and size of the installation. A 0.2 second contact selection seems rather critical in this respect. The operating temperature requirement comes down very slowly from here on with increasing contact time. For example, to reduce the operating temperature on acetylene by 30°F., it is necessary to increase the contact time to 0.3 second. That's a 10% reduction in operating temperature and a 50% increase in contact time, and you can readily see what that will do to either the size or pressure drop of the installation.

In 1956, L'Air Liquide suggested to MSA that "Hopcalite" filters might find application in air separation plants—and they had some data to support this contention. During 1957, two installations were made—a 45,000 std. cu. ft./min. bank at Rohm & Haas in Houston, Texas, and a smaller bank at Petroleum Chemicals, Inc. at Lake Charles, La. The former has been in operation for more than a year, and, to date, the operator has never had any evidence of acetylene downstream of the filters. They sample both from the air stream and the liquid pool with, among other things, infra-red

instrumentation with a full-scale range of from zero to 2 pts./million acetylene. Traces of other hydrocarbons such as ethylene have been detected, but this is to be expected because the operating temperature at the catalytic bed in this plant is only 315°F. If elevated to 375°F., all of the unsaturated hydrocarbons should disappear. The system was set up to have an initial pressure drop of 3/4 lb./sq. in. The mechanical pre-filters, which are necessary to any catalytic installation, were to be changed when the pressure drop reached 1 1/2 to 2 lb./sq. in. ga. I understand that the pressure drop has now reached about 8



R.B. Evans, who reported on catalytic oxidation, works on fluid purification equipment at Mine Safety Appliances Co.

lbs./sq. in., but no filter changes have been made in over a year of continuous compressor operation. They evidently do not need the full oxygen capacity at the moment. The second installation is in operation but we do not have a full report on its performance. MSA has also prepared two small sample cells for tests at the Dow Chemical Company at Freeport, and for the Atlantic Refining Company at Marcus Hook, but these results have not been reported.

MSA's development program has been aimed along two avenues; (1) to reduce the operating temperature of the catalyst, and (2) to reduce the pressure drop or the space requirement. In the former, there is nothing encouraging to report. We found many accelerators to reduce the required operating temperature for specific hydrocarbons, but none of them worked over the wide range of hydrocarbons you must consider. For example, we have one catalyst which will completely oxidize methane at 600°F., but this same catalyst requires 400°F. to oxidize acetylene; considerably higher than the "Hopcalite" now in use. The second avenue toward improvement has been more productive and we hope soon to have a few low-pressure-drop catalytic filter assemblies on the market. These are to operate at a few inches of water resistance rather than 3/4 lb./sq. in. in our present system. We certainly hope to be able to show new elements to you by the time of your next meeting.

CHAIRMAN WALTON: Thank you very much, Mr. Evans. Any comments?



R.L. Swope, treasurer and chief engineer at Southern Oxygen Co. in Washington, D.C.

SWOPE, Southern Oxygen, Washington, D. C. I'd like to know whether any

attempt to use this catalyst in a high-pressure air stream has been undertaken to date?

EVANS, M.S.A.: None to date, Mr. Swope. The problem there is the oil from reciprocating-type compressors. That has yet to be overcome before an installation of this type can be made.

SWOPE, Southern Oxygen: This then is particularly applicable to centrifugal air compressors. Is that correct?

EVANS, M.S.A.: Yes.

GRUNBERG, L'Air Liquide, Montreal, Canada: In the Rohm & Haas plant, which is a 350-ton plant, the conditions are especially favorable because it has a blower. The air is compressed to approximately 92 lbs./sq. in., and at the outlet of the compressor—before it is cooled down in the spray-tower—the air goes through the MSA unit. We have been satisfied with the low pressure drop obtained with the MSA unit. The problem of purifying a gas which has been going through an oil lubricated compressor is a bit tricky because here we are dealing with small amounts of oil vapor which in going through these units may be oxidized to a fair amount of CO₂ and this has to be removed by some other means. In a high-pressure plant the CO₂ can be removed by cooling. The general practice is to decarbonate at



J. F. Grunberg, manager process development at L'Air Liquide, Montreal, Canada.

about 400 lbs./sq. in. By high-pressure plants, I mean liquid plants with air at approximately 2900 lbs./sq. in., so the decarbonation units operating at 400 lbs. allow removal of the oil with the condensing water vapor which acts as a good scrubber. A special heating device has to be added to the MSA unit. These units at the Rohm & Haas plant operate at approximately 300°F., which is a good discharge temperature for a blower, although a slightly lower temperature would be desired where energy is costly. I think if we could operate these units at 270°F., it would allow us to use compressors with efficiency improved by inter-stage cooling. Even if a small amount of heat had to be supplied to the catalytic unit it would not be too costly.

We consider that the oxidation of acetylene in the air before it enters the low temperature separation plant is the best way to have a safe plant, because the remedy is taken at the source before the hydrocarbons enter the plant. If any unknown gas contaminant is, after compression, brought into contact with a finely divided catalyst, there is a better chance to avoid unknown reasons of explosion within the plant. The use of catalytic oxidation of acetylene does not,

however, eliminate the use of liquid filters, which will be mentioned later.



G.R. Walton Jr. is with the Houston, Texas, plant of Rohm & Haas as production area manager.

WALTON, Rohm & Haas, Pasadena, Texas: I do want to substantiate Mr. Evans' remarks. The only problem we have had to date is the developing of a high pressure drop (8 to 10 lb./sq. in.) across the filter after about six months operation. Unfortunately, we did not provide a bypass around the filter, thus the exact cause of the pressure drop cannot be determined until a future shutdown.

CHAIRMAN WALTON: At Atlantic, as mentioned by Mr. Evans, we have a sample cell which contains one filter element with which we are checking performance in order to justify full scale installation.



H.R. Lyles of Petroleum Chemicals at Lake Charles, La, is a process superintendent in the oxide glycol unit.

LYLES, Petroleum Chemicals, Lake Charles, La.: Is there any experience with the effect of trace sulfur compounds on this MSA catalyst, particularly hydrogen sulfide?

EVANS, M.S.A.: The sulfur compounds will destroy any catalytic surface if they are deposited as free sulfur or salts. So long as you operate the system at a temperature low enough there is no effect on the catalyst.

CHAIRMAN WALTON: Thank you. Any other questions or comments?

FUNK, German Linde, Toronto, Ont.: We have been experimenting with a pilot plant to burn hydrocarbons in air. The type of catalyst we have chosen was in use for the combustion of methane in oxygen-krypton mixtures at a temperature of about 750°F. The objective is to purify this stream to a few parts/million of methane. This contact material contains no precious metals. A temperature of 480°F is sufficient. At 85 lb./sq. in. ga., with space velocities of 3000-5000 cu. ft./hr. per cu. ft. of catalyst, and with 10-60 parts/million of hydrocarbons in moist air, there were burned:

98% of total	C ₂ H ₂
99%	C ₂ H ₄
91%	C ₂ H ₆
75%	C ₂ H ₂

Fortunately, acetylene burns very easily and completely. Likewise, as with precious metal catalysts, humidity in air decreases efficiency of oxidation. Satu-

rated hydrocarbons burn less easily than olefines. The temperature of the catalyst bed is mainly determined on the basis of whether saturated hydrocarbons like propane, ethane, or olefines and acetylene are to be removed. Normally, it is not necessary to remove methane at all. The presence of substances which shorten the life of precious metal catalysts has not influenced the catalyst-life during our experiments. Actually, a catalyst of this type has been in operation for several years.

To keep the heat exchange surface small enough for heating from 212 to 480°F, and cooling down from 480 to 212°, and then respectively to 68°, and also to minimize the costs, a gas-fired air heater is provided which operates on high



H.F. Funk reported on a pilot plant to burn hydrocarbons in air at German Linde Corp. in Montreal.

temperature differential and, therefore, with a small exchange surface. A steam boiler is used for cooling the first stage. The steam boiler also has a high transfer coefficient, and, hence, a relatively small heat exchange surface. Regenerators used as heat exchangers would need a heat exchange surface many times the area, resulting in higher costs. About eight cubic feet of methane will have to be burned with 1000 cubic feet of air, and a considerable amount of heating value can be recovered as steam at about 43 lb./sq. in. ga. In this way we hope to have an approach for an economical method of burning hydrocarbons in the air inlet before entering the cold box.

CHAIRMAN WALTON: How about lubricating oil? Is it a problem with your catalyst?

