

.... *Parts 2 and 3*

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

Continuing the CEP exclusive report of the Baltimore sessions, chemical engineers again bring their experience to the problems of the safe operation of air plants.

Part 2 Air plant safety

CHAIRMAN WALTON, Atlantic Refining Co.: This symposium is directed particularly to those concerned with, and responsible for, operation and maintenance of existing air plants. We are interested in operating safely what we have.

For each topic on the agenda we have a person who has had experience in that particular area and who will introduce the topic. He will attempt mainly to give the facts which are known or have been published, and avoid, in general, expression of his own opinions on the subject. Following that, the audience will be asked to give their opinions or other information which might be of interest to the group.

Air Intake location

There is a question that has been asked many times—is the intake location you already have a good one—should you change it if it is something that can be changed. The selection of your intake location may vitally affect the occurrence of accidents or operating difficulties. Mr. Gordon Cochrane of Sun Oil Co. will discuss this topic.

COCHRANE, Sun Oil: One of the important factors in safe operation of air plants is the proper location of the air intakes. Since almost all the contaminants enter an air plant in the feed air, it is imperative to use the purest air possible. Too often other

safety features within the plant are unnecessarily overloaded because of poor air intake location. When choosing such a location these factors should be considered: The known sources and types of contaminants, location with relation to air plant location, point sources versus fairly uniform distribution of contamination, and prevailing wind direction or atmospheric condition. Most of these subjects can be at least partially considered without extensive analytical testing. However, if possible, an analytical study should be made. Continuous analyses should be used in prefer-

ence to spot samples; we have found that contaminant concentrations can vary rapidly and that spot samples have only a limited value. Sampling methods which can be used include the use of a small compressor, vacuum pumps, or evacuated cylinders.

There are many analytical methods for measuring small concentrations of contaminants in the air. These include dispersive and non-dispersive infrared, mass spectrometry (MS), gas chromatography, and chemical analysis. Since a very high degree of sensitivity is required, it is usually necessary to condense the contaminants at liquid oxygen or liquid nitrogen temperature and then analyze by MS or chromatography. This method is excellent for all contaminants heavier than methane. A good method for total hydrocarbons burns the hydrocarbons to CO₂ and then analyzes the resulting CO₂ either chemically or by infrared. A long path dispersive infrared analyzer is valuable in identifying types of contaminants present. We have used this method successfully. However, they are not normally available and the sensitivity for some contaminants is very poor. There are available various chemical methods for measuring acetylene, nitrogen oxides, ozone, oxidants, etc.

Some of these analytical methods involve problems including representative sampling, obtaining the required sensitivity, and removing CO₂ and wa-

Four More Sessions At Salt Lake City

There will be four sessions on Safety in Air and Ammonia Plants at the upcoming Salt Lake City Meeting, Sept. 21-24. Again chaired by N. H. Walton, these sessions will go even deeper and wider into this vital subject. No engineer in this field will want to miss these continuing meetings.

ter without losing any of the contaminants present.

After an analytical study is complete, and the types, sources and concentrations of the contaminants are known, then the air intake can be properly located. Sometimes it is necessary to provide two or more air intakes which can be used alternately, depending on the wind direction.

It is also necessary to determine where the various contaminants will collect in the air plant, what their solubility limits are, and whether the safety features in the plant are adequate to remove all contaminants which enter.

WEIGERS Cyanamid, New Orleans: We have discussed alternate air intakes at great length at our plant and in order to qualify my remarks, I should tell you a little bit about our local conditions. We are in an essentially rural area. The only industrial complex that presents a source of air contamination is the Fortier plant itself. Consequently we have a fairly good control over the contaminants that are vented; the sources of contaminants are under the same management as is the oxygen plant. We make every possible effort to prevent a steady venting of acetylene or any other hydrocarbon which we consider potentially dangerous to the oxygen plants. Slugs, however, do occur when there is a process failure. This slug contamination factor should materially influence your choice of air intake location and whether you need an alternate intake at all. As to alternate air intakes, we are faced with a somewhat peculiar weather condition in New Orleans. Inversion conditions (invariably accompanied by practically no wind) are very frequent. Then, any gases vented hang close to the ground. We checked the local wind pattern and came to the conclusion that it is practically impossible to predict the direction a contaminant slug will take during an inversion condition once it is vented. For us, to be of any use whatsoever, an alternate air intake would have to be 2,000 ft. long and be sized for a flow of about 85,000 std.cu.ft./min. It becomes understandable, therefore, why we decided that an alternate air intake was not the answer. It would only be used on days when a steady wind is blowing. The cost of such an intake for those days would be, in our opinion, prohibitive.

We rely instead on three other factors: To keep the contaminants out of the air whenever possible; having a plant with as high an acetylene tolerance or digestive capacity as possible; and by operating the plant wisely.

WALTON: Any comments?

BOLLEN, Dow Canada: We have also given some thought to the installation of an alternate intake, and like a good many other air plants we found ourselves in a location that it didn't seem to matter where we put our intake because we would still run into some

WHO TOOK PART

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contamination.

To give you an idea of our problem—we have the Polymer Corp. plant to the extreme north, two refineries to the south (Sun Oil and Canadian Oil), our own ethylene plant directly across the road to the west, while our latex and styrene plants are directly to the east of us. We are completely surrounded. An air survey indicated we couldn't go any place in any direction without running an air intake line several miles away from our plant. We couldn't even take our air intake straight up, because our ethylene plant is a hypersorber unit with a vent stack running up to about 180 ft. Our only recourse was to monitor our gas streams by chemical analysis and try to keep close tabs on the acetylene and the hydrocarbons in the gas stream.

LAWRENCE, USI, Tuscola: A number of you have seen our setup. We have a rather elaborate system—both a wind direction and wind velocity meter, both mounted on the panel board. We have alternate intakes—one to the west and one to the north. Our big source of contamination is across from the south. Actually we can't trust our meter on the board because its sensing elements are located at the air plant, and our intakes are some distance away. Actually, an operator goes

out about every hour and checks the wind and switches the butterfly in the air intake. We have considered putting in a third intake.

WALTON: Air pollution studies have brought out that even with wind instruments showing velocity and direction, gustiness can produce unexpected results. Instruments are useful, but they must be used with intelligence and some personal common sense interpretation.

GORAND Sun Oil: This might sound simple but it is important. Wherever the locations of your air intakes, they should be posted as restricted areas especially where there is congestion in a refinery and where you give entry to outside maintenance contractors. If you turn your back for a minute you're likely to find they have put up compressors, welding machines, and acetylene welders right under your air intake.

WALTON: A good point. Now to pass on to the next topic.

The removal of particulate matter at air intakes

CHUBB, Atlantic Refining Co.: The removal of particulate matter at the air intake presents many problems similar to the location of the air intake. These can be categorized into three items we could discuss.

First—The necessity for removal of such matter concerning the prevention of fouling in the air plant, the trays of the tower, the silica gel or other filter cases. There has also been some discussion in recent months about the possibility of particulate matter being a source of static electricity.

Second—The degree of removal necessary, both in general and also the particular degrees for your location.

Third—The devices for removal. There are many on the market.

At Atlantic we have a rotating wetted-leaf and screen-type filter. The wetting agent is tricresyl phosphate. From discussion of these three general topics we might learn what others are doing about particulate removal.

WALTON: This is a topic which may be a problem to some and not to others. In our case we have right next to the ammonia plant a waste disposal plant for treatment of plant sewage. The sewage filter cake is burned in an incinerator. The ash produced is a very fine, fluffy material of extremely small particle size. We have used with success an air pollution dust level sampler called a High Volume Air Sampler (General Metal Works, Cleveland) which is very good for making studies of the conditions in one's area.

If you have reversing exchangers in your air plant you may believe that dust would not get past these and into your tower. We know that to be untrue. We had one experience where one of the cores of our exchangers ruptured and we had to remove it. We started up the plant afterwards without that particular core, putting caps on the manifold inlet and outlet. The outlet manifold cap when it was removed some months later for reinstallation of the column was found to contain about a gallon of very fine dust which had, to everyone's surprise, apparently entrained on through the reversing exchangers.

OHLSON, Pennsalt Chemicals, Wyandotte, Mich.: I couldn't quite follow why there should be much concern about particulate matter in the air intake. We have problems on fly ash and things of that sort which are a little hard on the first stage of the compressor but apart from that I don't think there would be any concern about safety involved. We have had difficulty further down the line, however.

You spoke about using reversing exchangers. In our air plant we have an alumina air dryer at the entrance to our cold exchangers and we installed a Dollinger filter beyond the dryer to insure that no alumina could pass into the cold equipment. We have had the experience of the bag in the Dollinger filter catching fire, melting the filter internals, and frying the paint on the outside of the vessel and

downstream lines. While some solids undoubtedly entered the cold equipment, there were no other untoward effects from the fire. Needless to say, we tried hard to find out what had happened, but never succeeded. There was some evidence of oil in the air line beyond the dryer, but the oil certainly could not have passed through the dryer because it is a very efficient oil remover itself; further, the dryer was equipped with a prefilter for oil removal. It was concluded that the oil must have dated back to the time of the initial installation; hence we simply put in another bag. I can't think yet what ignited that bag. The operating pressure was about 300 lb./sq. in. or perhaps a little less when it ignited. Incidentally, I have also heard of another bag filter igniting in the outlet line from the air dryer in another plant, but I have no details.

