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Argonne National Laboratory

MINUTES OF SYMPOSIUM

"NITRIC ACID - ORGANIC MATERIAL REACTIONS"

JUNE 11, 1953

at

ARGONNE NATIONAL LABORATORY

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ANL-5128
Chemistry - Separation Processes
for Plutonium and Uranium
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ARGONNE NATIONAL LABORATORY
P. O. Box 299
Lemont, Illinois

MINUTES OF SYMPOSIUM

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ANL-5128
Chemistry - Separation Processes
for Plutonium and Uranium

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SYMPOSIUM ON NITRIC ACID-ORGANIC MATERIAL REACTIONS

Held at Argonne National Laboratory

Lemont, Illinois

June 11, 1953

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INTRODUCTION

A symposium on the subject "Nitric Acid -- Organic Material Reactions" was held at Argonne National Laboratory on June 11, 1953. The symposium was suggested by Mr. D. F. Hayes, Chief, Safety and Fire Protection Branch, AEC Washington. Dr. Frank K. Pittman, Deputy Director, Division of Production, AEC Washington, was chairman. The names of those attending the symposium are given on the preceding page.

The meeting was informal: most of the talks were based on notes, rather than given as formal papers. This presentation is followed in the minutes, the talks being given verbatim as much as possible. If the information was covered in project reports, the talks are summarized with the inclusion of references. In one case, because of poor transcription, part of a talk was completely cut from the minutes. The authors did not review the minutes; consequently, there may be errors resulting from transcription or editing. In general, it was not possible to identify questioners and speakers in the discussion period; however, in cases where the identity seemed pertinent, tentative identification is indicated.

GENERAL EXPLOSION HAZARDS OF ORGANIC MATERIALS -
M. H. Wahl (du Pont)

I'm surprised to be posing here as an explosions expert after I've been out of contact with our commercial explosive business for about three years. Nevertheless, during my years of experience with commercial explosives, some of which were actually spent on testing hazards of chemical systems, I have developed a philosophy on the subject which I would like to present to you. I must admit that my philosophy is not shared by all my colleagues, although several unfortunate instances in the last few years are bringing more people around to my way of thinking.

I thought I would spend a little time discussing some of the general considerations of explosives to provide a background for the discussion today. I like to think of an explosion as a sudden uncontrolled release of energy. (That definition differs somewhat from what's found in the dictionary.) The chemistry going on in an explosive process is very similar to that which we study in plants and the laboratory. The chief difference is that the rate of release of the energy is uncontrolled.

In general, there are two types of explosives. There is the detonating type of explosion and the deflagrating type of explosion. Explosion is a general term, and you're safe in using it if you don't know the specific type of explosion you're referring to. The detonation type of explosion has a reaction time of the order of millionths of a second; whereas a deflagration type reaction is of the order of milliseconds. The detonation reaction propagates by means of a very steep front shock wave, and the outward manifestations of the two types of reactions are radically different. If a detonation reaction is shot in a vessel or pipe -- the pipe is broken into very small jagged-edged fragments which are widely scattered about. If you have a deflagration type of explosive shot in the same confined conditions, you will find that the pipe is more or less split open. Perhaps it is torn somewhat, but it is usually recovered in a few large pieces.

It is my question whether there isn't a third type of explosion that you might term the boiling type in which through steam pressure or gradual evolution of gases, the bursting strength of the vessel is exceeded. I think in damage it may be considered as comparable to the deflagration type of explosion.

There are a variety of detonating type of explosives which differ in sensitivity. You probably learned in freshman chemistry that one can be set off by the stroke of a feather. Others are heat sensitive, and they form the face of the blasting cap. In industry, typical compounds are lead azide, nitromannite, and mercury fulminate. Nitroglycerine, which is the base of the explosives industry, is somewhat more stable, although it is a rather treacherous compound. It is sensitive to friction, impact or flame. Probably

one of the most stable detonating compounds is TNT; it can be melted and cast and presents very little hazard. I think the interesting thing to point out is that with the exception of heavy metal salts, the bulk of the explosives of industry is based on nitro compounds and nitrates. This indicates that we , should be wary of any nitric acid derivatives.

There is another class of explosive mixtures -- explosives which are mixtures of oxidizing and reducing liquids. A mixture of concentrated nitric acid (I'm not sure whether I refer to 95% nitric or perhaps 70%) with nitro-benzene is quite sensitive and can be detonated.