FUNK, German Linde: In the large plants we are concerned only with non-lubricated turbo-compressors. Oil vapors are, however, burned in the catalyst bed.

CHAIRMAN WALTON: This seems to be one of the problems still with the MSA unit. Mr. Evans?

EVANS, M.S.A.: There may be a misunderstanding. It is not that the catalyst is destroyed by the oil, it is just that there's a possibility that there will be too much fuel applied to the bed instantaneously. Under these circumstances, the temperature in the bed would rise to a point where the catalyst would be sintered.

Solids in intake air

GRUNBERG, L'Air Liquide: I would like to come back to this question of pressure drop on the MSA catalyst. We are not too concerned about it. At our suggestion, MSA built for Rohm & Haas a unit which purifies 33,000 std. cu. ft./

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min. of air. Of course, the origin of the increasing pressure drop will have to be investigated during the next shut down. It is possible that the pressure drop comes from some minute amount of solids deposited on the bed.

(Mr. Grunberg has later advised that during the January 1959 shutdown the increased pressure drop has been found to be caused by the deposit of iron oxide on the catalyst containers.—EDITOR)

CHAIRMAN WALTON: The next subtopic is the necessity for removal of particulate matter. This has been a matter of concern to some of us, who wonder about whether our air tower trays are, in a matter of time, going to fill up with dirt. We, at Atlantic, made a dust survey, and I'd just like to mention the figures which we obtained. This was about six months ago. We found that in our air intake to the compressor we varied between 18 and 16 lbs. of dust per billion cu. ft. The effectiveness of the wetted leaf filter was such that we had 1 to 4 lbs./billion cu. ft. going to the reversing exchangers. In our plant it takes about 3 months to process a billion cu. ft. In the air distillation tower we found 0.75 to 3 lbs. of dust per billion cu. ft. This dust actually passed through the reversing exchangers—we have actually found dust when we have opened the lines. From the reversing exchangers to waste air, we found 0.25 to 1 lbs./billion cu. ft. of dirt. In the nitrogen we found 0.2 lb. per billion cu. ft. In the blowdown the amount was extremely variable. It cycled up and down as the cycling took place in the intake air. This study was made with the High-Volume Air Sampler, available from General Metal Works, Cleveland, Ohio. The MSA filter also takes out particulate matter. That's one of its advantages.



G.U. Weigers, is in the Oxygen Department of American Cyanamid's New Orleans Plant.

WEIGERS, American Cyanamid, New Orleans, La.: Have you had the opportunity to open your column and find out whether this particulate matter was depositing on the trays?

CHAIRMAN WALTON: No, we haven't, but we have done this in the past. We did take out the internal thermowell in the re-boiler, and saw a very light deposit of dust on the re-boiler tubes.

WEIGERS, Cyanamid: We opened up one of our low-pressure columns last month, and, to our surprise, found no evidence of particulate matter on the trays after 4½ years of operation. We're sure that some particulate matter is getting through our filters, but we have had no evidence of a build up in any particular part of the plant.

CHAIRMAN WALTON: That's an interesting observation.

LAWRENCE, U. S. Industrial Chemicals, Tuscola, Ill.: Mr. Walton, did you analyze the dust?

CHAIRMAN WALTON: Yes. We have, very close to our ammonia plant, a waste water plant. All the waste water from the refinery goes through there, and solids are filtered out and burned in an incinerator. The dust was found to be fly ash from that incinerator.



J.A. Lawrence is superintendent of the Ammonia Plant of U.S. Industrial Chemicals at Tuscola, Ill.

LAWRENCE, USI: We probably have more solids due to corrosion in our suction line. We've analyzed them and found they're mostly iron sulfate. We found it in our exchangers when we derimed. It gets stuck in the ice in the exchangers. We don't have reversing exchangers. I was wondering, would MSA's filter be ruined if one didn't use a pre-filter? Also, would a filter be improved with tri-cresyl phosphate in it, or is this material considered a hazard in an air plant?

CHAIRMAN WALTON: I can say that we have a wetted leaf filter which uses tri-cresyl phosphate, and so far we do not believe that to be a hazard. We're not really sure of that.



F. Himmelberger is safety director at Air Products, Allentown, Pa.

HIMMELBERGER, Air Products, Allentown, Pa.: I have a brief comment on tri-cresyl phosphate. We have taken a number of the phosphate ester-type lubricants, slurred them in liquid oxygen, and ignited them either with a flash bulb or a small blasting cap. We were always able to produce explosions when the stronger source of initiation was applied.

CHAIRMAN WALTON: There is a pre-filter which is designed to remove particulate matter before the Hopcalite section in the MSA filter. Isn't that correct, Mr. Evans?

EVANS, M.S.A.: That is correct, it is an extremely efficient "ultra filter" which will take out all particulate matter with efficiency in the order of 100% down to 3/10 of a micron. Obviously, you should not expose this type of filter to particulate of 10 microns or larger in size; you would just waste its usefulness.

ROTZLER, Monsanto Chemical, Texas City, Texas: At the meeting last year

I described an explosion which occurred about three years ago in a reboiler in our plant. I raised a question which existed in our mind as to whether soot, which we know to be present in the air around our plant in rather small but very definite quantities, might cause an explosion; therefore, whether the removal of this particular kind of particulate matter might be a special problem in oxygen plants. Work since that time has indicated that although it is certainly possible to get detonations between finely divided carbon (soot) and liquid oxygen, the conditions are somewhat special. Not every mixture of liquid oxygen and carbon will produce a detonation, nor are these mixtures easily detonated; it takes a considerable amount of energy. So while I don't think soot can be ruled out as a safety problem in oxygen plants, as a progress report let me say that we do not feel it was the cause of our explosion.



R. W. Rotzler, manufacturing superintendent in the Plastics Division at Monsanto's Texas City, Texas, plant.

CHAIRMAN WALTON: Thank you. It's good to tie in some of these things which were discussed last year and left open.

KNAPP, American Messer, New York, N. Y.: I would like to make one more remark regarding gas removal. In our regenerator plants we use a system for cooling the air working on the following principle. There are two towers. In one, water is contacted with the effluent nitrogen and cooled down by heat exchange and by evaporation of water into the dry nitrogen coming from the plant. In the second tower the incoming air is cooled and scrubbed with this water, after having passed the aftercooler of the turbo compressor. We found that this water scrubber serves very effectively in removing dust from the incoming air before the air enters the low temperature plant.



H. Knapp, process engineer at American Messer Corp., New York City.

Air compressors

CHAIRMAN WALTON: Air compressors have been a problem for many years, and one which is not entirely solved as yet by any means. Mr. W. F. Cummings of Shell Chemical has consented to introduce this topic.

CUMMINGS, Shell Chemical, Pittsburg, Calif.: Fires originating from deposits of carbonaceous materials in air

compressors and auxiliary piping, surge vessels, and inter-coolers are a serious industry-wide hazard. This topic is included on the agenda to highlight the potential hazard present wherever air compressors are operated.

The fuel for these fires or explosions is usually the lubricating oil and the carbonaceous products formed by oxidation of this oil. Many theories have been advanced concerning the mechanism of initiation. A few of these are: (1) ignition of deposits by glowing carbon blown



W.F. Cummings,
manager of Shell
Chemicals Opera-
tions Department
at Pittsburgh, Cal-
ifornia.

from the cylinder area; (2) auto-ignition of oil vapor-air mixtures; (3) formation of organic peroxides with the lubricating oil leading to further exothermic oxidation reactions; (4) auto-ignition of carbonaceous deposits by the exothermic reaction which occurs during formation of a carbon-oxygen complex when oxygen is absorbed into the deposit, as theorized by investigators of the Bureau of Mines. On application of above-normal temperatures, and we feel that somewhere in the neighborhood of 300°F, this complex breaks down into CO₂ and CO. If the net heat generated is not removed, spontaneous ignition may result.

Regardless of which mechanism actually causes ignition, a high operating temperature is the common factor in all the theories. This high temperature may result from one or more of the following conditions: (1) broken, dirty or leaking valves; (2) leaking piston rings; (3) insufficient jacket cooling or inter-stage cooling. However, under certain conditions, excessive cooling could cause condensation which will destroy your lubricant and result in scuffing and high local heat. A hot piston might then result. (4) Unusually high compression ratios.