Prior to the incident discussed, we had some trouble with chafing holes in the filter bag, which let some alumina dust get into the cold exchangers. As a double check, we installed a sintered metal filter farther down the line to take the dust out and I assume a lot of others do the same thing. It is also good for protection against plugup by particulate material.

WALTON: Let's pass on to the next topic.

Permissible levels of hydrocarbons and other contaminants

There has been a great deal written on this, with some differing opinions. Frank Himmelberger from Air Products will introduce the subject.

HIMMELBERGER, Air Products, Inc.: We at Air Products are both designers and operators, and are most happy about this particular cooperative effort. In considering how to make oxygen plants safe from explosions, it is first necessary to consider what type of condition in the plant may be prerequisite for such explosions.

By the very nature of the plant, liquid oxygen is always present. When sufficient fuel and oxygen are in contact, ignition will provide a potent energy release.

Igniters of sufficient strength to explode oxygen-fuel mixtures are known to be available; they include static charges, ozone, or certain chemicals. Not all igniters are known nor perhaps, even suspected. Of the three contributors necessary to cause explosions, oxygen is always present; an initiator may appear at any time. Hence any control over air plant explosions must be derived by control of the fuel essential to the reaction.

The most frequently encountered fuels are hydrocarbons, both saturated and unsaturated, C₁ to C₆ and their derivatives, oxygenated and otherwise. Some inorganics are hazardous. Most of the active candidates are gases. The most widely accepted culprit in air plant explosions is acetylene. Undoubtedly it is often responsible for trouble,

however, until recently it was ALWAYS BLAMED. Operators of air separation equipment have practiced acetylene control for more than three decades. To cope with its hazard, precise data were required. Adsorptivity information enabled designers to size silica gel adsorbers and to prescribe regeneration schedules. Knowledge of the solubility of acetylene in liquid oxygen, along with analytical techniques for its detection, allowed operators to establish "safe" limits. As it had been demonstrated that solid acetylene could be exploded in the presence of liquid oxygen, and since the solubility of acetylene in liquid oxygen was generally accepted as being slightly below 5 pts./million, maximum allowable concentrations somewhere between ½ and 2 pts./million were set by many operators. Adherence to the philosophy of acetylene control served air plant operators well . . . for several decades a creditable record of safe performance was achieved.

In the light of analytical findings in the atmosphere of today's petrochemical plants, many other combustible materials must be suspected as trouble-makers. The findings of recent Air Products experimental work on solubilities, densities, vapor pressures and lower explosive limits of fuel materials serve to add to the growing belief that the consideration of acetylene as the only cause of explosions must be rejected as too narrow.

To establish maximum permissible concentrations of any contaminant requires the use of precise data on solubility and lower explosive limits in liquid oxygen. For highly soluble materials the maximum permissible content (MPC) is the lower flammable limit. For the less soluble ones it is, for all practical purposes, the solubility limit.

The significance of solubility becomes apparent when one considers the levels of concentration above the solubility limit can result in localized concentrations of fuels above the lower explosive limit. Thus, if either the explosive limit or the solubility limit is exceeded, a hazardous condition exists. Accordingly, if either of these limits is approached corrective measures are required.

Some of the steps in achieving fuel control include: 1.—Continuation of effective acetylene control which also reduced concentrations of other materials. 2.—Examination of properties of combustibles, such as solubility, densities, vapor pressures, flammable limits, adsorptivity and chemical reactivity—particularly over catalysts. 3.—Collection of information on environments and its application in both design and operation. 4.—Careful study, with the aid of better analytical tools, of the effectiveness of equipment design and operating techniques. 5.—Setting safe limits and applying adequate controls. 6.—Measuring the approach to a hazardous condition

through analytical monitoring.

The variable nature of air pollution must be considered in formulation of operating procedures. Allowance must be made for temporary surges in contaminations greatly exceeding the typical values. Thus, on rare occasions when the pollution levels override the design safety factors, corrective procedures may be required. In such contingencies, continuous monitoring provides the necessary guidance.

Obviously, individual monitoring for each conceivable fuel is not practical, but total hydrocarbon analysis, expressed in terms of methane equivalent, satisfactorily simplifies the problem in many locations. In addition to the fact that most fuels are hydrocarbons, it can be justified as effective on several grounds: 1.—Available fuel energy is roughly proportional to the carbon atom content. 2.—The lower flammable limit of the hydrocarbons, expressed as methane equivalent, is approximately constant and does not drop below 5 mole percent. This is, of course, useful in predicting flammable limits of soluble hydrocarbon mixture. 3.—Very important is the fact that the more soluble hydrocarbons are, in general, displaced from the silica gel adsorbers by the less soluble ones.

Total hydrocarbon analysis is most effective in process areas characterized by a frequently changing composition of a wide variety of impurities. It is least effective where a number of very insoluble materials are present or are potentially available.

Non-hydrocarbons and insolubles, certainly including acetylene, must be treated separately as required in particular plant environments.

As to the subject of other contaminants, I have not included them in this part of the introduction. In the discussion we may bring out how they fit into the philosophy of fuel control.

WALTON: I'd like to confine the first part of the discussion to hydrocarbons and leave other contaminants for the next part of the discussion. There are a great many different ideas about the hydrocarbon content limits that can be tolerated.

BUTIKOFER, Standard Oil, Indiana:

We have established limits in this hydrocarbon analyzer of our own development and later partially replaced it with a long-path infrared. At present we are able to analyze for the various hydrocarbons such as methane, ethane, acetylene, ethylene, and propane, and some nitrogen oxides.

We have established limits in this order: On incoming air we have a maximum of about 0.3 pt./million of acetylene, on total hydrocarbons about 10 pts./million. Oxides of nitrogen are about 0.3 pts./million. In the liquid oxygen streams we allow as much as 300 pts./million of methane and ethane and about 150 pts./million for all other hydrocarbons. The acetylene limit is about 0.5 maximum. Oxides of nitrogen are down around 0.5. Actu-

ally, in operation we have found up to 180 pts./million of total hydrocarbons except methane and ethane in liquid oxygen, which was a shutout condition. We have never been particularly worried about exceeding acetylene limits.

WEIGERS, American Cyanamid: Our plant is a tonnage gas plant. The oxygen is used for the production of acetylene by the partial oxidation of methane. Therefore we find ourselves in close proximity to a large acetylene plant. Actually the distance is something like 1,500 ft. Consequently acetylene has been of prime concern.

I think that the maximum permissible level of acetylene in an oxygen plant is a function of the design. Consider that an essentially stable and undisturbed liquid interface in the main reboiler can produce droplets splashing up from the walls and evaporating totally. Such conditions could conceivably produce solid acetylene deposition with a concentration as low as 0.1 pt./million. If you have agitation, or if your walls are washed, or you raise or lower your liquid levels, you can disperse this accumulation. If you have a gas plant, you can get rid of only a very small amount of your acetylene through volatilization with your gaseous products. To be safe, you must provide a liquid purge directly from your main reboiler. In our plants we have an auxiliary vaporizer, which permits us to concentrate in it the acetylene and other contaminants and then purge a more concentrated liquid. In other words, we use fewer gallons of liquid to get out the same ounces of contaminants.

Preliminary calculations have shown that to be completely safe one should not use an auxiliary vaporizer if the acetylene concentration in the main reboiler exceeds 0.2 pts./million. We reason that: There is no guarantee that all the tubes in an auxiliary vaporizer are running wet. Naturally this is something aimed at, but about which there is no guarantee. So we

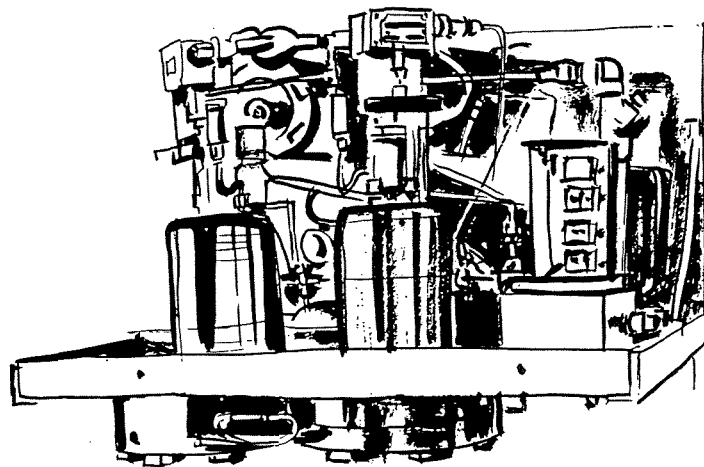
take the worst, possible condition of tubes that have liquid entering at the top and the liquid evaporating totally within the tube. Under these conditions it can be demonstrated that with 0.2 pts./million acetylene in your entering liquid, one does not run into danger of deposition in the tubes. So this becomes the upper permissible limit for utilizing an auxiliary vaporizer to get rid of the acetylene. Actually, the liquid purged from the main reboiler in terms of the intake air stream is about 3%. Once the acetylene concentration in the main reboiler exceeds 0.2 pts./million, we feel it is safer to purge liquid directly from the main reboiler and get it out of the plant to an outside tank where it can evaporate without damage to the plant should there be an explosion.

With the refrigeration limitations that are common in gas plants, this does entail a slight reduction in production capacity. We feel that the risks involved more than justify temporary reduction of this sort.