We know from experience with detonation explosions that there are certain factors of importance. One is the so called oxygen balance. We know, for example, that the greatest energies are obtained when there is sufficient oxygen to convert all the combustible material to carbon dioxide and water. So I think in setting up a reaction system we should stay as far away from that point as possible -- on either side. There is a so-called mass effect that we really can't evaluate quantitatively. We know that some explosions which can't be shot in small quantities can be shot in large quantities. Ammonium nitrate, for example, is very difficult to detonate in small quantities, yet we're all familiar with the Texas City disaster where destruction was very serious. We also know that explosives can be toned down by use of diluents, and I think that point can be used in setting up an operating process. One of the diluents, of course, might be one of the reactants present in excess. .

Typical deflagrating explosives are black powder, which is an intimate mixture of sulfur, sodium and potassium nitrate and carbon, or smokeless powder, which is a nitrate of cotton. Here again we see that the base of these are nitric acid derivatives. This type of explosive really is not too hazardous unless confined. When you burn small quantities of black powder that are unconfined, you get a quick flash but you don't get a crack. The same is true of smokeless powder. It takes confinement; that is, the rate of pressure release is a function of pressure. The fact that all these compositions are capable of giving a sudden release of energy is indicative that they are thermodynamically unstable. Any system which is thermodynamically unstable should be considered a potential hazard until proven otherwise. There are free energy and thermal data available in handbooks, and I think for preliminary consideration we can use such data. If we can write equations to indicate that there will be a sizeable energy release, we should consider the system to be a potential hazard until experimental results indicate or define those hazards.

I find that most of our people class compounds and mixtures as non-explosive or explosive, and I just don't think that the line of demarcation is that sharp. I would like to think in terms of a sort of twilight zone or gray zone between those two classes. I'd like to talk a few minutes about the compounds I think should be classed in that particular zone of doubt.

Ammonium nitrate is one of those. Ammonium nitrate can undergo a reaction forming water and nitrogen with an energy release of the order of 28 kilocalories/mol. It is treated according to shipment classification as an oxidizing agent, and it is manufactured as though it were a safe chemical; yet we have had a number of unpleasant incidents associated with its manufacture; so it is my contention that ammonium nitrate should be classed as a weak explosive. It undergoes a self-sustained exothermic reaction and should be treated accordingly. TNT is another chemical in this category. It's used in the dyestuffs industry as an intermediate, and I think little attention is paid to its potential hazard. Yet we have had an instance or two where it has caused some damage. Acetylene is capable of undergoing a decomposition into its elements with a release of energy of the order of 54 kilocalories/mol, and I think there is no doubt but what most of us recognize that it presents an explosion hazard. Ethylene on the other hand is also unstable -- the heat evolution is somewhat smaller, but I recall that the British had one instance in which ethylene exploded under very high pressure. Two other compounds which fit in the same category and which should be considered in our nitric acid subject are NO and N_2O. They're both endothermic compounds. The literature reports that N_2O can also be exploded under certain conditions, generally high pressure. The same is also true of NO.

So it seems to me in analyzing the explosion hazard of any system, the question to ask is: is this system thermodynamically stable? You should look at both the liquid phase and the vapor phase during normal operation and also take into consideration the compositions you are likely to get through equipment misoperation or operating bulls. The goal of the analysis is to determine if a system at any stage is explosive, and if so, what are the limits.

In conducting tests to assist the analysis, I think we should aggravate the conditions because it's usually when your system gets out of control that you run into trouble. I'm very suspicious of negative results. It shows that there were not severe enough conditions -- temperature, pressure or ignition; and I feel much better about it when we approach the explosive limit from both sides and have it well defined.

In testing liquid systems, we heat them in either unconfined or confined conditions to elevated temperatures. We frequently test them in bombs where we determine and measure the rate of pressure development. There's a Bureau of Mines bulletin which gives very good coverage on how to test gases and vapor mixtures (Bulletin 502, "Flammability Limits of Gases and Vapors"). I've found from my own experience that the ignition basis of those mixtures is very important. If you get negative results on a spark, you try something else (e.g., hot wire or a thermite type of ignitor), generally an ignitor that gives a high temperature for a fairly long period of time. If you can't design to operate outside the explosive limits for any system, then of course you have to design to cope with it.