Suggested methods to minimize likelihood of fires

Certain metals act as catalysts in the oxidation of oil, of which bronze and many other copper-containing alloys appear to be the most active. We have found that pistons and rider rings constructed of non-copper materials, such as molybdenum disulfide impregnated bakelite, should be used. When designing your compressor auxiliaries, it has been our experience that piping runs should be as short as possible, especially where high temperatures might be encountered, such as between the compressor stage discharge and your coolers. Also, locations where carbonaceous materials might collect, such as baffles and excessively large surge vessels, should be minimized.

The formation of carbonaceous deposits in air compressors depends on the type and the amount of lubricating oil used.

It is essential that the minimum quantity necessary to provide lubrication be determined. Any excesses will promote carbon deposition. Numerous non-combustible compressor lubricants which have been recommended for use in air compressors are on the market. The majority of these lubricants are phosphate esters which provide good flow, high glow and wetability characteristics with a subsequent low carbon formation.

High temperature alarms may be installed on the discharge of each compressor stage if sufficient operator supervision is not available. However, it must be pointed out that the reliability of these alarms is questionable in the event the thermowells become insulated by carbon deposits. Another detector is the barium hydroxide bubbler. Based on a theory by the Bureau of Mines, formation of CO₂ is indicative that conditions necessary to cause a fire have developed. Installation of a barium hydroxide bubbler on a side stream from your compressor discharge should provide warning of this CO₂ formation.

Carbonaceous deposits should be cleaned from air compressors, auxiliary piping, and intercoolers, at frequent intervals to avoid excessive buildup. A six month timing is suggested.

Here, in summary, are some useful rules for the operation of air compressors. (1) Take the inlet air from a cool, clean location. Use an adequate air filter and service it regularly. (2) Use adequate intercoolers. Maintain jacket and inter-stage suction temperatures low, but never below the dew point of the gas for the discharge pressure involved. A good rule here is never to let the incoming gas be above the temperature of the water jackets. The number of stages selected should provide moderate compression ratios for each stage. (3) Maintain clean intercoolers and jackets. Inspect discharge piping, reservoirs, cylinders, etc. regularly. Clean as required. Provide sufficient clean-outs and drain valves. (4) Check operation of valves frequently. Repair as soon as they are found faulty. (5) Use the least amount of a good, inhibited oil that will lubricate the cylinders satisfactorily, and. (6) clean air compressors with soap solution rather than with inflammable or volatile substance. Provision should also be included that, in event of fire, the location may be purged with nitrogen or flooded with water.

CHAIRMAN WALTON: There's a great deal of interest in Teflon rings. I know in one instance of their use with reduced lubrication. Is there anybody who would like to comment on experience with Teflon rings with no lubrication at all?



W.A. Mason, group
leader with Dow
Chemical's Proc-
ess Engineering
Department, Mid-
land, Michigan.

MASON, Dow Chemical, Midland, Mich.: We have tried Teflon piston rings

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in circulating pumps operating at 5000 lbs. pressure at Midland. Garlock Rockhard Piston Rings have been used previously with lubrication. These rings operated satisfactorily for three months before removal for examination. They were satisfactory except for severe wear at a point where the cylinder had previously been badly scored. This does not necessarily mean that Teflon piston rings would be perfectly satisfactory for use in a new cylinder liner. This particular application gave the piston rings every opportunity because the cylinder had been previously polished to a mirror finish by the lubricated Rockhard Piston Rings. This trial looks promising. As to the source of these Teflon piston rings, they were purchased from Koppers Company, Inc., Baltimore, Maryland.

CHAIRMAN WALTON: France Packing Company I know, also makes Teflon rings.

SWOPE, Southern Oxygen: We're using Teflon rings in an expander operating at about -100 to -150°C with no lubrication. This set has been in operation for about a year and is working satisfactorily. A previous set of rings wore out in about 30-45 days, as we were warned in advance. Apparently there is some polishing of the cylinder walls which takes place.

CHAIRMAN WALTON: I think Teflon offers one of the greatest possibilities in this problem of getting rid of the lubricant entirely. Ingersoll-Rand is working on a proposal for our particular installation, for changing over to Teflon rings. I think there are two types. One is a glass fiber strengthened Teflon, and the other is copper. Mr. Swope, which were yours, do you know?

SWOPE, Southern Oxygen: I would say they may have been glass fiber. I don't recall any copper. The rings are backed by a stainless expander spring.

FUNK, German Linde: We have so-called labyrinth compressors which do not use lubrication at all. They run on so-called labyrinth seals.

Referring to explosions or fires in air compressors, I would like to say that we once experienced a fire in an air compressor and traced the cause to carry-over from the caustic wash tower between the second and the third stage of compression. This explosion occurred in the third stage. Apparently the caustic lye had deteriorated the lubricating oils in the cylinder, then carbon had deposited on the third stage cooler and auto-ignition set off the detonation. Therefore, a carry-over of lye should be prevented.

PUTMAN, Superior Air Products, Newark, N. J.: We have also used Koppers glass-Teflon rings in a low tem-

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perature expansion engine and discovered that the first set of rings apparently wear in to the cylinder's surface and then you get a service life on the second set of rings ranging anywhere from 5,000 to 7,000 hours. These rings are used at low pressure ranges, expanding from 600 to 60 lbs./sq. in.



L.E. Putnam, chief engineer at Superior Air Products, Newark, N.J.

CHAIRMAN WALTON: Those of us who have to use oil lubricated compressors, either air compressors or others, have some concern about oil removal devices, and I'd like to report on our experience. We have tried silica gel, F-1 alumina, H-151 alumina, cotton batting and felt. The silica gel and also the F-1 alumina have given us trouble with powdering so we ruled those out. The H-151 has not powderd, but it leaves something to be desired on oil removal. We recently had a visitor from the government helium plant at Amarillo, and he spoke about the use of cotton batting and felt as being one of the most effective means. We have just installed several layers of felt and cotton batting and we don't have anything to report on it as yet. Does anybody have any comments on oil removal devices, down to the last trace?

EVANS, MSA: We have just recently developed a filter for the Kinney vacuum pump effluent, and it removes particulate matter down to 3/10 micron size at high efficiency. This filter handles 150 std. cu. ft./min. It is about 10 inches in diameter and perhaps 20 inches high. It picks up about 10 lbs. of oil, oil mist or fog (very finely divided particulate which appears as smoke if it is left free in the atmosphere) every 4 days, then the element is cleaned by soaking overnight in naphtha. To date we have not established how many cleanings can be repeated, but we know it is more than ten.

CHAIRMAN WALTON: Any other comments?



D.L. Stockbridge, Jr., of Southern Nitrogen, Savannah, Georgia.

STOCKBRIDGE, Southern Nitrogen Co., Savannah, Ga.: We had some problems with oil in our instrument air. We thought we had it licked when we used a cresyl lubricant, but we found that this carried into our instruments. Many of these have neoprene bellows and the lubricant deteriorated those to such an extent that we had to discontinue the use of the so-called non-flammable lubricants.

We have been using wool felt in our filters for about six months, and it seems satisfactory.

FAATZ, Foster Wheeler, New York, N. Y.: Our early experience with removal of oil from air streams indicated that two problems are involved, and they have to be considered separately. One is the removal of oil fog, and the other is removal of oil vapor. In the first plant we built we used an alumina adsorber and the fog tended to go through it. It was necessary to agglomerate the fog with a felt filter before passing the vapor into the alumina or charcoal bed for adsorption. The idea is to prevent the vapor from condensing on cold surfaces of subsequent equipment.

GRUNBERG, L'Air Liquide: We have found it advantageous to cool the air down to around 40°F before removing the last traces of oil vapor. At 40°F, a substantial amount of water is simultaneously condensed, which seems to facilitate oil removal.



R. F. Bollen is Ammonia plant Supervisor for Dow Chemical Ltd. at Sarnia, Ontario.

BOLLEN, Dow Chemical of Canada, Sarnia, Ont.: We had quite a problem with the excessive amount of oil in the high-pressure nitrogen stream to our nitrogen scrubbing unit. Our installation had a felt pad filter and we tried increasing its efficiency by installing special knock-out pots, without success. Since that time, we have installed an activated carbon (10-20 mesh) filter ahead of the felt pad filter, and now find very little oil on the felt pads. We are hoping this will extend the operating period of our cold box. We have also installed an ammonia refrigerated pre-cooler (to -10°F.) on the high-pressure nitrogen stream ahead of the carbon filter.

ANONYMOUS: The activated charcoal—what grade is it?

FUNK, German Linde: It is a little difficult to remove oil vapors from dry gas. For that reason, we inject steam and under these circumstances it is very easy to remove oil.