We've established 0.5 pts./million as the maximum allowable acetylene level in the main reboiler. As to when we reach this maximum, with a gas plant such as ours, the liquid-making capacity can be increased radically by revalving the plant. Unfortunately, once you have revalved it you can no longer make gaseous product. We believe that if one is in excess of that 0.5 pts./million, he is more than justified in stopping all gas production in order to make liquid as rapidly as possible, to dilute the acetylene in the main boiler and purge it out.

We are now just getting interested in the analysis of total hydrocarbons. The proximity of the acetylene plant has dominated our thinking in the past four years.

We are faced with the problem of having no idea as to the background level of hydrocarbon in the main reboiler. So our step-by-step procedure is this: We want to characterize the hydrocarbons that we have and find out the normal background level and



Liquid oxygen vaporizer

above all, to find out how much of the total is methane. Once we have done that we feel we will be in a better position to decide what sort of monitoring instruments we can best use in order to control our hydrocarbons—methane and otherwise—in the main reboilers.

WALTON: A point there which is of great importance is that one's own particular situation has to be carefully considered. In our case we have a cascade refrigeration system. The refrigerants are propane, ethylene and methane. Ethylene has been considered troublesome; also propane. So in thinking of tolerance of quantities of compounds, their likelihood of concentrating due to leakage, safety valves lifting and other things of that sort, are something to be borne in mind.

We have in print the statement by an air plant designer that no pts./million of hydrocarbons should be allowed. We go from there to the statement that 50, another 200, another 250 to 300 and in our own case, before we were much concerned, we had 2,000 in our reboiler.

KERRY, Air Liquide: My remarks will be restricted to my company also being an operator of oxygen plants.

I will cite our own specific cases. I concur with what Himmelberger of Air Products said; let's not blind ourselves only to acetylene. In our own plants in the past 15 years we have had two specific cases where we have had mishaps which occurred just after we had completed an analysis for acetylene of the liquid after the rich-liquid filters. There are other hydrocarbons than acetylene.

Secondly, we are talking of parts per million and frankly, not many of us know or are sure of the precision of these terms. In our own plant after we had made up a gas chromatography analyzer for our own specific use, we asked our operating people about the results they were getting from one of our large plants. They said—". . . our liquid after the rich liquid filters is very clean." We took a sample, analyzed it by chromatography and found no acetylene. But we did find practically everything else right down to C's in very, very small traces or parts per million. With ordinary analysis we would get zero, and I think if there is any difference of opinion as to allowable limits, it occurs because we are as yet not too sure of the accuracy with which we use the instruments available to us for analysis.

KARWAT, The Linde Co. (Germany): Mr. Karwat read a statement at this point which will be the subject of a separate paper to be published in a subsequent issue.

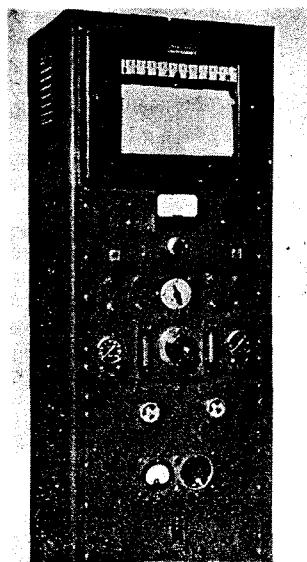
WALTON: Mr. Karwat's information showing the behavior of mixtures

and sensitizing effects of nitrogen oxides and ozone is quite interesting. Those of us who have been in the oil business know of the difficulty in trying to predict the behavior of mixtures of compounds.

Representatives from Monsanto are ready to speak on the subject of hydrocarbons.

ROTZLER, Monsanto: The general location of our large tonnage oxygen plant (judged by even normal oxygen plants of standard size) is Texas City, Texas.

Our plant is located on Galveston Bay, a large body of water just off the Gulf. The oxygen unit is closest part of the plant to the water. This is significant because our prevailing wind is rather consistently from the water. Therefore, we probably have less of a problem than most people in getting a good air supply. The wind is, of course, not always prevailing. The



Hydrocarbon analyzer for monitoring air separation plants

idea of an alternate air intake is not particularly attractive to us in view of the practical difficulties in putting an air intake at a point where we would have reasonable assurance of doing better than you would in the present location.

The oxygen is used in the partial oxidation of methane to make acetylene. It is a process similar to the one described by the representative from Cyanamid.

Our interest in the subject of safety in the oxygen plant was triggered in a big way by what is sometimes called an incident, or a mishap, but which we call a reboiler explosion. One occurred in our plant about a year and a half ago. We are fortunate in that there were no personal casualties. There was no external damage to the oxygen plant but there was a considerable amount of damage to the tubes in the reboiler.

From the standpoint of keeping a plant in operation, which is the only way you make money with it, an explosion is a matter of considerable importance quite aside from the cost of repairing the damage. And of course the possibility of personal injury is of prime importance, even more important than economics.

Without going into the details of this explosion, from what we have been able to determine by consultation with experts, the explosion was caused by the detonation of a solid material which quite distinctly sank and lay along the bottom of the reboiler. We have in our reboiler some horizontal baffles and there was apparently a small accumulation of this same solid material, along the top of these baffles. I mention that point particularly because the characteristics of the explosion—the detonation of a solid material—naturally made acetylene one of the materials most suspected. However, according to the information that most people have, solid acetylene floats in liquid oxygen and here we have a material which sank.

The characteristic of the damage was of a tremendously fast energy release. Metallurgical examination of the reboiler tubes indicated the damage was not caused by temperature. The characteristics of the metal had not been changed. The energy was released as a pressure or shock wave, and the damage was mechanical.

Just in general, I might say that considering the operating conditions at the time—as compared with the total of five years we have operated the plant—this was the least likely time to expect an explosion. Our acetylene plant at this particular moment was down completely; and had been down for about 24 hours, and was purged completely at the time it was shut down. There was very little chance of any acetylene, let alone a sudden surge of it, getting into the reboiler at this time. A number of other conditions indicated this just wasn't the time to suspect an explosion, but we had one. We have since given this a good deal of study. We've concentrated perhaps more on the particular causes of this one than we have on the general investigation of hydrocarbon levels in the reboiler.

We have done investigation along those lines, however. We've used chromatography, infrared spectroscopy and mass spectroscopy. We have not found any method for continuously monitoring either air or reboiler content that satisfies us. We simply don't get consistent results with any of the methods and apparatus which we've tried. While we are concerned with establishing a method of continuous monitoring with setting limits, we think it equally important not to call "wolf" to the people who operate the plant, any more than necessary. We are continuing work on the problem.

Our general hydrocarbon level is, I think, comparatively low, well within the accuracy of our investigation—under 500 pts./million for all hydrocarbons. Our acetylene content is constantly in the range of parts per billion and we set a maximum limit of 0.2 pts./million which is an order of magnitude above what we usually run.

As a result of this explosion we have sharpened our operating techniques.

We have paid more attention, for example, to the regeneration of our silica gel adsorbers, to the sampling of the reboiler for hydrocarbons in general and for acetylene in particular. We have added a secondary air filter. We have installed, downstream of a wetted rotating blade air filter, a filter with a solid medium intended to take out even finer particles. Our plant was not originally equipped with either an auxiliary reboiler or a vaporizer, and we have installed an auxiliary reboiler.

We are interested in investigating two things as to the cause of our explosion. One is this—around a partial oxidation plant for making acetylene, I think it is no secret that there is a good bit of soot. There is certainly some soot in the general atmosphere. A very slight concentration of soot in the large volumes of air drawn into the plant will in a year accumulate several pounds of soot in the reboiler. This would sink in liquid oxygen and is regarded as a possible cause of our explosion. The commercial explosive LOX, which is active carbon on which liquid oxygen is poured, is well known. We're not completely satisfied that soot had anything to do with our problem. We did take the precaution of adding the secondary air filter, however.

The other possibility which is even more speculative, is the chance of solid CO, in the reboiler playing a role in accumulating acetylene by anchoring it. The other role which would probably be required is that the CO₂ insulates the solid acetylene either against re-solution in the liquid oxygen or against showing up in the analysis of the reboiler liquid. I can't say that CO₂ is playing this role, but we're looking at it with suspicion.

WALTON: Now we'll welcome theories, hunches, and opinions.

KARWAT, Linde (Germany): I would like to tell of the work we have done in suspending finely divided activated carbon in LOX and igniting it with a primer of copper. The mixture proved not to explode. Explosion will occur under the condition that the solid carbon is not finely distributed within the liquid, but is agglomerated or thickened. It is difficult to understand how this could occur in a reboiler as there is an enormous ebullition. For this reason, I believe there is no possibility for such carbon deposits to occur.

HOLSTEIN, Atlantic Refining: I

think it is highly possible that the carbon deposits could have absorbed some hydrocarbon in the reboiler and then by having something trigger them off could have caused the explosion at the bottom of your reboiler. This would depend upon the kind of fuel present and absorbed in the carbon.

KERRY, Air Liquide: During the war I was personally involved with acetylene generating plants and pipe lines in an acetylene cylinder plant. We had quite a few acetylene explosions in cylinders, pipelines, and even in generators. Our standard policy was to cut the metal into strips and give it a complete metallographic and physical analysis. In almost every case we rarely found metal fatigue or defects. The metal was just as good as it was before the characteristic acetylene detonation, which is so sudden and so violent it doesn't affect the physical properties, such as the tensile yields and impacts, of the steel. This type of detonation in a pipeline is such that the entire pipe bursts instantaneously rather than progressively, from one end to the other. In all probability acetylene is Monsanto's particular culprit.