Question: I'd like to know about how reliable are these methods for indicating that there are mixtures or conditions which are explosive.

Answer: We have two methods that we employ. One is the use of a ballistic mortar -- it's really a mortar mounted on a pendulum confining a small amount of material in question (usually 10 grams is what we test), and we try to ignite it with a very heavy blasting cap. It's about the most severe test that we have available, and if we get any show of strength at all out of such a mixture, I always consider it as potentially hazardous. Another way we do it is to take a bomb. Again we put in 10 grams of mixture or compound in question, ignite it with a gram of nitrocotton which is enough to bring it up to an appreciable pressure and temperature. If we get any show of strength from that, we consider the system potentially hazardous. So those are two ways that we usually use in our department. If the results are negative, under these conditions, we consider the thing reasonably safe.

Question: Wouldn't you use the first method for solid or liquid explosives and use the second method for gaseous mixtures?

Answer: Well, I would use both of these tests for solids. For gases, I'd be inclined to use some of the techniques described in the Bureau of Mines bulletin. Usually I use a tube that is at least 2" in diameter and 4 or 5' long and fill this tube with the vapor mixture under question, ignite it at one end, and see if the flame propagates to the other end. When you get in high pressure systems, I'd use the bomb method.

It is important to make sure that your ignition conditions are potent enough. I've seen mixtures in the gas testing chamber where we'd shoot one of our "squibs" which throws out a fairly hot flame for maybe several hundredths of a second or several milliseconds. It just wasn't strong enough to ignite a borderline mixture.

Question: The borderline chemicals you listed as ammonium nitrate, acetylene, ethylene, nitrous oxide, etc. -- were these considered in their pure form or with contaminants present?

Answer: They all, when properly primed and confined, give an exothermic self-sustained reaction if pure. Ammonium nitrate, for example, is more hazardous if it has combustible materials present in it. It undergoes a decomposition with release of oxygen; so if you've got something there to use up that oxygen, you've got a more potent mixture. Commercial dynamites today are made up largely of ammonium nitrate with some combustible material, wood pulp or meal, that are sensitized a little more with nitrogylcerine, so that the large energy producer is ammonium nitrate plus a fuel.

Question: There was a question on one of the statements; you mentioned that ammonium nitrate in particular did not ignite in less than some certain minimum quantity. Do you have any idea as to what quantity you were speaking of?

Answer: Well, in a bomb you'd get strength out of 10 grams. Just put it in a paper package, and I don't think you'd get any strength out of 25, 50 or 100 pounds. It probably requires ton quantities, or something like that. There I think the large volume provides its own confinement.

Question: In defining the types of explosions as deflagrating or detonating, you mentioned that one of the systems -- nitric acid-nitrobenzene -- could be detonated. Could any ordinary reactions of that category be of a detonating type?

Answer: Only if ignited with a detonating type ignitor. I know of no instance where such a reaction got out of control, or if it's been set on fire and turned into a detonation type reaction. I've never seen extremely large quantities of that get out of control so I don't know what the mass effect there is. I doubt whether such a mixture once it gets out of control would turn to a detonation type of reaction.

Question: Are we apt to run into any compounds in which the mass effect might only be established by experimenting with greater than 10 gram quantities?

Answer: Well, I think it's doubtful if you use very severe conditions for your small test quantity. I know of no instance where the larger tests showed some of the potential hazards that didn't show up in this bomb test, for example. I think if you were to take a small quantity and test it in the test tube and find negative results, there is a possibility that a larger quantity would show up to be hazardous.

HAZARDS OF NITRIC ACID-ORGANIC SYSTEMS – M. H. Wahl (du Pont)

From my chemical training I grew up to think that nitric acid was a simple and innocent compound. But based on my experience with the Explosives Department, I've modified my ideas considerably. Any time we use nitric acid, I think we have to consider ourselves preparing a potential hazardous salt. Be careful. Actually in a liquid system containing nitric acid, we may have any of the following substances present: oxonium ion, which is a hydrated proton, OH_3^+; the nitrate ion, NO_3^-; molecular nitric acid; the nitronium ion, NO_2^-; and there is another ion the name of which I don't know, $H_2NO_3^+$. You might also have nitrous acid present. In the gaseous phase in addition to molecular HNO_3, you might have HNO_2, NO, N_2O, NO_2. So you see with nitric acid you have a very complex system.