Silica gel adsorbers

CHAIRMAN WALTON: The next topic on the agenda is silica gel adsorbers. This has been fairly well covered in papers which have been published in *Chemical Engineering Progress* and discussed at Baltimore. We are particularly interested at this time in anything new in experience or thoughts which have come up in the past year. Are there new developments on service life, difficulty with powdering, regeneration temperature, or testing to determine how critical the regeneration time is and what is the optimum time temperature for regeneration? Dr. Grunberg of L'Air Liquide is going to introduce this topic.

GRUNBERG, L'Air Liquide: Whatever are the means for removing hydrocarbons ahead of the plants as with catalytic units, it is always necessary to use liquid filters. At the present time no air separation plant is built without liquid filters or cold filters. The main purpose of these filters is to remove acetylene, which has a very low vapor pressure at the temperature of liquid air and oxygen. Its solubility at the temperature of boiling oxygen does not exceed 5 to 6 parts/million. The maximum concentration which is generally considered as safe in the air to be treated is 1 part/million. However, this concentration is at times often exceeded. Provided higher concentrations of acetylene in the air do not last too long, the filters can usually take care of them, but is not a very safe type of operation. Liquid filters should be preferably used on the whole stream of air or rich liquid treated.

Various types of adsorbents are being used in these filters, and it appears that the best one is "SOVABEAD" mainly because the loss by attrition is negligible. Plain silica gel has a tendency to powder, and is more sensitive to temperature changes. The basis of design is of the order of magnitude of 600 lbs. of adsorbent per vessel and for 100 tons/day of oxygen produced. This amount is sufficient to take care of 1 part/million of acetylene for a period of approximately 7 days. An important factor in the operation of these filters is the temperature at which they are regenerated. It appears that the temperature of 250°F. is optimum. The SOVABEADS can withstand temperature as high as 450°. It is preferable to leave no trace of water and heavy hydrocarbons on the beds after regeneration.

These filters do not adsorb methane in appreciable amounts, but do adsorb some higher components. Another type of filter has been introduced in some plants. It is a cold filter in the gas phase. It seems to effectively adsorb some high boiling components like butane and propane at low concentrations.

If gas phase adsorbents are used, very good screens must be installed in order to stop the micron-size particles produced by attrition. These would be detrimental in the operation of high speed turbines.

MASON, Dow: One of the items on the agenda included measuring the amount of material adsorbed on the gel. When our air separation plant at Midland was started, we regenerated the adsorbents every day. We also determined the amount of adsorbed material, and the concentration of hydrocarbons in the liquid oxygen, every day. After six or eight weeks of operation, our data convinced us that we should regenerate the adsorbents only twice per week, and determine the total hydrocarbons desorbed from the adsorbents only once per week.

The procedure for determining total hydrocarbons desorbed from the adsorbents consists of several steps. During the entire regeneration process, the effluent nitrogen from the adsorber is

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divided into two parts. The major part of this effluent is metered and vented to the atmosphere. A small but constant proportion of the effluent is passed through a trap, cooled to liquid nitrogen temperatures to condense any hydrocarbons and CO₂. It is metered with a wet test meter. After the regeneration period is completed, the trap is warmed and the condensed hydrocarbon and CO₂ is transferred to an evacuated volumetric flask by flushing with dry nitrogen. The mass spectrometry department then analyzes the sample and reports its composition and standard volume at 0°C. and 760 mm. of mercury. With the composition and standard volume of the sample, and the metered volume of the total nitrogen used for regeneration, we calculate the total amount of each constituent that has been desorbed in the complete cycle.

On the basis of these examinations, we believe we are operating with a factor of safety of 10. That is, the adsorbers have a capacity of about 10 times as much as has accumulated during our worst cycle. This might be of interest to some others who would like to make such determinations.

CHAIRMAN WALTON: We use silver sova in our silica gel adsorbers and after three years, when we had a shutdown, we changed it because we thought it might be a good idea to see what it looked like. There was very little powdering and very little change in color. Examination in the laboratory indicated that it was about as effective as it had been when it was new.

WEIGERS, Cyanamid: My question concerns the useful life of the silica gel adsorbents. We too have changed the silica gel in our gas phase as well as our liquid phase adsorbers after three years of plant operation. The initial layers of gel (perhaps 6 inches to 12 inches in depth) in both the adsorbers were discolored. The top layers were quite dark brown. Going down in the bed this brown color got progressively lighter, and even after the brown had disappeared, the silica gel, instead of being a semi-transparent crystal, was opaque milk white. An analysis of this discolored gel indicated something like 0.3 percent hydrocarbon by weight. However, we did not characterize the hydrocarbons. We have decided to change the new gel after a two year run. I'm curious as to whether any of you have experienced similar hydrocarbon contamination of the gel, and if you have, what is your program for changing gel?

MASON, Dow: At Dow in Midland we, too, have found discoloration of the silica gel on the top of the bed. Our Spectroscopy Department reported that the discoloration was caused by a small amount of carbonization. However, there was no appreciable effect on the adsorption capacity of the gel.

COCHRANE, Sun Oil, Philadelphia, Pa.: We have two sets of silica gel adsorbers. One set is on the stream between our low pressure column and our reboiler

condenser, and has been in service about 20 months. We have periodically checked the efficiency of these adsorbers for removing all C₂ and heavier hydrocarbons, mostly saturates. We have found that in a period of about a year, the adsorption efficiency has remained about the same. We plan to change the gel after possibly a three year run.

WRIGHT, Standard Oil Co. Whiting, Ind.: I wonder if anyone was working on adsorbent filters for removing ethane and methane from the rich liquid stream?

HIMMELBERGER, Air Products: As to adsorption of ethane on silica gel, Dr. McKinley and Dr. Hsu of our laboratory are running extensive tests on adsorption, and they will be prepared to present a paper on the subject entitled "Adsorptive Purification of Liquid Oxygen" at the AIChE meeting in Cincinnati in December, 1958. (Shortly to be published in CEP . . . Editor)

CHAIRMAN WALTON: Any other comments on gels?

KNOX, St. Paul Ammonia Products, South St. Paul, Minn.: It appears to me the real problem is whether you have had any indication of reaching a breakthrough point in your filters. On your three-year basis, did the actual operating levels of hydrocarbons in your low pressure column show any tendency of rising?

CHAIRMAN WALTON: In our case, no! We didn't feel that we were anywhere near the point where we had to even change our regeneration or our 7-day onstream time.

WEIGERS, Cyanamid: We found exactly the same thing as far as the adsorptive capacity of the gel was concerned.

STEVENS, Phillips Petroleum, Idaho Falls, Idaho: I'd like to tell you about some of our lab experiences with silica gel as an adsorbent for radioactive nuclides, specifically ruthenium tetroxide, from an air stream. These, of course, can be analyzed for in very low concentrations. We are testing silica gel at a moderate temperature, with large amounts of nitrogen oxides and water vapor present.



J. I. Stevens, is with Phillips Petroleum as Group Leader for Process Design in the Atomic Energy Division.

We found that after the silica gel had been saturated, after perhaps 20 times the saturation volume of water had passed through the beds, it still has an affinity for adsorbing the ruthenium tetroxide. However, the over-all efficiency while good (decontamination factor of perhaps 1000) still gives us a tailing-off curve, even though we are having these very high decontamination factors. I'm sure that you aren't going to be concerned with the same problems as I. However, what is your experience in regeneration?

How many cycles have you gone through before you had excessive pressure drops, etc., during the regeneration of silica gel beds?

CHAIRMAN WALTON: We in this three-year period regenerated each gel case once a week and we had no indication of increased pressure drop during that three year period.

Reboilers (or vaporizers)

The next topic is reboilers or vaporizers, which will be introduced by Mr. Himmelberger.

HIMMELBERGER, Air Products: What we've heard up to now deals with keeping things out of air plants. Now let's consider the traces that get in. We'll discuss:

1. The kind of hazard which can occur in the reboiler.
2. How the hazard can be defined during plant operation.
3. How it can be measured quantitatively.
4. How it can be eliminated.