WEIGERS, American Cyanamid: I have a question, if one has an acetylene-CO₂ mixture (both in solid state), what is the resulting density of the mixture? Does it still float or does the solid CO₂ carry solid acetylene down to the bottom of the reboiler?

KARWAT, Linde (Germany): The density of solid acetylene is 0.8. Therefore it must float. But having suspended it in LOX and having been able to see it through a sheet of heavy glass, it has been found that its location in the LOX depends on the adherence of gas to the surface of the solid crystal and controls the behavior of the solid, which can remain on top, bottom, or center.

KNOX, St. Paul Ammonia: It has been interesting to consider the possible combinations of contaminants. The point that comes to my mind is, do the normal deriming procedures that operators use to clear up their plants still apply, or is there some other protective operation that we should take such as solvent wash or something like that? Are these substances gummy, do they stay in there, or does deriming get rid of them, or what? This has just given me something else to worry about so far as I can see.

ROTZLER, Monsanto: The general policies in regard to deriming are particularly important. Again, going back to our particular incident, I think that the theories we have, except for the idea of carbon, would be prevented by a complete deriming—a complete warming up at periodic intervals. We have set a policy which stands so far—but like all policies can be changed by economics—of deriming

our plant once a year. Maybe that isn't often enough but we are planning to do it whether it is needed or not.

WALTON: On the matter of acetylene as a contaminant it is interesting to consider the maximum allowable contents which various people say they permit before they drop the plant to see how much variation there is. For instance, Weirton Steel has the lowest I've ever seen—0.12 pts./million; at that point they drop liquid out of the plant. This goes up to 2.0 pts./million for some other well known air plant operators. In our own case we drop liquid out when we go beyond 0.4 pts./million.

On oxides of nitrogen there has been nothing really published or stated by anybody about what limits they feel can be tolerated in the reboiler. Some people, whose knowledge we respect, feel that possibly the maximum tolerance should be the same as for acetylene. Our average obtained until now has been 0.01 pts./million with very little variation. Any comment?

BUTIKOFER, Standard Oil: Our maximum tolerance of oxides of nitrogen in our liquid oxygen streams is .05 pts./million. The most we have found so far is about .01.

KARWAT: If we have in the auxiliary condenser 0.1 pts./million acetylene, then the oxygen from the vaporization of this liquid will contain 0.1 pts./million of acetylene. The last drop of liquid in the auxiliary condenser will be in equilibrium with 0.1 pts./million in the gas phase. This concentration of liquid is then nearly 3 pts./million of acetylene and that is half of the solubility of acetylene at this temperature and pressure. Therefore we are, for theoretical reasons, free from danger in the auxiliary condenser. That is why we say 0.1 pts./million of acetylene as a safe limit in the main condenser.

HOLSTEIN Atlantic Refining: I'd like to comment on Dr. Karwat's statement which upholds our operation at a reboiler liquid concentration .01 pts./million of acetylene. Our air fractionation plant is used only to produce nitrogen and we take a ½% blowdown from the reboiler continually. So the data seem to fall together.

WALTON: Anybody else had any experience with concentrations?

HIMMELBERGER: I'd like to add another concept in the philosophy of establishing limits. If you know that a contaminant is dangerous at a certain level, and if you know that you can operate 95%, or more than 95% of the time at some level far below that dangerous level, maybe only 1% of it, then I think it a very good philosophy and a good practice to set 1% as your maximum operating limit but not your max-max limit. In other words, when you exceed such limit as the 1% in the example, that is the time to get curious about the plant environment

and the operation of the plant, even the performance of the operators themselves, and determine what is causing the change in the level of contamination. You need not shut down your plant at this level—merely get curious and try to take corrective action before drastic action is required.

WALTON: Another contaminant which has been discussed to some degree is ozone. Nobody has set any particular limits on ozone, but one of Kerry's articles stated that 0.1 pts./million on the inlet air should be the maximum. Has anybody set limits on the ozone content in their reboilers?

ANONYMOUS: The analysis of ozone is at very low levels and I don't think we know at what level of ozone we should worry. We may have to analyze ozone in the fractional part per million range and I think that daily analyses in the air plant would become a difficult problem. The setting of limits is going to be dependent on our ability to analyze at these levels.

KARWAT: No ozone has been found in industrial oxygen plants but only in krypton plants where concentrations reach far higher limits.

WALTON: A number of us are concerned about ozone because we have compressors in our plants driven by motors of several thousand horsepower. We know that some ozone is produced in those electric motors and it seems a point on which nobody has taken a definite stand. The gentleman from Dow points out that in severe electrical storms you get a quantity of ozone.

KERRY: I would refer to some excellent work done by the Armour Institute. This work on ozone is published in two volumes. It gives a very comprehensive bibliography, complete analytical procedure and a good deal on occurrence of ozone. It shows that many industrial cities do have air containing small traces of ozone. So we can say that ozone is caused not only by motor discharges or electrical storms, but has also been found to be part of the normal air. We, therefore, have to be on the watch for it.

WALTON: As I recall, the Armour Institute traveled around the country with a mobile lab and determined ozone levels in the various cities as part of its air pollution studies.

Analysis by instrumentation:

COCHRANE, Sun Oil: For many years air plant operators have had to rely entirely on chemical tests to determine what contaminants were to be found in various air plant streams. With recent advances in instrumentation it is now possible to monitor some contaminants on a continuous basis. Continuous monitoring is an invaluable tool for safe operation of

an air plant. Unusual concentrations of contaminants can be detected and corrective action taken before they reach a dangerous level. These devices are helpful in making contaminant balances, studying contaminant distribution in a plant, locating air intakes, and studying adsorber efficiencies.

As to what contaminants should be monitored, each plant has its own particular problem. Air plants near an acetylene generator would probably want to monitor acetylene; whereas, plants in an oil refinery would probably want to monitor total hydrocarbons. There is a difference of opinion as to whether it is more important to monitor possible fuels or possible detonators. It is possible to monitor such things as hydrocarbons, acetylene, and nitrogen oxides. Hydrocarbons have been successfully monitored using infrared analyzers. They can be sensitized to a particular hydrocarbon or to a mixture of hydrocarbons; when this is done the reading is only approximately proportional to the weight of hydrocarbons present. Composition of the hydrocarbon mixture affects the reading to some extent. A more exact total hydrocarbons method is to catalytically oxidize the hydrocarbons to CO₂ and then monitor the CO₂. This has the advantage of being exactly proportional to the pounds of hydrocarbon present. It is also a more sensitive method, as CO₂ is a stronger infrared absorber than hydrocarbons and also since each mole of hydrocarbon heavier than methane produces two or more moles of CO₂. If a stream being monitored already contains a small quantity of CO₂, then only the increase in CO₂ upon burning must be measured. This can be done by passing the sample, before combustion, through the reference cell of an infrared analyzer, and after combustion, through the sample cell. The increase in CO₂ content is a measure of the hydrocarbons in the stream. Using a 30- or 48-in. cell it is possible to detect quantities of about a 0.5 pt./million at atmospheric pressure. If the average carbon number of the hydrocarbons is about 3, this is equivalent to less than 0.2 pt./million on a mole basis. Even greater sensitivities can be achieved at higher pressures.

Several makes of commercial analyzers are available. In general, they have good stability, rapid response, and require a minimum of maintenance. Hydrocarbon analyzers have the disadvantage of requiring supplementary testing to determine which individual hydrocarbons are present, inasmuch as hydrocarbon solubilities vary widely. This problem may be at least partially overcome by adjusting the temperature at which the oxidation occurs. In this manner methane can be separated from C₂ and heavier hydrocarbons.

For the future, gas chromatography offers great potential in measuring in-

dividual hydrocarbons on a continuous basis.

Another useful analyzer is the acetylene infrared analyzer. Getting necessary sensitivity is, however, difficult since acetylene is not as good an infrared absorber as is CO, and since the required range of operation of the analyzer is lower. Instruments are available which have full-scale ranges of either 0 to 1 pt./million or 0 to 2 pts./million full-scale. These analyzers operate at pressures up to 1,000 lb./sq. in.

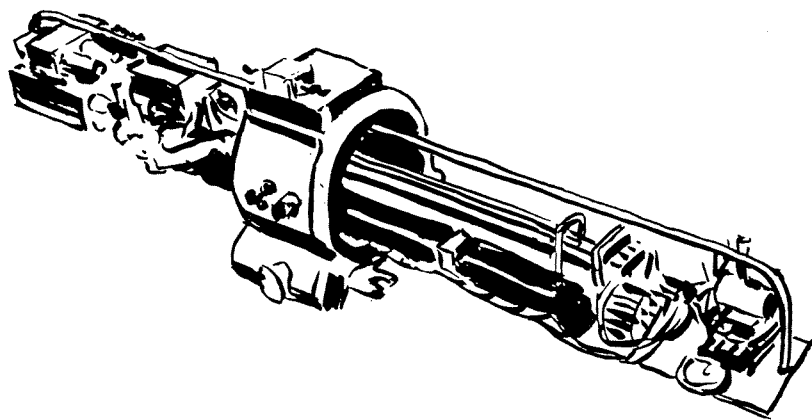
Several instruments are available which can monitor nitrogen oxides. These analyzers are mostly used in smog control work, and as far as I know, have never been used in air plant operation. One problem common to all continuous analyzers is that of getting the sample into the analyzer. Sample tap location is extremely important especially in the reboiler or vaporizer where large concentration gradients exist. Sometimes, if the vessel is very large, it is necessary to alternately use two or more sample locations. All liquid sample lines should be as short as possible, and samples should be vaporized immediately upon leaving the cold box to keep the lag time to a minimum. In vaporizing a liquid sample, care must be taken not to concentrate the contaminants or to deposit them in the vaporizer. We have successfully used a coil of tubing immersed in a boiling water bath; others have successfully used small electrically-heated vaporizers. It is possible to vaporize the liquid sample on a batch basis, vaporizing the sample at the same time the pressure is raised. The pressure may also be raised by using a small diaphragm pump. Stream pressure increase is often desirable where high sensitivity is required. The entire sampling system can be made automatic by using solenoid valves, including 0 check and span check. Often one analyzer can scan more than one air plant stream.