We might briefly run through the types of reactions you get with various classes of organic compounds. With alcohols under some conditions you get nitration to form the alcohol nitrate ester. Under other conditions you get oxidizing type reaction and end up with acetic acid. In case of butanol, you get butyric acid. Aldehydes oxidize rather easily to acids; ketones oxidize to smaller acids somewhat more difficultly, although in the case of cyclohexanol and cyclohexanone, they both oxidize down to adipic acid. Ethers oxidize with some difficulty to acids, and we do know that ethers in the presence of oxidizing agents form ether peroxides which are hazardous and treacherous compounds. I don't know in what volume they form, but I would suspect that they might be the cause or the initiators of some of the reactions that take place in these systems. Hydrocarbons are very stable or as stable as any class of compounds with nitric acid, although we do know that according to the Hass process they can be nitrated under rather severe conditions. (With temperature of the order of 400° to 450°C, propane and ethane can be nitrated.) Unsaturated hydrocarbons react very quickly with some of the nitrogen oxides and give you a complex mixture of unstable compounds. We have worked on those to considerable extent. Some of the reaction products can be kept overnight and some not that long; there is a constant evolution of oxides, sometimes you get fume-offs. So that I would be very wary in introducing any unsaturated compounds into the nitric acid system. In some of the explosions, although it is possible subsequently to determine the chemistry involved, we can very seldom determine the cause of the ignition; and I suspect that maybe derivatives of unsaturated compounds are the igniting agents. Aromatic compounds nitrate fairly readily, and aliphatic side chains on aromatic compounds usually oxidize down to the acid. Isopropyl benzene or toluene would oxidize down to benzoic acid.

One point that I intended to make earlier and didn't, it seems to me in analyzing the system you should consider mainly whether it's thermodynamically stable, and I wouldn't waste much time trying to answer the question what ignited the explosion. It seems to me it's a statistical proposition to be assumed that sooner or later if the system is thermodynamically

unstable, something is going to ignite it. You might consider the elimination of the igniting agent a second line of defense, but not the first line of defense. I question whether any of these reactions that we have just talked about are the primary reactions of the explosion. They may get out of hand and give rise gradually to a pressure that would rupture the vessel, but I doubt whether they are the rapid deflagration type of reaction. The heat evolved on oxidizing butyl alcohol to the acid is of the order of 100 kilocalories/mol, yet the heat of combustion of butyl alcohol is 640 kilocalories. So I think that vapor phase deflagrating reactions are probably reactions of butanol, butyl nitrate and butyric acid with NO or N_2O or NO_2.

One thing we have observed is that in some of these nitric acid systems there is an induction period, so that if you are not alert the nitric acid will build up, or your other reaction products will build up, and you are liable to get into trouble. Sometimes the reaction is associated with the use of brown or yellow nitric acid in contrast to white nitric. You have noticed that reagent grade nitric is received as white, but after it stands around for a while (particularly after it's been opened), it turns brown, which means that it has dissolved NO_2 in it. NO_2 seems to be more reactive than the other various nitric acid species present in this system.

Question: Would you mention that nitric reaction with aliphatics?

Answer: Yes, that is the so-called Hass reaction. The vapor phase reaction between nitric-NO_2 with propane, ethane, methane. The higher up in the series you go, the less severe the conditions have to be to cause the nitration. I think some of those higher ones will react very, very slowly with nitric acid and on boiling in very concentrated nitric acid for days, but on the whole they are as stable as any class of compound.

Question: You mentioned the possibility of reaction with NO or N_2O. Have you had any experience in your nitric acid recovery systems with explosions due to this under normal operating conditions?

Answer: No, I don't think we're operating at high enough pressure to get us into trouble. I don't think NO or N_2O will explode or get into trouble alone at pressures less than maybe 200 to 400 pounds per square inch, and our recovery systems operate at atmospheric or 50 or less.