Most of the larger air separation plants in the chemical industry today employ a double column. An integral component of the cycle is a reboiler-condenser, which condenses nitrogen to provide reflux to both the columns. Refrigeration for this is obtained by vaporizing liquid oxygen. Heat exchange surface is generally provided by a tube-in-shell type reboiler-condenser, in which low-pressure oxygen boils vigorously. Much of the liquid oxygen entering the reboiler leaves in the vapor phase. In spite of judicious location of air intakes and careful operation of air purifying units, minute traces of impurities may reach the reboiler. Since boiling takes place near -300°F., most of the impurities will have extremely low vapor pressures, causing them to concentrate in the liquid fraction. If no liquid is withdrawn from the oxygen side of the reboiler, the concentration of impurities depends upon the inlet composition, vapor pressure of the contaminants, and time. Hazards arise when contaminants reach their lower limit of flammability or exceed their solubility in the liquid oxygen. Maintaining the concentration below the solubility level is important for two reasons:

1. Explosive local concentrations, even though average impurity levels are below the flammable limit.
2. Splashing of undissolved particles onto the cold walls above the liquid level, forming a combustible interface with the oxygen vapor.

Knowing what impurities to expect, accurate data on solubilities and flammable limits can help to establish safe operating conditions.

Fortunately, gas phase lower com-
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bustible limits are well known; extensive publication in this field has been sponsored by the U. S. Bureau of Mines. Their bulletin 503, *Limits of Flammability of Gases and Vapors*, by Coward and Jones, is a valuable reference for air plant operators. The book by Lewis and von Elbe, *Combustion, Flames and Explosions of Gases*, is of interest to those curious about the underlying theory of combustion. Although the data on flammable limits of combustibles in air are more complete than those in oxygen, it will be noted that where both have been investigated, the lower flammable limits in air and gaseous oxygen are almost identical, and so it is safe to generalize on this. The next comparison necessary is the relationship of gas phase lower combustible limits with those in the liquid phase. To sustain flame, energy produced by the reacting gases must be sufficient to excite the unreacted portion to flame activity. To meet this requirement in low-temperature liquids, more energy, hence more fuel, is needed and the lower limit can be predicted as being higher than that of the gas phase limit. Experimentation in our laboratory indicates this to be true for methane, ethane and propane.

Another experimental finding, useful in air plant safety work, is that mixtures of soluble hydrocarbons in liquid oxygen did not explode when their C_1 or equivalent carbon atom concentration was maintained below 5 percent.

Figure 1 depicts flammability limits of the system, methane-oxygen-nitrogen. Any mixture within the hatched area is flammable in the gas phase; flammable liquid compositions are contained in the envelope within the dotted line. For rough estimation these values may also be considered to apply to other soluble hydrocarbons, providing concentrations are expressed in terms of equivalent carbon atom percent, rather than mole percent. A composition as pictured at "A" is safe; a composition at "B" is capable of ignition.

Another aspect demonstrated by our laboratory explosion studies was that explosions were readily initiated below the gas phase limits in ethylene, acetylene, and other hydrocarbon mixtures with liquid oxygen when their solubilities were exceeded. Formulation of safe limits, then, requires accurate knowledge of solubilities. To supplement rather meager published data prior to 1956, our laboratory initiated a program to investigate the solubilities of hydrocarbons and other substances in liquid oxygen. Some early results were published in an article on "Oxygen Plant Safety Principles" in the March 1957 issue of *Chemical Engineering Progress*. At the Cryogenic Engineering Conference in Cambridge, Massachusetts, in September 1958, a more complete discussion of solubilities and their determination was presented in a paper by Dr. McKinley and Mr. Wang of our laboratory staff. Figure 2 is a plot of some of the data as solubility vs. temperature for saturated hydrocarbons. Note

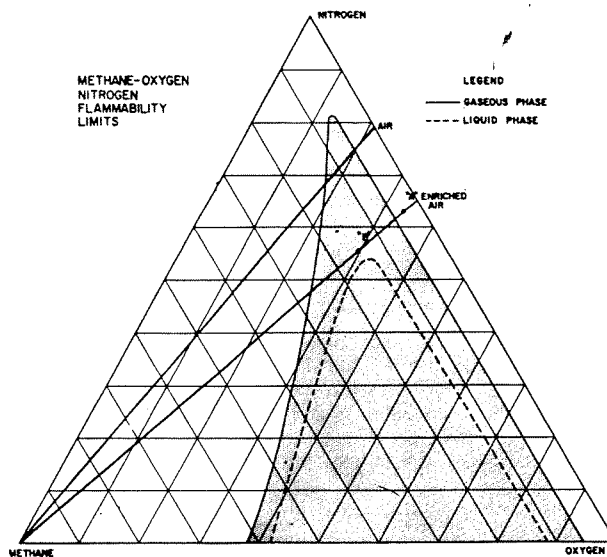


Figure 1. Flammability limits (methane-oxygen-nitrogen system.)

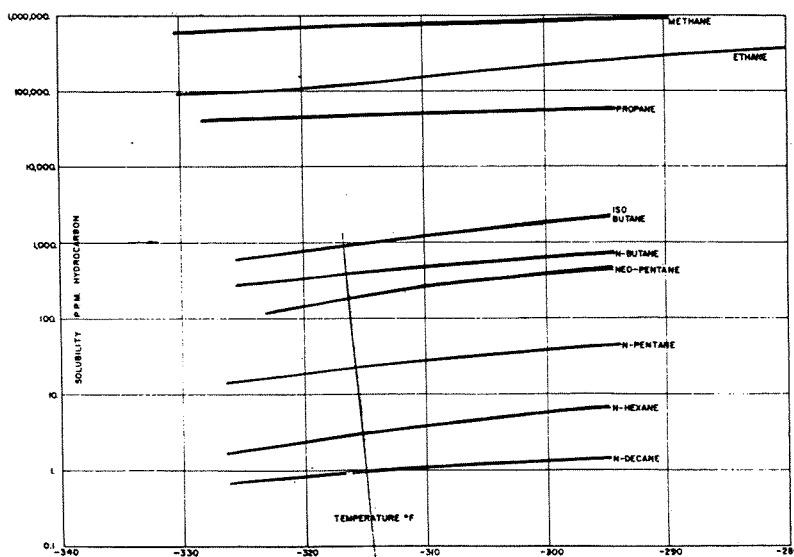


Figure 2. Solubility of saturated hydrocarbons in liquid oxygen.

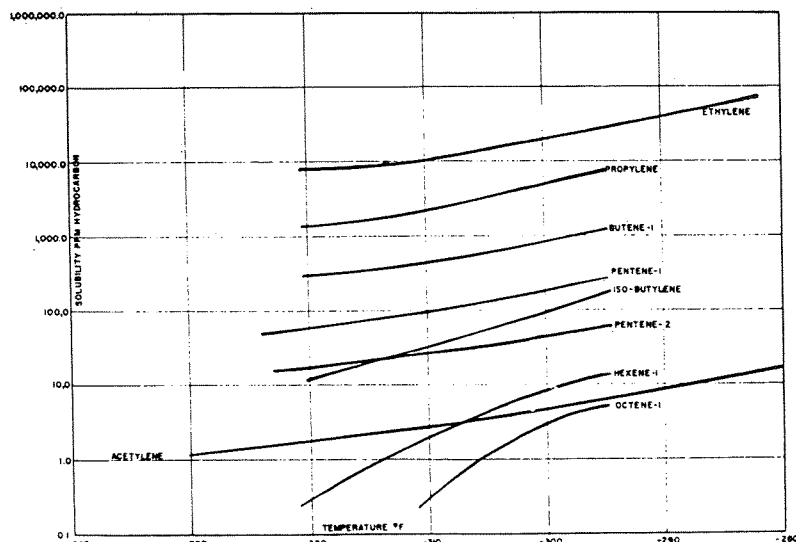


Figure 3. Solubility of unsaturated hydrocarbons in liquid oxygen.



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that the solubilities of methane, ethane, and propane are above the lower explosive limit and hence could become hazardous while still in solution, but only at concentrations in excess of 50,000 pts./million when analyzed in terms of carbon atom equivalent. These three compounds have boiling points below 0°F. and are comparatively small molecules. They are the ones most likely to penetrate the air purification barriers of freeze-out and adsorption. The C₄'s and higher, on the other hand, have boiling points above 0°F. and are relatively larger molecules. They are, therefore, more easily removed by normal purification methods. In fact, if an adsorber is subjected to excessive loading, beyond design expectations and safety margins, the higher boilers will preferentially displace ethane and propane. (Oxygen itself displaces methane when the inlet methane concentration is low.) One's ability to remove the less soluble compounds more readily and the fact that they tend to preferentially displace the more soluble ones from adsorbers becomes an important factor in setting maximum tolerable impurity levels. These levels must be compatible with practical operating experience and appreciably reduce monitoring requirements.