Part 3

Air plant safety

N. H. WALTON: Mr. Chubb will discuss the use of chromatography.

CHUBB, Atlantic Refining: There are no commercial instruments that I know of for the continuous gas chromatography analysis of any of these liquid air streams. There is one method that we are using at Atlantic, which gives us the accuracy required—the fractional pts./million of from one to 15 different hydrocarbon contaminants in liquid air. We have had repeated results in picking up acetylene in the range of 0.05 to 0.5 pts./million in various samples. This method has been developed by Shell Development in conjunction with its Los Angeles



Acetylene analyzer

air pollution studies. This is not a commercially available instrument, but is made up of commercially available parts put together in a special method and coupled with special columns, and operating techniques. We obtained the information from them and from the Franklin Institute. We have this method on a test basis, and are satisfied with the results obtained. We intend to apply this to our air plant operation as follows: We hope in the near future to have a continuous MSA infrared acetylene analyzer installed in the air plant. With this continuous indication of the acetylene content of the reboiler liquid, masked somewhat by some cross sensitivities of other hydrocarbons, we should have a level in pts./million that we normally run in the reboiler. Once that safe level is established we would run the plant with the aid of this instrument. When this level increases for some reason, we would withdraw a liquid sample from the reboiler, run it through the gas chromatographic equipment and within one hour we would have the answer as to what caused the increase in hydrocarbon content—acetylene or possibly methane about which we wouldn't be too concerned.

We can certainly make available to any of you who are interested in this information, what we have, or at least put you in contact with others.

WALTON: Mr. Waters will now talk about their acetylene analyzer and total hydrocarbon analyzer.

WATERS, James L. Waters, Inc. We got into this field primarily from the aspect of using an infrared analyzer to continuously measure contaminants in both the oxygen pool and in the inlet stream. In trying to analyze acetylene in the concentrations in which you people have an interest—a range of as low as 0 to 2 parts/million, capable of accuracy of better than 1/10 part/million—becomes difficult for the more conventional infrared analyzers mainly because there are not enough absorbing molecules in the

sample cell. We have overcome this difficulty primarily by measuring the sample at a higher pressure, packing more molecules into the cell.

We have developed a system operating on the principle of taking a liquid sample, containing it within a vessel and evaporating it at a high pressure. In this way we can operate these systems at pressures up to 1,000 lb./sq. in. and from that we can actually operate our analyzer at 800 lb./sq. in. after a pressure regulator.

Incorporated is a method of obtaining a sample at high pressure which is a representative sample of the liquid pool. By operating at such high pressure we are able to increase the sensitivity of the infrared analyzer and supply acetylene analyzers capable of analyzing to .02 to .01 parts/million of acetylene.

In addition, we can also use the gas from our sampling unit to feed first an acetylene analyzer and then a hydrocarbon analyzer. In a hydrocarbon analyzer we sensitize so that essentially total carbon-hydrogen bonds are measured. This works very well for the saturated hydrocarbons—ethane and above in weight, and for the unsaturates—propylene and above. We have some sensitivity to methane and a rather reduced sensitivity to ethylene and fairly low sensitivity to acetylene. If we have 100 units of sensitivity to normal butane, we could provide an analyzer with 85 units of sensitivity to propane, 50 units of sensitivity to ethane, 30 units of sensitivity to propylene, 25 units of sensitivity to methane, but only 5 units of sensitivity to ethylene. This would be a single analyzer sensitive to a wide range of hydrocarbons.

It is not necessary to be as sensitive to these other hydrocarbons as to acetylene. Hydrocarbons are stronger absorbers than acetylene and, in general, it is not necessary to use the higher pressure. Adequate sensitivity is available without high pressures.

Another way of analyzing hydrocarbons is to burn the hydrocarbons to

carbon dioxide catalytically and then measure the carbon dioxide. This has been introduced as one extra step but it has some very decided advantages because it measures total carbon atoms.

WALTON: Any questions?

MASON, Dow (Midland): I wonder if you have attempted to use multipath cells, rather than high pressure, to increase your sensitivity?

WATERS: We've considered this but in a nondispersion instrument, the multipath cells do not work out very well. You lose more beam strength than you actually gain in terms of increased sensitivity and I think the answer to your question is no. It doesn't look as promising as a dispersive type of instrument that takes a focused beam.

WALTON: Air Products was probably the first to develop to total hydrocarbon analyzer. As I recall, they did so in the interest of safe operation and were not interested in marketing the instrument, and I wonder if they would like to say anything at this time.

HIMMELBERGER: I don't believe I have any further comments. Both Weigers and Waters pointed out the use of total hydrocarbon analyzers and in discussion on fuel control, this morning, I tried to cover the usefulness in certain locations. So, I have nothing further to say at this time.

WALTON: Mr. Mason has mentioned that Dow makes use of model 210 Consolidated Mass Spectrometer on a monitoring basis and they are happy with it. Does anyone else have any other instruments?

ANONYMOUS: We use the 3.3 micron wave length. Actually, the 14 micron wave length is a little stronger right in the middle or at least it is on the spectrographs that you observe. But because we are using a non dispersive instrument, the amount of energy in that very strong tip at 14 microns is so much less and it isn't really much stronger and the highly resolved band at 3.0 microns is better.

WALTON: Mr. Waters, are there any acetylene analyzers in use right now, commercially?

WATERS: I think there are. Let me add that we have delivered them but I don't know whether they have been installed. Standard Oil and Cyanamid, I think, have one each. Dow Chemical also has one, I think.

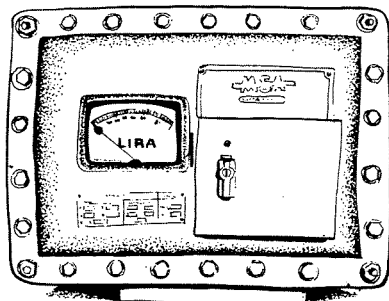
WALTON: Anybody from these firms want to comment on his experience with these units?

BUTIKOFER: We have essentially continuous instrument units on our air plant. At the front end of the plant we have an infrared CO₂ analyzer to watch the air entering the box. We have a total hydrocarbon analyzer of our own development which continuously monitors and reports into the

control room the total hydrocarbon C_1 plus entering with the air stream. In the laboratory we have a total hydrocarbon analyzer for use with liquid samples from the plant. We also have in the lab a laboratory-type dispersive infrared with a 10-meter multiple reflection cell which we use both on contaminants in the inlet air and on liquid samples.

We do have an acetylene analyzer installed in the plant but so far we have not been able to make it work.

COCHRANE, Sun Oil: We have several total hydrocarbon analyzers. One is on the feed air entering the plant and the other is on the liquid oxygen stream from the reboiler. We are satisfied with them. We burn all the hydrocarbons to CO_2 over a catalyst and then monitor the CO_2 . The analyzers show rapid response to changes in hydrocarbon concentrations. We supplement this by a daily test of complete hydrocarbon breakdown by mass spectrometry using a freeze-out method of concentrating the hydrocarbons. The analyzers have a long-path 35 in. cell and, as they operate at atmospheric pressure, we have no problem with raising the pressure. We vaporize the sample, as I mentioned,



Total hydrocarbons analyzer

in a coil of tubing immersed in a boiling water bath and so far we have had no trouble.

WALTON: I now call on P. T. Martin of Spencer Chemical to introduce the subject which is particularly interesting to operators of air plants where reciprocating compressors are used for compression.

LUBRICATION

MARTIN, Spencer Chemical Co.:

In any discussion of air plant safety, lubrication must necessarily be included. Most of the lubricants in general use today are hydrocarbons and this class of materials is a potential source of fuel for fires or explosions when in contact with oxygen. Oil entering an air plant with the air, tends to accumulate in the oxygen circuit where it not only causes operating difficulties which I just mentioned but presents the greatest safety hazard by

virtue of being in contact with the highest concentration of oxygen present. It also presents certain operating difficulties such as fouling of exchanger surfaces with constant loss of heat transfer performance and plugging of passages resulting in a loss of capacity.

At Spencer's Vicksburg, Miss., works we operate an air plant with a rated capacity of 185 tons/day of oxygen. The two major sources of oil contamination in this plant are lubrication of the reciprocating compressor rods and cylinders in the final air compression stages and lubrication of the centrifugal expanders. The possibility always exists of introducing oil by improper lubrication of valves in the oxygen lines, but this is a minor source compared to the other two. In our plant oxygen is pumped as a liquid in a centrifugal pump, followed by vaporization. Pump bearings are lubricated by the pumped fluid and the motor bearings are sealed with a lifetime lubricant. Thus these pumps offer no possibility of oil contamination. If they contain oil from another source and lose suction, the heat generated in a dry bearing could be sufficient to ignite this oil. We think something similar to this happened to us and destroyed one of our pumps about a year and a half ago.