SOME OBSERVED REACTIONS OF NITRIC ACID WITH TBP -
E. D. Arnold, ORNL

The most important effect of nitric acid on TBP is hydrolysis to di- and monobutyl phosphates. Degradation to dibutyl phosphate is most important in affecting plutonium and uranium stripping efficiency. However, the solvent recovery system is efficient enough to keep dibutyl phosphate concentration below the toleration limit. It is found that 0.01% DBP can be tolerated without serious effects. Build-up of impurities in the IB column increased plutonium losses. Experiments have indicated that 0.2% plutonium loss in the IB column may be due to impurity build-up or to lack of stages. However, study at KAPL has been done using mixer-settlers which indicate that our losses may be due to insufficient stages and not to impurity build-up.

The second notable effect of the nitric acid on the extraction solvent is degradation of the diluent. In this case nitration of the unsaturated hydrocarbons takes place much as iodine additions to double bonds. However, this effect is not too serious. At the ORNL metal recovery plant, the Amsco diluent contained only 0.02% fixed nitrogen after 160 cycles use.

A third effect occurs with the reaction of organic nitro compounds and TBP. Organic nitro compounds react with TBP to form surface active agents which are not washed out in the solvent regeneration cycle. These surface active agents accumulate and exert an effect to cause formation of a water-oil type of emulsion in the extraction columns. Any such formations will cause immediate shutdown of equipment.

Question: I've noticed in the discussions concerning hydrolysis of the TBP, no mention has been made of the fate of the butyl alcohol.

Answer: Nothing has been done (at ORNL) with this work so far. Have any of the other sites any information on this?

Statement: The formation of butanol by hydrolysis is used as a measure of the hydrolysis in the study of some of the phosphonate, phosphinate and phosphate esters.

Statement: KAPL has detected butyl nitrate.

Question: What can we do in acid systems with butanol and some butyl nitrate in the aqueous phase?

Statement: It seems likely that the system will end up with a volatile compound such as butyric acid or butyl nitrate or butyl nitrite, which compounds may give trouble in the vapor phase. This is particularly so if there is NO_2 or some oxidizing agent present.

Statement: Butyl alcohol is difficult to remove from organic streams by ordinary caustic washing techniques.

REACTIONS OF HEXONE WITH NITRIC ACID – R. M. Wagner (G. E., Hanford)

A resumé of reactions that take place between the nitric acid and hexone is given in Figure 1. The first reaction is initiated by the addition of HNO_2 to hexone to make an oxime. By further action with HNO_2 or HNO_3 it goes to the diketone which is not shown in the figure but goes in between acetic acid and the isonitro acid. As soon as the oxime is formed, it is attacked by N_2O_4 which gives a compound known as a pseudonitrole. It is then attacked by HNO_3 giving a dinitro compound that decomposes in water and goes to a true dinitro compound and with further attack down to acid. Another way the same reaction may take place in water is to go through what is known as nitrolic acid, which under further attack by nitric acid goes into a dinitro compound and on down to an acid. Direct attack of nitric acid on hexone gives nitrolic acid directly, but it suffers further nitration to nitro-isobutane down to the intermediate and further down to isobutyric acid. It is noted that in all these steps there is HNO_2 formed. This series of reactions accounts in part for the fact that we have quite an induction period in the reaction of HNO_3 and hexone; and furthermore, after a certain temperature is reached, the secondary reactions supply further HNO_2 so that the reaction remains self-sustaining.