Figure 3 depicts similar data for unsaturated hydrocarbons. At C numbers 2 through 5, the unsaturates exhibit lower solubilities in liquid oxygen than the corresponding saturates. Above C₆ this distinction requires more careful definition because of a different slope in the solubility curve with respect to temperature. Again, where silica gel adsorbers are employed, nature has compensated reduced solubility with increased facility for adsorption. Generally speaking, if the adsorption bed capacity for the mixture is exceeded, the unsaturates in a liquid oxygen or liquid air stream will displace saturates of comparable C number.

Notice acetylene, as it stands out as a special character. It has a low solubility comparable to compounds which boil above 100°F., but sublimates more than 200° lower. In spite of the fact that adsorption is effective in removing acetylene, its extremely low solubility, its sensitivity to relatively low energy initiators, and its frequency of occurrence in air feeds demand that acetylene gets special treatment. More about this later.

Other factors relative to plant cycle and location must also be considered in setting tolerable impurity levels. The lower combustible limit and solubility of fuels in liquid oxygen are universal parameters which must be acknowledged. They are the primary guides. For each fuel, the tolerable level must be set at some fraction of the lower combustible limit or the solubility, whichever is smaller. The size of the fraction chosen determines the safety margin. Idealistically, this would entail frequent or continuous analysis of each fuel by mass spectrometer, chromatograph, or infrared absorption. Some operating plants are able to approach this ideal procedure.

Others simplify the analytical problem by utilizing knowledge of their plant environment, the capabilities of their purification units, the equivalent carbon atom concept of combustible limits, and the significance of solubilities. A workable solution at a number of locations has been to select a limit in terms of total soluble hydrocarbons and a separate limit on acetylene. An acetylene limit of 0.5 pts./million represents a safety factor on the order of 10 when related to its solubility of 5 p.p.m. in liquid oxygen at -300°F. If complete circulation is not afforded in the reboiler, a more stringent level may be chosen to cover the possibility that liquid oxygen containing acetylene may splash on the walls above the liquid level, evaporate oxygen preferentially, and leave a residue of solid acetylene. Here, the vapor pressure of the solid acetylene becomes important. At a reboiler temperature of -290°F., the vapor pressure of solid acetylene is very low (about 4.5×10^{-6} lb./sq. in. abs.) In low-pressure, non-circulating reboilers, a safe acetylene level should be set somewhere below 0.2 pts./million.

The selection of a total soluble hydrocarbon limit in the reboiler can be based on at least three factors:

1. Air contamination levels.

In most locations hydrocarbon contaminants in air decrease in concentration as their C number increases; concentrations above 30 pts./million in air are unusual. C₄'s or less are most common, and in many cases methane is greater than the sum of all other hydrocarbons combined. Site conditions can never be taken for granted, however.

2. Prepurification equipment.

The air purifying units will alter the impurity content. For example, where silica gel adsorption is employed, C₄'s and above are more readily removed than lower hydrocarbons. In the event that breakthrough occurs, the lower hydrocarbons are preferentially displaced.

3. Solubilities.

The solubilities of C₄'s and lower, when expressed in carbon atom equivalent, exceed 600 pts./million.

Based on these considerations, a total soluble hydrocarbon limit of 500 p.p.m. expressed in terms of carbon atoms is very realistic in many plant locations. Lowering this limit to provide an even greater margin of safety is advisable where the plant location or plant cycle will permit it. Tolerable limits, however, need not be set so low that the plant will be shut down unnecessarily.

With respect to any contaminant or any group of contaminants, the practice of setting safe limits in two steps may have merit. One level, a normal operating maximum, can be set at a value somewhat above normal or average operating concentrations in the reboiler. At some particular plant, it might be 100 pts./million for total hydrocarbons (or 0.5 pts./million for acetylene). When this level is exceeded, corrective action might be taken, such as increasing a purge or putting a fresh adsorber on stream. Diagnostic action would also be initiated

to determine why an abnormal level is occurring. Action taken at this lower level of contamination may eliminate a costly plant shut-down. A second limit, including a reasonable safety factor, would represent the maximum safe concentration. It might be 500 pts./million for total hydrocarbons. When concentration exceeds this level, emergency shut-down is dictated.

Aside from hydrocarbons, other contaminants, such as initiators and sensitizers, should be mentioned, even though they are not hazardous in liquid oxygen in the absence of fuels. Ozone can be classed as an initiator and a sensitizer. Experiments have shown it capable of triggering liquid oxygen-hydrocarbon mixtures in the flammable range. Experiments have also indicated that less impact energy is required to initiate flammable mixtures in the presence of ozone. In both cases, however, ozone concentrations have been much higher than ever detected in air plants. In fact, air plant tests for ozone are seldom, if ever, positive. Nevertheless, since it is an initiator, all possible precautions should be taken to prevent ozone from entering the plant.

The oxides of nitrogen, NO and NO₂, have both sensitizing and inhibiting effects on combustion. Experiments, where NO₂ has been added to liquid oxygen-hydrocarbon mixtures just below the explosive range, have shown NO₂ to have very little or no effect on the combustible limit, nor has it shown any capability for spontaneous ignition of mixtures within the flammable range.

In the trace impurity range, oxides of nitrogen have reacted with ozone and hydrocarbons in the presence of sunlight to produce complex molecules in smog areas. At low temperature in coke oven gas plants, explosive "gums" have been formed by reactions of oxides of nitrogen and unsaturated hydrocarbon, but in concentrations of several percent rather than parts per million. These reactions prompt us to be suspicious of oxides of nitrogen, but do not define their predictable behavior in air plants such that operating limits can be set.

Toward the further understanding of their behavior, experimental work is continuing. The solubilities of NO and NO₂ in liquid oxygen at -300°F. have been determined as 6 and 15 pts./million respectively. Analytical results have shown plant concentrations to be far below this level. A tolerable limit for oxides of nitrogen might be set at 2 pts./million, or even 0.2 pts./million in many places, without handicapping operation. Setting limits below their solubility level may provide protection against some hazard as yet not clearly defined—and possibly non-existent.

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There is more to learn about initiators and sensitizers, and we are hard-pressed to select safe limits based on scientific criteria. Emphasis on prevention of hazardous fuel levels is a more certain line of safety defense. With the selection of safe limits of concentration, guideposts are set up. The next step is to prevent reboiler concentration from exceeding safe levels. One approach is to minimize contamination entering the reboiler through prepurification of the feed stream. Here, low temperature adsorption and catalytic oxidation are in established use.

The other general approach to reboiler purity is through withdrawal of all or a portion of the liquid oxygen phase which is susceptible to contamination. These include intermittent purging, continual withdrawal of a side stream to an auxiliary vaporizer or liquid pump, and other variations.

Where only part of the liquid is drawn off, the questions of how much and how often must be answered. Where analytical monitoring of the reboiler is practiced, the answers are in the safe limits. Through experience, the required withdrawal rate for a given cycle at a particular location can be predetermined approximately. On this basis, it has been possible to design so as to maintain refrigeration balances and to recover all or part of the refrigeration and product lost through partial withdrawal. Since the auxiliary vaporizer further concentrates impurities, special controls are applied. It is customary to install such units in a separate or remote part of the cold box to avoid major plant damage in the event that the additional concentration of impurities reaches hazardous proportions.

A type of reboiler system permitting complete circulation of liquid and gas taking place through a common inlet and a common outlet is shown in Figure 4.

Note that no distinct liquid level exists on the oxygen side of this reboiler. Liquid and vapor circulate completely, no unwetted walls are exposed, and continuous liquid withdrawal is taken overhead. Since the vapor phase which contains essentially no impurities forms part of the circulating stream, the most impure portion, all liquid is fed to the pump which acts as a continuous purge.

In cycles where pumps are not required, an auxiliary set of low-temperature adsorbers may be placed in a liquid stream circulating through the reboiler and the column.

The final step of maintaining a safe level of contamination in reboilers is monitoring, which provides both the windshield and the rear-view mirror to the road of safe operation.

CHAIRMAN WALTON: Thank you Mr. Himmelberger. Any comments? Has anybody had the experience of determining ozone and oxides of nitrogen concentrations above, say 0.02 pts./million? Our own analyses have not given us values greater than that. One of the

questions that has been raised is the desirability of intermittent and continuous blowdown. In our own case, we practice continuous blowdown. It seems to be required to maintain a hydrocarbon concentration down to about 100 pts./million which we strive for.