With regard to lubrication of reciprocating compressors in air service, a hazard exists which is not limited to air plant operation but can occur wherever compression ratios result in fairly high discharge temperatures and pressures. This hazard is that of spontaneous ignition of the oil present in the discharge lines resulting in fires or explosions. We experienced these several times in the initial 2½ years of operation.

Reduction of these reciprocating compressor lubrication hazards has been accomplished by a variety of practices. The first is to avoid excessive lubrication, and experience is the best teacher in this matter. Second, the use of oil-removal equipment downstream of the compressors is, I think, a common practice. In addition to line separators, activated alumina and carbon are used to my knowledge. The third is to observe maximum temperatures at the discharge of the compressors and take the necessary corrective action. For instance—broken valves should be promptly replaced, loading and unloading procedures can be written which will minimize high compression ratios when starting and stopping machines. The fourth is the use of synthetic lubricants. About a year and a half ago we switched over to Monsanto's Pydraul 600 for use in the air cylinders in our reciprocating compressors and have experienced no fires or explosions since that time. We have used Pydraul AC for the past 3-4 months, and its lubricating properties have been very satisfactory. There are other good synthetics but

we have had no experience with them.

Finally, the presence of oil in compressed air can be recognized by the use of a Bureau of Mines (#8485) type dewpoint indicator which deposits fog upon a mirror. By making routine checks of this nature, a hazardous situation can be corrected before it becomes a major problem.

Several steps have been taken by the manufacturer and ourselves to reduce the hazard of oil from the expander system. The only possibility of contamination from this source in our plant is from oil used to lubricate the forward bearing that might find its way along the shaft and be discharged into the air stream in the expander housing. The labyrinth seal and insulating block around this shaft was drilled to receive an air purge at a slightly higher pressure than that in the expander housing. This purge flows along the shaft effectively blocking any tendency of oil to flow in the reverse direction. Should the oil drain line become plugged, resulting in an accumulation of oil in the chambers surrounding the shaft and bearing, the level will rise in a volume chamber connected to the bearing chamber in parallel and equipped with a high level alarm. What I am saying in effect is that we have a surge pot with a level alarm that will accumulate oil at the same rate as the bearing chamber accumulates it. This volume chamber (or pot) has about five minutes capacity of oil allowing the operator sufficient time to take corrective action. Should no action be taken the oil will eventually discharge from a vent normally relieving the labyrinth purge. We do not believe oil can now enter the plant from this source. However, operators continue to keep a close inventory on the expander oil reservoir and to make periodic checks at telltales in the air line downstream from the expander as secondary precautions.

Use of synthetic lubricants has been considered for expander service, but we prefer to undertake to keep all lubrication from this source out of the plant rather than merely introduce a material with a higher flash point.

Several points may be worth mentioning regarding proper lubrication of valves in oxygen service. I think this was mentioned earlier. We completely disassemble and degrease all oxygen service valves at our plant-site before installation—in addition to specifying, when they are purchased, that they are for oxygen service. This includes replacing the packing with a new packing which has been previously soaked in a solvent to remove chance traces of oil. Packing and lubricants should contain no straight hydrocarbon greases or oils. Several alternates are available including silicones and halogenated hydrocarbons. Improper use of a hydrocarbon grease can be made quite difficult by provid-

ing special lubrication fittings and guns for oxygen service only. Valves or fittings can also be color coded—painted, as a warning measure.

It is well known that lubrication of oxygen compressors presents certain hazards, but we have no experience along these lines and I don't intend to discuss that subject.

In spite of all efforts to prevent it, oil may get into the air plant. When this occurs, how is the fact to be recognized and corrected before a fire or explosion occurs? Telltales, which are simply continuous purges into clean alumina or some other material which will show the presence of small amounts of oil, may be installed at strategic points in the air and oxygen circuits. Larger amounts of oil can be detected by a rapid loss of reservoir inventory (with no obvious spill), loss of exchanger efficiency, and restriction of the oxygen circuit. To remove the oil, part or all of the plant is warmed and a suitable solvent used to flush the affected parts. We've used trichloroethylene because it is readily available and is less toxic than carbon tetrachloride. Even so, its use requires great care to see that the toxic vapors are not inhaled and that skin contact is avoided. Care must also be taken that the solvent does not freeze inside the equipment and present the operator with a new set of difficulties. We follow the flushing and draining with a hot air stream until solvent vapors can no longer be detected. Proper planning and execution of these operations will minimize the operating hazards.

WALTON: Anyone care to comment on lubricating practices?

ANONYMOUS: With the Bureau of Mines dewpoint analyzer is quantitative data obtained or is qualitative detection? What about breakdown fractions of oil—can you pick those up at different dewpoints with any degree of accuracy? We've actually tried that and I was just curious to learn whether Mr. Martin has any information on this?

MARTIN: This dewpoint tester involves only an oil film on the mirror, and it isn't quantitative. Answering your second question—we haven't reached any conclusions about breakdown fractions.

WALTON: Mr. Maune, who had to leave, told me that in his air plant he compresses air to 600 lb. in three stages. They've been using Pydraul. About two weeks ago a discharge valve in the third stage broke and before they could get the compressor shut down the temperature had gone up to 700°. A fire developed at that point and proceeded on to the after-cooler. It points up the fact that although synthetic lubricants are more desirable, they do contain carbon atoms and are combustible to some extent.

NORRIS, New England Gas Products:

We have been using Cellolube 220, a tricresylphosphate, since 1953. We've had no trouble with it. We do find a little more cylinder ring wear, but not enough to compensate for returning to oil. We have had a number of flashes with oil. We first used a regular good grade of oil which developed considerable carbon on the valves. We then switched to a high detergent oil which carried through our filters into our columns, which resulted in an explosion in the after boiler. We have had wonderful success with Cellolube 220.

SANDERS, The Texas Co.: Mr. Martin, is the problem one of breakdown products of the lubricant or is it the oil itself that is being carried through and in that case is the synthetic lubricant any different? Before he answers, I want to mention something that has been done in our air compressors in Hydroformer operation for a number of years which is a way to prevent final discharge stage fires. It is simply the injection of water into that point. We are installing this system on our installation at Lockport.

MARTIN: My opinion is that it is the oil itself but that is a personal opinion and isn't necessarily justified or verified by any work we've done.

ANONYMOUS: We have essentially the same setup as Mr. Martin. We have checked the air downstream of the alumina dryer through a Dollinger filter and have found that a minor quantity of synthetic lubricant gets through there to the air plant. It will not register at -90 dewpoint. We have not found that it has given us any trouble in the quantities present. Our experience with Pydraul is that it cleans up the lines in the inner coolers, etc.

ROTZLER, Monsanto: A tool that we have found useful in construction of a new plant to learn whether piping had been degreased to the extent we think it should be, is an ultraviolet light which fluoresces any hydrocarbon. The particular disadvantage is that it is so extremely sensitive that other things will also fluoresce to some extent, and it may take a little longer to get the plant built.

CHUBB, Atlantic Refining: We have a similar oil problem with compressors in the synthesis loop of the ammonia plant. We are going to try within the next week, a method that may be of assistance to others in tracing down their oil troubles. We will introduce into one of the compressors a radioactive oil and with Geiger counters we will try to follow that oil throughout the plant and find out just how far it goes, how much of it gets past our activated alumina filters, etc. Maybe next year we will be able to report on how we made out.

WALTON: We are quite interested in seeing how this tool works.

ANONYMOUS: Our problem is somewhat different from those which have

been expressed here in that ours are not tonnage plants, but small, principally liquid oxygen plants for shipboard use. For that purpose in our air compressors we use small, usually 4-stage, compressors which give us a rather serious lubrication problem. We have done some preliminary laboratory testing of the fluor lubricants and although these are expensive and might be inappropriate for larger plants, it appears that they might be justifiable for our smaller plants. We must have much better cooling in the successive stages if we are going to use them as they do not have a good viscosity index.

KARWAT, The Linde Co.: Permissible concentrations of oil in the air entering separators should not be higher than 0.1 pt./million. Normal methods of eliminating the oil from the air coming from the compressor are inadequate. But I have heard of one means which is in use but have not confirmed it. This is to introduce after compression hot (70° to 100°C) air which is saturated with water vapor, and then cool it down. This produces a mist which entrains all drops of oil.

In vaporizing liquid oxygen which contains oil, the oil is entrained and deposits in the tubing in very thin films which are so sensitive that an explosion is to be expected, based on experience with films in tubes or steel flasks or similar apparatus.

WALTON: Has anyone tried a synthetic lubricant in an expander?

ANONYMOUS: We've used tricresylphosphate in reciprocating expanders from 2,500 to 70 lb. discharge, for about three years. Actually I'm not so sure that this is any better than a low flash point oil, the reason being that the tricresylphosphate in the oxygen system itself is not in my opinion as safe as some may think.

HOLSTEIN, Atlantic Refining: The lubricating systems for expanders are not completely foolproof and present an even greater hazard since oil leakage at this point is deeper in the plant system. Our own experience has been with a plant served by a centrifugal compressor and expander. These have shown nil oil entrainment in four years of operation. We, however, are seriously concerned with this problem and have plans for solvent deoiling should it become necessary. The solvents used are carbon tetrachloride, perchloroethylene, or hexane. We have had experience with deoiling our cascade refrigeration system and there we chose to use hexane due to the proximity of our ammonia system and our fear of halogen poisoning of our synthesis catalyst.