Figure 1
TYPICAL REACTIONS OF HEXONE WITH NITRIC ACID
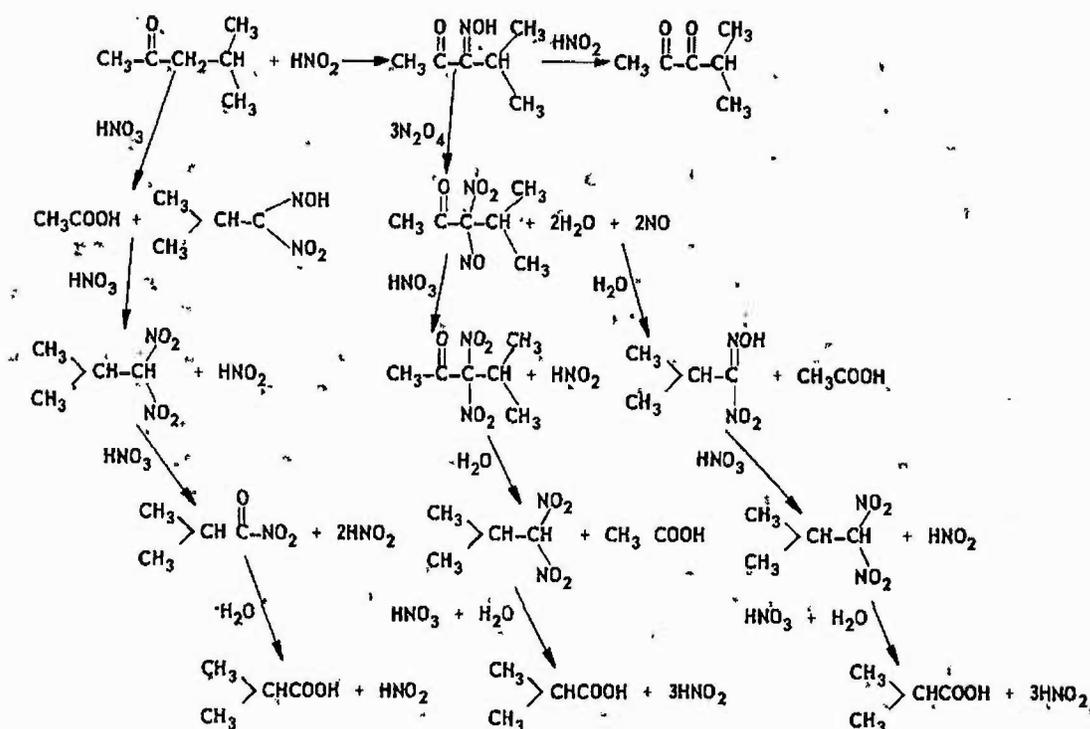
If we established a series of solutions of HNO_3 and hexone containing varying amounts of HNO_2, at both 25° and 40°, starting with the HNO_3, less than 0.3 molar and the HNO_2 only 0.0001 to 0.01 $\underline{M}$, the HNO_2 disappeared with no self-sustaining reaction, and we had no vigorous reaction ensuing. However, with the HNO_3-HNO_2-hexone system in which the nitric acid concentration initially was between 0.3 molar and 2 molar, the HNO_2 decreased initially due to the first equation in Figure 1. The HNO_2 concentration goes through a minimum and thereupon increases by the secondary reaction until it reaches a steady state. At the concentration due to using about 0.3 to 0.2 molar nitric acid, we found an equilibrium value of about 0.01 molar nitrous acid. If the temperature is increased from 25° to 40°, both the initial disappearance and the final build-up of HNO_2 were accelerated greatly. The concentration of nitric acid to make the reactions self-sustaining seemed to vary distinctly between 0.2 and 0.2 molar in solutions with original HNO_2 concentrations of 0.001 $\underline{M}$.

At 40° where the initial HNO_2 is 0.01 molar or greater, there is no limiting concentration of HNO_3 for which the reaction will become self-sustaining. Stated differently: if at 40° the initial HNO_2 is 0.01 molar or greater, there is no limiting nitric acid concentration for which it will not remain quiescent and become self-sustaining. In the HNO_3-HNO_2-hexone systems, the initial reaction is first order with respect to HNO_2 and independent of the HNO_3 concentration.

In attempting to find the effect of increases in concentration in oxime (first equation), trying to step up the secondary reaction, we found that there was no effect at all by adding oxime to the solution. That is, as far as the initial reaction rate is concerned (as it approaches the minimum); but it did increase the secondary build-up to the constant state of HNO_2. Reducing agents such as iron which increased HNO_2 concentration, increased the rate markedly while reagents such as sulfamic acid or ammonium ion which destroy HNO_2, of course, quenched it. We found that as yet unknown oxidizing impurities which result in photochemical decomposition of pure hexone, react more readily with HNO_2 than the secondary products. In the same investigations, a photochemical effect of uranyl nitrate resulted in a removal of HNO_2. The HNO_2 concentration of both organic and aqueous solutions of UNH decrease when exposed to light. In darkness the effect is not noticeable. Of course, we are worried about the effects of the hexone reactions on the plant process; we found that all these various products (of which all except one we were able to find in the experimental systems which we studied in the laboratory) were satisfactorily removed by a caustic strip.