FUNK, German Linde: On the question of nitrogen oxides, last year Dr. Karwat has issued a comprehensive paper on this subject, but since then we have discovered some new occurrences of several hundred parts/million of nitrous oxide, which was found in a main condenser. Of course, we had to find out whether this was of any concern, but fortunately it does not seem to be a sensitizer for explosions. It does not seem to result in or promote explosions.

CHAIRMAN WALTON: One thing that has concerned some people has been methane. Methane is rarely analyzed for. Yet we know in the cases where it has been analyzed that you'll find methane in the reboiler liquid being extremely high in number of parts/million. This is certainly a fuel and yet, it's one which is pretty well discounted in most peoples' thinking. Does anyone have any different thoughts? The analytical techniques usually, of course, miss methane in your analyses for hydrocarbons.



G. S. Cochrane, Sun Oil, is intensely interested in air plant safety, especially infra-red analyzers.

COCHRANE, Sun Oil: Perhaps we are a little conservative in measuring total hydrocarbons, but for shutting down the plant or for taking corrective action, our hydrocarbon limits include methane. This requires the use of a separate analytical technique, gas chromatography, for measuring methane. We have

developed a test which is quite sensitive in the very low parts per million range.

GRUNBERG, L'Air Liquide: Mr. Himmelberger mentioned a limit of 100 pts./million of total allowable hydrocarbons in the air treated. We have also found that it is difficult in practice to set a lower limit. Otherwise, the plants would have to shut down too frequently. When it comes to methane, its vapor pressure and solubility are so high that a much higher concentration is safe. However, the total allowable hydrocarbons in the air would have to be limited to approximately 150 p.p.m., unless very accurate and rapid methods of analysis could instantly certify that only a very small amount of hydrocarbons heavier than ethane are present in the air feed and the vaporizers.

MASON, Dow: We did some work in Midland on the solubilities and explosion limits of some various hydrocarbons in liquid oxygen, including methane. The procedure was carried on by remote control behind a barricade. We introduced measured quantities of oxygen gas and hydrocarbons into a copper vessel in which the mixture was condensed by cooling with liquid nitrogen. This condensed solution was tested for explosibility by detonation with a No. 6 Blasting Cap about 2 inches above the liquid surface. Solutions of methane up to 10% by weight did not explode, however, a solution of 33% methane exploded violently and destroyed some of the apparatus. However, the solubility of methane is so high that, as Dr. Grunberg suggested, its relatively high vapor pressure would prevent its accumulation to a dangerous concentration.

HIMMELBERGER, Air Products: In our experimental explosion work at Air Products, we ran several mixtures of methane and oxygen. Below 10% methane, no explosions resulted; mixtures above 12% exploded every time. Between 10%-12% methane, results were less consistent. We set 11% as the approximate lower explosive limit of

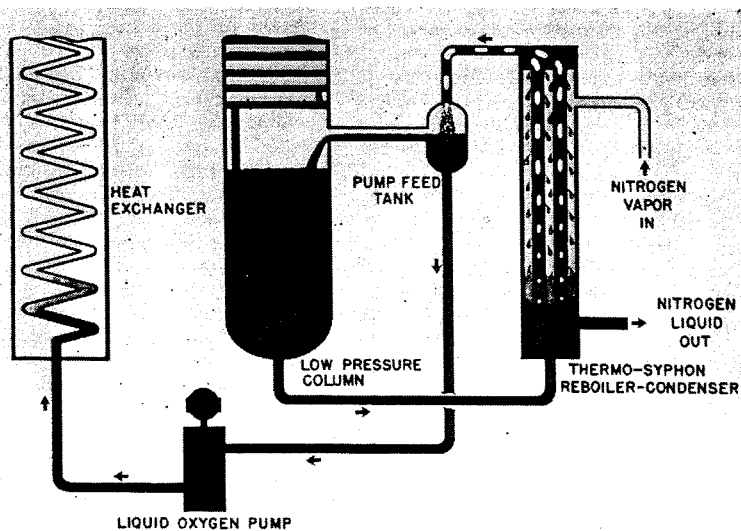


Figure 4. Circulating oxygen system.

methane in oxygen in the liquid phase. A dynamite cap was used for initiation.

DE PAUW, Carbo-chimique Testre, Belgium: There are some interesting facts about blowdown which we have experienced in our plant. We operate a plant which now has an auxiliary condenser. Some 2 years ago we were operating in a regular way. One day there was an alarm given by the plant operator who was noticing that the purge from the auxiliary condenser was showing a white color which most of you attribute to CO₂. This assumption was made by us too, but about half an hour later, a little explosion took place. This was not really dangerous but it was a warning. The findings were that there had been some CO₂ in the oxygen, although nothing indicated that the silica gel adsorbers or the heat exchangers (or regenerators) had gone wrong. On the contrary, we did not find acetylene or other hydrocarbons to be above permissible levels. Our theory is that the white color of the oxygen indicated some oxidation had already taken place initially as a kind of slow flame. Later, the reaction grew explosive. We haven't been able to trace anything further, because nothing has happened since.

WEIGERS, Cyanamid: We had an experience six months ago which may be of interest to some of you here who have auxiliary vaporizers. We make it a practice to analyze for acetylene every hour and a half in the liquid separator located underneath the auxiliary vaporizer, as well as analyzing in the main condenser reboiler of the oxygen plant. We try to run with a continuous purge by doing a partial evaporation of the liquid withdrawn from the main condenser. We had been operating for several months with absolutely no acetylene indicated when suddenly we had an appreciable concentration of acetylene in the liquid separator underneath the auxiliary vaporizer. The concentration found was much higher than what you would expect if the acetylene levels in the main vaporizer were its source. We occasionally find the merest trace of acetylene—0.02 pts./million, in this liquid oxygen separator, and under those conditions one can predict that he won't find any in the main condenser. But this time we found 3 p.p.m. and still had found nothing in the main condenser. We have theorized that the auxiliary condenser was not running with all the tubes wetted, and that in some tubes we had total evaporation taking place and that over a period of days, some acetylene crystals deposited. We had been trying to re-establish a continuous drop-through of liquid, and just prior to this incident the operator *over-controlled* and passed too much liquid into the auxiliary condenser. We have, therefore, modified our procedures so that even when we are running with a controlled continuous liquid drop-through we still flush the additional condenser once a shift by opening the liquid feed valve so that all tubes will

be wetted, preventing the accumulation of crystals in dry tubes. Since we've adopted this procedure we have no recurrence of this particular incident. Has anyone else run into a similar situation?

CHAIRMAN WALTON: As far as I know, this is the first concrete proof of the thing that has been talked about a great deal—that you could have a development of crystals above the liquid surface in a pot-type reboiler.

LAWRENCE, U.S.I.: We have had the experience that Gordon Weigers mentioned, on several occasions and we went through the same reasoning he did, except that we haven't started flushing the thing out yet. If flushing seems to work all right, it sounds like a good idea. We've noticed that we apparently on several occasions have had a dry tube suddenly get some liquid on it and wash out. We have the same type of auxiliary vaporizer as Mr. Weigers described.

WEIGERS, Cyanamid: I might add that to our minds this is the best argument for deriming your auxiliary condenser from time to time whether its fouled with CO₂ or not.

CHAIRMAN WALTON: Does anybody have any comments on intermittent blowdown as compared with continuous?

BOLLEN, Dow: Ours isn't intermittent at the present time. However, when we first started operations we were using the intermittent blowdown and we found that we got up into some pretty high concentrations of hydrocarbons. When we started operating with continuous blowdown we found it effective in keeping the concentrations down below 100 pts./million. Normally the concentration was in the order of 50 pts./million. Just recently we installed a new air compressor to supplement the air flow to the air plant. We were able to put approximately 15% more air into the air plant, but we found that we couldn't handle all of the extra liquid oxygen that was produced. Our oxygen take-off is in the vapor phase and we found that the oxygen level built up so rapidly in the vaporizer section that we had to purge a great deal more oxygen in order to control the level. Since that time, with the increase in purge we have found that the hydrocarbon content in liquid oxygen has dropped down to as low as 5 pts./million.

KNAPP, American Messer: Considering the withdrawal of the liquid oxygen from the condenser reboiler, we think that the shape of the tube sheet is an important factor. Looking at the few pictures that have been released concerning reboiler explosions, one can notice that the tubes have been damaged often near the lower tube sheet. From this one must assume that crystals that precipitate out of the over-saturated liquid settle down on the tube sheet and are not removed even if the liquid oxygen is drawn continuously from the bottom of the tube sheet. We, therefore, provide our condensers with conical lower

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tube sheets where the liquid oxygen is withdrawn on the lowest point in the cone and experience seems to indicate that this is effective in this respect.