WALTON: Has anybody used any in a centrifugal expander—30,000 rev./min. or 20,000 rev./min.? Many of us have talked about it but none of us has tried it, so far as I know. Mr. Martin mentioned safety devices that prevent oil from entering the air in expander

streams, but safety devices don't always work.

The next topic is **SILICA GEL ABSORBERS AND PREFILTERS**. Mr. Frank Kerry of Air Liquide will introduce this subject.

KERRY, Air Liquide: This subject is so very well known that I will be brief in introducing it. I will report on experience based on the operation of our own plant, plus some of the plants we have recently designed.

We have found that in plants that stop and start often, in other words, producing oxygen on a batch basis, alumina was a little better than silica gel because silica gel would absorb water and a certain amount of attrition would ensue. For plants operating for long periods of time silica gel had an obviously higher adsorption rate for acetylene. Silica gel proper has a higher absorption capacity for acetylene than pellet form silica gel or Sovabead. However, we have preferred Sovabead because it has better resistance to mechanical attrition.

Concerning filters regeneration, our policy has been to oversize these silica gel filters, so they would be switched long before the entire filter was contaminated. The deriming period of such filters is determined after the plant is started and it is possible to find out what the actual plant capacity is, and what the entrainment of hydrocarbons is. Finally, one determines the most suitable combination of temperature and time to dispose of not only acetylene but also traces of other hydrocarbons and small amounts of oil vapor. A minimum of 180° F. is necessary. Acetylene desorbs quickly. In some cases we raise to as high as 350° F. to make sure.

It is almost hopeless to design the silica gel (rich liquid) filters to take care of any sudden slugs of contamination. We have installed in two plants prefilters or silica gel filters in the vapor phase. One of these plants has been in operation now for several months and in two instances of slug contamination, these prefilters were able to handle the extra load.

If both the prefilters and the rich liquid filters fail to stop the contaminants from entering the main vaporizer or auxiliary vaporizer, what do we do? Obviously, one can shut down the plant. This gives a choice of dumping the liquid from either auxiliary vaporizer or the main vaporizer, and if so when does one safely dump it? Our rule is to fix certain safety limits for contaminants contained in the main vaporizer and in the auxiliary vaporizer. We divide these into "operating limit," "dangerous limit" (which, although it is perfectly acceptable to run the plant, means the operators are required to find out what is wrong), and "unacceptable limit"—as soon as

the contamination reaches this limit—the liquid has to be dumped.

WALTON: Mr. Kerry has added to this introduction the **SHUTDOWN PROCEDURES** topic and I think it might well be discussed with absorbers and prefilters.

WEIGERS, Cyanamid (New Orleans): We use hot nitrogen for deriming, aiming for an outlet temperature of 180° F. to make sure we remove such strongly adsorbed materials as ammonia and HCN present and we know that when we reach 180° F., these materials have been removed. We haven't had sufficient experience to be able to say how often we are going to have to change whole silica gel charge, but as a start, we plan initially to change every two years. Whether we'll have to change it in a shorter period of time, we don't know.

BUTIKOFER, Standard (Indiana): We have in effect three sets of limits for the various contaminants: 1. The normal operating range. 2. A "caution" set (which means extensive purging). 3. The limit which means "shutdown" of the plant. In the third circumstance we would cut the air out of the box and again carefully check our contaminants. If we find them high, we would blow down. We have a brass line through which we can blow the liquid oxygen out into a tank, from our box where we can let it evaporate. In the course of checking our plant, we do shut it down, for as long as a two-hour limit. If the downtime exceeds two hours, then we automatically blow it down. The reason for that is we feel the primary exchangers will warm up enough so that when we reintroduce the air into the plant on start-up, we can probably displace CO₂ off the primary exchangers, which in turn would be caught by our vapor phase filters and displace hydrocarbons on them directly into the liquid oxygen.

I would like to hear some discussion about a proper length of time to hold the plant with its liquids in a static state but not in operation, before you blow it down.

WALTON: There have been a number of statements made and articles written saying that when you shut the plant down you should not hold the liquid for more than a short time. But no one has defined what a short time is. Anyone care to comment?

HIMMELBERGER, Air Products: Again, the use of good analytical tools is the best way to determine how long you can hold liquids. If you can analyze frequently enough, you can check the pattern of the increase in contaminants in any liquid reservoir and judge your dumping procedures accordingly.

HOLSTEIN, Atlantic: I know your problem and we have been faced with it many times. I think we are of a highly nervous nature so our choice is usually to dump the liquid.

Usually these things come on rap-

idly. You don't know how long repairs are going to take and you go along for 15 to 20 min., possibly more, and then decide "let's get rid of it." The primary reason is that analytical procedures require more time than we wish to risk.

WALTON: There you have quite a divergence of opinion—from 15 min. to 2 hr.

WEILAND, Ketona Chemical: I'd like to comment on one part of Mr. Butikofer's remarks. I would warn against purging your oxygen into a tank. We did that—both our normal purge and any dumping that we did went into a tank that was partially buried. We did not get enough heat exchange out of the tank so we did not boil off all the liquids completely. Over a period of time we apparently accumulated in that very small tank some hydrocarbons or other explosive materials. The whole thing blew. Fortunately no harm was done but we now purge our oxygen on to the ground or to an aluminum plate above the ground.

BUTIKOFER, Standard (Indiana): The tank I described has no bottom. It rests on gravel. I shouldn't have called it a tank.

WALTON: It might be of interest to note here that we just installed a blowdown system which consists of an aluminum heat exchanger with bayonet-type tubes so that we get complete vaporization of the liquid which is dropped out.

LAWRENCE, USI, Tuscola: We have been down as long as 36 hr. and started up by just getting the level down in the main vaporizer long enough to see the level. We don't dump the bottom traps and as long as we didn't have any hydrocarbon to start with we run a quick test for acetylene before and as soon as we start up. We have never seriously worried about the time limit.

KARWAT: There is a question of simultaneous presence of CO₂, acetylene, and perhaps other hydrocarbons on the surface of silica gel. We have made the following experiment. We have had a stream of nitrogen containing some CO₂ and have loaded a layer of silica gel with carbon dioxide up to the saturation point. We then stopped the stream of nitrogen-CO₂ and replaced it with a stream of nitrogen mixed with acetylene. We wanted to see whether the acetylene comes past the silica gel. The result was that no acetylene came through; only the CO₂. This shows that the acetylene is more strongly adsorbed than the CO₂. On the other hand, CO₂ cannot drive off acetylene from a surface of silica gel. At the moment I am not in a position to report on other hydrocarbons.

NEUMANN, Texas Co.: As to previous actual experience at our plant at Brownsville, we had two sets of silica gel filters and one of them was on an air stream going to the expand-

ers. The other was the usual rich liquid filter. It so happens that on our plant piping arrangements one filter regenerated concurrent flow where the material went through it in normal operation, and the other went counter-current. In the deriming of these filters some analyses were made by mass spectrograph on what came off at which temperature and there was a peculiar pattern of removal. In one set of filters, CO₂ came off first and in the other set, the acetylene came off first. This could be entirely explained on the basis of CO₂ displacing the acetylene.

WALTON: Anyone else have any data on this subject?

CHUBB, Atlanta Refining Co.: We have made one set of tests on the regeneration of a Sovabead or Mobilbread filter. To do this, we regenerated with nitrogen to a bed temperature of 108°F. We sampled the regeneration stream continuously and got the following rough set of data represented by a plot of the bed temperatures versus the percent of the total desorbed materials, as shown in Figure 1. The acetylene curve is kept separate. The saturated hydrocarbons are grouped in one curve and the unsaturated hydrocarbons are grouped in the other curve. This is the extent of our data on regeneration of Mobil bead filters to date.

WALTON: We intend to repeat this test a number of times more in order to refine and prove the data. This is just the first attempt and we thought it might be of some interest to you.

KNOX, St. Paul Ammonia: With regard to this problem of CO₂ carrying through, that is what we normally consider a cold start-up. It is our practice to reestablish the temperatures in the warm end again by means of the start-up by-passes and thereby again reach operating temperatures. Any CO₂ that could be carried through initially while the front end exchangers are warmer, goes back into the atmosphere through the waste nitrogen vent. By following this procedure we do not feel that we have any problem of this kind because by establishing our operating temperatures before the flow is put on through into the high pressure column, any residual CO₂ is frozen out and contained in the same parts of equipment as would occur with normal day-to-day operation.

LAWRENCE, USI, Tuscola: Even on a two or three hour downtime, when you start up it is with a very small flow whereby your exchanger never really warms up. I couldn't see the possibility of slugging it even if you are shut down for 8 to 12 hrs. One doesn't have to use the by-pass if you still never warm the exchangers enough to get CO₂. When you do get CO₂, in our case, I know we can't start the turbine. The CO₂ will flood the suction screen on the turbine and it will not run and we can't get a very large flow into the plant. So, in our case, I'm going to rule the CO₂

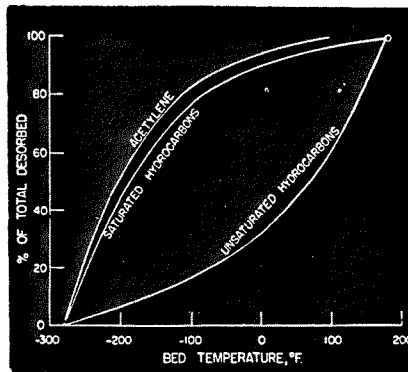


Fig. 1. Hydrocarbon desorption from Mobil bead using nitrogen for regeneration

theory out, I think.