Experiments were performed investigating the kinetics of the HNO_2-hexone reaction. The initial HNO_2 was 0.001 molar and the temperature was 40°. The starting HNO_3 concentrations varied from 0.2 to 1 molar. As nitric acid concentration was increased, there wasn't much change in first order k values until the HNO_3 was above 0.5 molar; but the time to reach the minimum nitrous acid concentration decreased rapidly. These experiments show

that nitric acid affects the hexone reaction by formation of nitrous acid.
The effect of the increase of nitric acid on k and formation of HNO_2 is sum-
marized in Table I.

Table I

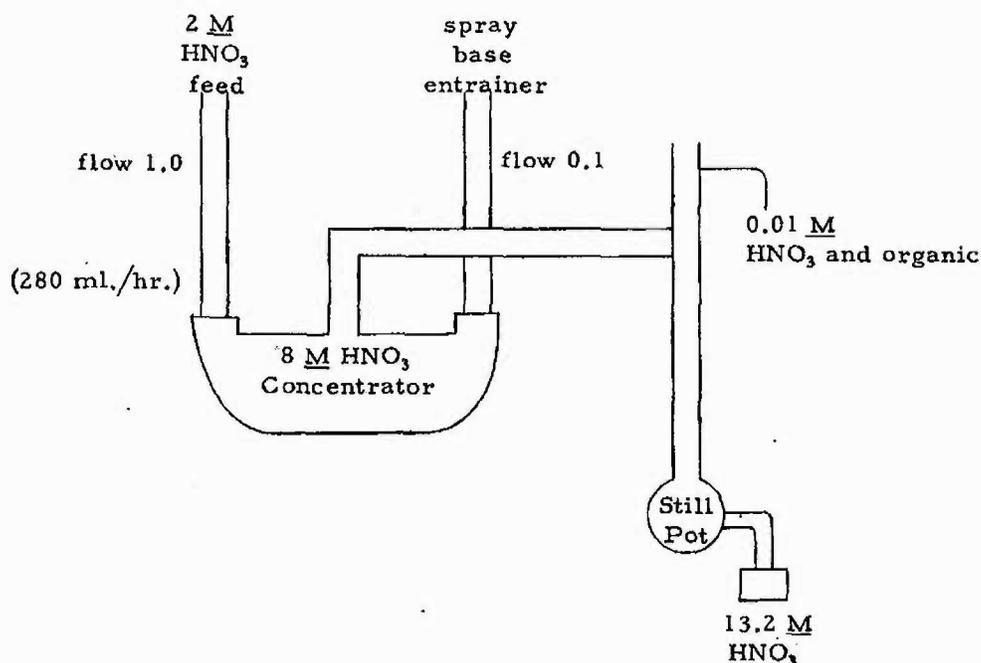### EFFECT OF NITRIC ACID ON NITROUS ACID-HEXONE REACTION

Initial reaction rate of nitrous acid with hexone, experiments at 40°C,
0.001 M initial HNO_2 concentration

Concentration of HNO_3 (M)	k (min^{-1})	t (hrs.) to reach minimum HNO_2 conc.
0.2	0.0548	4
0.4	0.0552	1.5
0.5	0.0550	0.8
0.6	0.0990	0.5
1.0	0.1080	0.2

NITRATION OF PUREX HYDROCARBON DILUENT -
R. M. Wagner (G. E., Hanford)

The possible nitration of kerosene diluent during the concentration of aqueous process streams was considered for conditions including entrainment of as high as 1 per cent organic. When such streams are evaporated in the plant, nitric acid is removed continuously from the vapor. A laboratory apparatus which more or less simulates evaporators was prepared. A schematic drawing of it is given in Figure 2. The concentrator started with 8 molar nitric acid in the pot; 2 $\underline{M}$ HNO_3 and spray base were added separately with flow ratio of 100/1. The overflow was fed into a 1-inch ID glass column packed with 1/8-inch helices with a still pot full of commercial nitric acid bottoms. The unit was operated for a period of some 18 to 20 hours continuously. The organic appeared as flash entrained with the overhead of 0.01 molar nitric acid. The organic-containing acid was fed to the overhead during the entire run; samples from the nitric acid left in the concentrator after the run, the nitric acid left in the still pot, and the acid take-off were washed with carbon tetrachloride, and the carbon tetrachloride was washed with caustic. The caustic was examined in ultra-violet. We could find no differences in the ultra-violet between the nitric acid from the concentrator, still pot, and acid take-off and ordinary commercial nitric acid. The overhead contained some organic; it showed traces of dinitro-isobutane which represented a decomposition of approximately 0.001 weight per cent of the over-all organic for the total run.