FUNK, German Linde: It is an old practice in our shops to supply the main condenser with the conical tube sheet.



J.A. Glass, supervising engineering for the production Technical Service Department at Monsanto.

GLASS, Monsanto Chemical, Texas City, Texas: We have studied nitrous oxide, nitrous oxide-acetylene, and carbon dioxide-acetylene mixtures in the presence of liquid oxygen in an effort to explain the detonation which occurred at the bottom of our reboiler, as described by Bill Rotzler at the Baltimore meeting. We have found that certain mixtures of solid nitrous oxide-acetylene as well as solid carbon dioxide-acetylene will sink in liquid oxygen. We have also noted that we were unable to get an explosion of solid carbon dioxide-acetylene mixtures which are dense enough to sink in liquid oxygen. However, we found that certain mixtures of solid nitrous oxide-acetylene which sink in liquid oxygen will explode under certain conditions.

We have measured the nitrous oxide content of our oxygen reboiler drain and on several occasions found that the concentration has been in excess of the 70 p.p.m. solubility limit. These facts may explain certain detonations which occur at the bottom of the reboilers.

Instrumentation

CHAIRMAN WALTON: The next topic is instrumentation. We have Gordon Cochrane of Sun Oil Co. to introduce this topic. His company has done considerable work on instrumentation and has a great deal to offer.

COCHRANE, Sun Oil: As an introduction to the discussion on air plant instrumentation, I would like to briefly describe the infra-red analyzer installation at the Sun Oil Co. air plant at Marcus Hook, Pa. (See Feb. '59 CEP, pp. 54-58—Editor).

ANONYMOUS: Mr. Cochrane, do you analyze the same stream with both the catalytic oxidation unit and the hydrocarbon unit itself, or do you monitor different streams with the different analyzers?

COCHRANE: We normally monitor different streams with different analyzers. The reason we installed the two types of analyzers was that when we first

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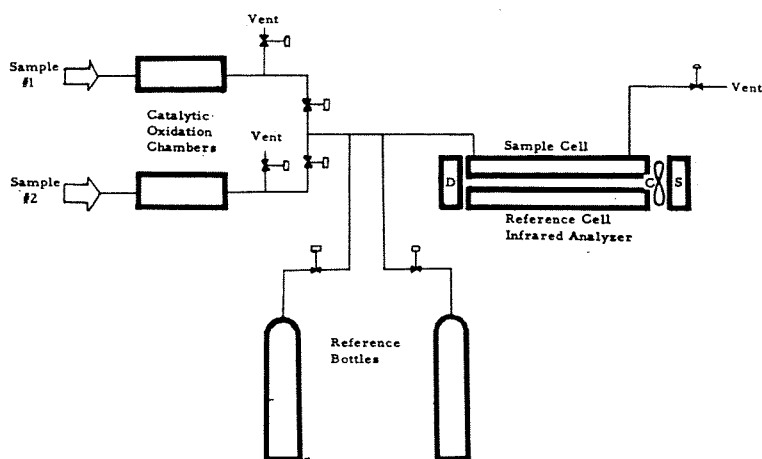
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investigated the analyzers there was no experience with the catalytic oxidation catalyst. So we installed the one analyzer which did not involve catalytic oxidation as a check on the effectiveness of the catalyst in the other analyzers. We normally use it on a separate stream. However, we have compared the results of the two analyzers on the same stream.

ANONYMOUS: When you're using catalytic oxidation, is there any possibility of your being deceived by picking up, say, a heavy molecule and getting a lot of CO₂ where actually you have an acetylene molecule, which is actually much more critical?

COCHRANE: That's right. In measuring total hydrocarbons by catalytic oxidation a heavy molecule will show up as a much greater concentration of carbon dioxide. It will be proportional to the total pounds of carbon present in the sample. That is why it is essential that the analyzer readings be supplemented by a complete hydrocarbon breakdown. As far as acetylene is concerned, it is a completely different problem. We analyze it separately in a chemical test. We do not rely at all on the analyzers to tell us the concentration of acetylene in the stream. I know that MSA has a special analyzer which you can sensitize to acetylene in areas where acetylene is a problem. We do not have such an analyzer.



Infrared analyzer installation for monitoring total hydrocarbons. (Sun Oil.)

WEIGERS, Cyanamid: You mentioned that you analyzed the rich liquid stream from your pressure column. What's the significance of the analysis? I'm assuming that you have liquid phase adsorbents which I gather are not too good for some of the lower hydrocarbons but why do you analyze there in addition to the liquid oxygen in your main reboiler condenser?

just about this time back home they're putting it on again with an improved sampling device. Anybody else have any comments on MSA?

MASON, Dow: At Midland, we have a continuous hydrocarbon analyzer which was built by our Spectroscopy Department using the Mines Safety Appliance Detector. This unit has been in operation on compressor air intake for nearly a year

COCHRANE: We do not analyze the high pressure column bottoms. The high pressure column feed is what we analyze.

CHAIRMAN WALTON: As I recall, there's a period of about 1 to 2 hours from the time that you get a big surge on the intake until you can see it in the reboiler. So this is a marvelous protective device if you have problems with high hydrocarbons in your air intake. In the Philadelphia area, one of the things which is significant is you normally always have a fishtail type of wind. The wind is continually going back and forth over about a 25-degree range and that is one of the things which tends to give you these ups and downs in the hydrocarbon content of your air intake. Rohm & Haas has an MSA Acetylene Analyser, an installation that has been in service for about a year. I wonder if they would care to comment on it.

WALTON, Rohm & Haas: We have an analyzer, the MSA-type analyzer. We've had it in service approximately six months. However, we have not yet made use of it as far as determining acetylene goes—our chemical methods do not indicate any.

CHAIRMAN WALTON: You get zero reading on it and that checks with your chemical methods? Well, we have an MSA analyzer at Atlantic which has been installed but has not been in operation yet because of purely sampling problems. We've been having difficulty in getting a liquid sample to the analyzer. The analyzer itself has checked out well on knowns. I think probably

with very little trouble. There was some electronic noise introduced at one time by some dirty contacts. This trouble was eliminated by a thorough cleaning. At one other time, a tube failure gave us a scare. Also, there seems to be some drift of the zero point from day to night which worried us at first. This instrument usually reads at, or very near, zero, but has gone up to as high as ten p.p.m. for very short periods of time. This analyzer is tested daily using a sample of known composition of ethane and air.

WEIGERS, Cyanamid: We also have one of the MSA infra-red analyzers which is sensitized to acetylene. We are using it to sample the incoming air stream. We are getting the liquid sample devices in the hope of setting up for an acetylene determination in the liquid oxygen. Our analyzer takes the sample from the air feed to the high pressure column. We've had it continuously onstream since October of 1957 and our operating experience is unfortunately rather limited. There's been only one incident of acetylene since the analyzer went on stream and that was corroborated by chemical analysis. The particular analyzer that we have has a zero to 4 p.p.m. full scale deflection and with the noise level that we're experiencing a trained observer could probably interpret 0.2 of a p.p.m. but as far as our operators are concerned 0.3 of a p.p.m. would be the minimum significant deflection.

SANDERS, Texas Co., Lockport, Ill.: We're doing something a little bit different, however. We're monitoring the separator liquid oxygen as the most concentrated source of contaminants and we're applying the same, or essentially the same, contaminant limits as most everyone appears to be applying to their low pressure tower or reboiler liquids. We've used this to its greatest advantage in telling us when we had corrected some particular contaminant problem by either purging or by switching the rich liquid or the cold filters. And just a comment which applies to what we've said this morning—the fastest correction we've found is by switching the cold filters on high hydrocarbon counts.

COCHRANE, Sun Oil: I would just like to mention briefly some of the other uses to which we have put our infra-red analyzers. One has been to study defrost of the silica gel adsorbents and defrost of some of our exchangers. We have tried also to measure the hydrocarbons removed from a plant during defrost and where those hydrocarbons were coming from.

CHAIRMAN WALTON: That's a very good point because I know some of us have had difficulties with blockage in nitrogen wash systems in hydrogen purification and the use of the analyzer to try and determine just what it is that is causing that blockage would certainly be a very valuable tool.

Part 2 of this three part report will appear in the July issue of CEP.