WALTON: Well, let me try to answer that in this way. From our own experience we know that it gets all the way through to the main vaporizer—we think by a combination of two things. One is physical entrainment at the end of our reversing exchangers. Two, is the fact that it definitely does have some partial pressure. We're sure that it is CO₂, because over a period of three or four months the pressure drop in our reflux exchanger builds up and it is necessary for us to shut down and warm that up to about -150, at which time the drop clears. Any other comments?

MOODY, Air Products: One suggestion for extended downtime. When the plant is shut down all the liquid in the high pressure column can be transferred to the sump in the low pressure column diluting any hydrocarbon concentration there. Since any further concentration is due to the heat leak entering the column from the outside atmosphere, the period of shutdown before draining is extended without running into any dangerous hydrocarbon concentrations.

WALTON: We have had Sova beads in our original filters and after about three years' operation we shut down the plant and decided, on general principles, to change this material. An analysis indicated the Sova bead had lost very little of its efficiency. As we use a centrifugal air compressor, lube oil contamination wasn't a problem. There was little dust found in filters.

Another discovery: with a thermocouple on the regeneration line downstream from the bed and with the heater that we had, the highest regeneration temperature we were getting was about 80°. But by installing a thermocouple in the bed itself, it showed the bed actually to reach 180°.

The next topic—**FREQUENCY AND METHOD OF CLEANOUTS**—Will be introduced by Mr. Holstein of Atlantic Refining.

HOLSTEIN, Atlantic Refining Co.: The frequency and method for cleanouts will vary with each plant, and are basically related to plant location, at-

mospheric conditions, and plant design. Once a plant is in operation, the need to clean out is determined by economics and safety considerations. The materials which concern us are CO₂, water ice, oil accumulation, and atmospheric dust and dirt.

The deriming of almost all CO₂ or water ice occurs during the standard cycle for the primary exchange system. It is, however, possible for these materials to pass into the plant system and accumulate at various points with the result that the operating efficiency is impaired. This can occur gradually during normal operation or rapidly as a result of plant upset such as power or equipment failures. The remedy for this situation is to warm the plant to a suitable temperature and purge all, or a particular section of the plant. It has been our experience that partial deriming may be required every few weeks or months (usually brought on by some equipment malfunction such as sticking rotovolve) and complete deriming about every year.

Have had no knowledge or experience about dirt removal although periodic inspections have indicated some entrainment of particulate matter. We anticipate it will be necessary to clean the system, particularly the fractionation tower, if an increase in this building should be noted. We hope that periodic complete deriming will minimize the problem since some dirt removal is accomplished at these times. We know of at least one operator who is seriously concerned about the purity of his product due to dirt accumulation.

WALTON: I am seriously concerned as to what will happen some time when dirt accumulates in the towers and affects their fractionating efficiency. With some towers, the top can be cut off and the tray cartridge lifted out. This does represent, however, a long shutdown. Other towers are so designed that one is not able to do that. Has anybody had any experience with cleaning out a distillation tower?

KERRY: In our own oxygen manufacture operating department we do clean out the distillation tower with a grease solvent. We have found that even with silica gel filters, etc., there is a film of grease which does accumulate in the tower and we have used carbon tet and trichloroethylene to clean it out. We do this quite regularly and about once a year we stop for general overhaul and you might say for preventive maintenance. We do know of one plant that ran for three years without stopping and frankly we don't recommend it.

NORRIS, New England Gas.: We used to wash down our distillation column once a year but that was when we were using potash as a drying agent ahead of the fractionating column. At that time we used to wash with a mixture of warm vinegar and water, and then finished with carbon tetrachloride.

SAFETY *continued*

Since then we have been using activated alumina as a dryer, we've been washing out once every two years with carbon tet, but plan to use something else.

ANONYMOUS: We have in operation, I think for over ten years, a small liquid nitrogen column with an oil lubricated expander and we had occasion to replace the column after ten years of operation. We took it apart and carefully examined it. At no time had we cleaned it out and still there was no indication that we had either oil films or excessive particulate material in the column. One of the reasons for this, we believe, was that the column was periodically defrosted on a weekly schedule with complete defrosting and bringing the equipment up to well above room temperature each time.

WALTON: The next subject—**METAL INSPECTION**—will be introduced by Mr. Chubb.

CHUBB, Atlantic Refining Co.: Metal inspection as a topic was covered thoroughly as far as ammonia plants are concerned, at the earlier session. I will introduce only one new aspect. This is the inspection and use of aluminum for exchangers, pipings, etc. We have quite a bit of aluminum in our air plant and our experience generally has been favorable. We had quite a bit of difficulty in some sections of the plant with poor original welds, in the original construction stage. These did not show up until after about three years of operation. At that time we had several leaks. I think Mr. Walton told you about the explosion we had, and minor as it was, it was still quite a warning. Upon examining the piping and exchangers, where we had all these leaks, we found something in the order of 30 to 40 places where faulty aluminum welding was leaking—and certainly could have gotten us into even more trouble if it had gone much farther.

We would like to hear from anyone who has had experience with faulty aluminum welding, aluminum failure, etc.—what kind of inspection periods they have, what type of inspection they use for aluminum welding and aluminum piping.

WALTON: Anyone like to comment on that subject? I don't know how many of you are in states that have been recently reviewing their laws governing inspection of pressure vessels. Pennsylvania's code is getting quite a going over at the moment and we are told that it is liable to become much more strict than it has been in the past. It's quite possible that we may be faced with some kind of regulatory requirements for inspection of pressure vessels in the air plant. I think it is something we might devote some thought to and find out, if we

don't already know, what the climate is in your own states in this regard.

ANONYMOUS: With respect to the problems with aluminum, one that is particularly difficult to police is the selection of the right welding wire. In the construction of some of our plants we use a number of different aluminum alloys which from outward appearance appear to be the same. Some rods with some alloys will form a very brittle weld that does not develop the strength of the base metal nor does it even approach it. We have undertaken to take a good many steps to insure that the correct welding wire is used and even in spite of that, we've found the wrong ones can slip through. Particularly bad is the welding of type 61 alloys to 52 or 54 alloys.

With respect to metal inspection, one area which we found requires attention is in the discharge piping from the air compressors to the air separation plant. Often there are corrosive materials in the air which along with the condensate form acids that corrode the pipe. We find it essential that metal inspection policing be done in this area.

MASSEY, Monsanto (Texas City): We got into a problem during a recent construction program which might help others to know about. We have the aluminum brazed exchangers and during construction, we put water in

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them to hydrostatically test the whole system. Our water is slightly alkaline. After draining the water out, and during the heading up, we had a fire due to hydrogen accumulation. This amazed us. We hadn't realized that aluminum would evolve hydrogen with a very slightly alkaline water and I believe it will also do this with slightly acid water. I think it might be an advantage to anybody going into construction with brazed aluminum to remember that if you get water in them you are definitely going to get hydrogen. We dried the exchangers and had no more trouble.

WALTON: That's an interesting point.

HOLSTEIN, Atlantic Refining: When we were shut down for extensive repairs after our explosion, and after we had removed all of our insulation from the cold box, we had a few gashes in some of our Trane exchangers due to the use of sharp tools. It has been our experience that repairing these aluminum exchangers is not a

"do it yourself" job. We tried it several times and failed, and finally decided to get the manufacturer's service man who did a very fine job.

WALTON: One thing that concerned me in reviewing the available literature on the subject—I believe Dr. Karwat made a statement at Boston—that some oxides of nitrogen are corrosive. Would you care to amplify that any, Dr. Karwat?

KARWAT: In the case of having some nitrogen oxide and some nitrogen dioxide present after warming up the apparatus, these with water may form nitric acid.

WALTON: The difficulty we had with aluminum welds was mainly with small piping. Where aluminum welds are made in piping large enough to use chill rings, the welds were good and sound. But in the smaller lines where you can't use a chill ring, there were many, which on examination showed fine cracks on the inside. These cracks grow very slowly. It is extremely important that the technique of welding small aluminum lines be well understood by the welder and welding supervisor. We sent a supervisor and three or four welders out to the Alcoa plant at New Kensington for training in the methods which they recommend. I'm sure the Aluminum Company would be glad to assist others.

STOCKBRIDGE: Southern Nitrogen: I'd like to ask Mr. Walton what method was used to determine the cracks? Did you have to destroy the welds?

WALTON: To show up the cracks which were there we used dye checking. Then on welds that we suspected we cut out and cut them in half and used dye check in microscopic examination.

WALTON: I would like to comment briefly on the catalytic oxidation of the air intake for air plants.

A successful and economical device would remove substantially all the hazards that we discussed. The difficulty in the past and to the best of my understanding at present, is that with the catalysts tried so far, too high a temperature is required to be practical and economical. Reasonable temperature suffices for some compounds but for others it is necessary to get up into 800°, or so.

KERRY: Our work has shown results which so far are optimistic for plants which have centrifugal compressors, and not so good, unfortunately, for plants using oil lubricated compressors. Most of the catalysts tried so far show very well for acetylene but not too well for ethylene-propylene. One has to go to a higher temperature. It's not impractical but you might say it would be desirable to eliminate these higher temperatures.

Sessions held at A.I.Ch.E. National Meeting in Baltimore, Fall, 1957.