Figure 2

2 $\underline{M}$ HNO_3 feed

spray base entrainer

flow 1.0

flow 0.1

0.01 $\underline{M}$ HNO_3 and organic

(280 ml./hr.)

8 $\underline{M}$ HNO_3 Concentrator

Still Pot

13.2 $\underline{M}$ HNO_3

We found quite different results when we were not operating continuously and merely operated by reflux with 8 $\underline{M}$ nitric acid and either straight Shell spray base or spray base with TBP (say 30% TBP-70% spray base). There was heavy nitration under reflux, contrasted with a flash distillation where there was no replenishment of the nitric acid lost with the vapor. We have evidence of what appears to be an intermediate between a dinitro compound and a product of the addition of N_2O_4 to an aliphatic straight chain, the identification from ultra-violet comparison with other known compounds from the lab. With the flash distillation the amount was between 0.08 and 0.09 weight per cent, whereas with continuous operation (which was what we were interested in mainly for process considerations), the amount was possibly 0.001 weight per cent. So the continuous run seems to show that using low aromatic diluent will not give us as much trouble in decomposition as TBP itself.

EXPLOSIVE CHARACTERISTICS OF PUREX SOLVENT DECOMPOSITION PRODUCTS - R. M. Wagner (G. E., Hanford)

When Purex solvent is contacted with typical ICU solution for a prolonged period, there is produced a red-orange liquid called "red oil" (or sometimes "third phase"). This substance is known to contain uranium salts of TBP decomposition products and, possibly, nitrated hydrocarbons. The "red oil" has a density of about 1.3 to 1.5; in Purex systems it will appear at the bottom of a vessel, a layer of aqueous phase above it, and the regular solvent phase on top. It may form in a Purex plant if there is continued re-cycling and concentration of aqueous UNH solutions which have contacted the solvent.

By a series of laboratory experiments reported in Hanford document HW-27492, we have found that under plant conditions "red oil" will explode only when systems containing it are evaporated to incipient calcination. Under less severe conditions there may be evolution of NO_2.

Editor's Note: Dr. Wagner also presented information on the stability of organic phosphorus compounds. Unfortunately, this talk was not transcribed.

Question: In your experiments on diluent nitration, you mentioned that both in the continuous apparatus and in the flash installation there was little nitration but there was a large amount of nitration under reflux conditions. How much was it with reflux?

Answer: We didn't determine it, but I estimate that approximately 1/2 to 3/4 the amount of organic present did nitrate.

Question: In the reflux experiments did you try introducing an external source of ignition to see if the vapor mixtures were explosive?

Answer: No.

Question: Can you form red oil with TBP and uranyl nitrate without nitric acid being present?

Answer: I think that we did.

THE EFFECT OF IRRADIATION ON TBP AS A SOLVENT - E. D. Arnold, ORNL

In considering the chemical processing of homogeneous reactor fuels of the slurry type, economics may require process operation at a high enough radiation level to damage TBP and preclude an extraction process. The experimental work that has been carried out in the laboratory was to determine what effect irradiation has on TBP and how this damage changes the effectiveness of the Purex process. The irradiations were by exposure of the solvent to a high energy cobalt-60 gamma source, which simulates the beta absorption that would occur in processing of short-cooled materials.

Preliminary tests on exposed solvents show that radiation-induced hydrolysis of TBP to mono- and dibutyl phosphates was the major irradiation damage. However, the magnitude of this effect indicated that irradiation damage would only be noticeable in Purex process operating at 10 to 100 times the radiation level expected in 15-day cooled material. Two series of Purex batch countercurrent tests have now been completed which confirm this conclusion, one series using irradiated 30% TBP in Amsco and the other using solvent irradiated in the presence of nitric acid and uranyl nitrate.

The effect of irradiation was shown by losses noted at irradiations of 2.5 watt hours per liter of solvent and higher; the losses were greater in the second series where irradiation was in the presence of nitric acid and uranium. Very large changes in decontamination factors and residual solvent activity only occurred at 30 watt hours per liter.

Another type of damage was that due to evolution of relatively large amounts of hydrogen and methane from the TBP as well as from the hydrocarbon diluent. This apparently leads to an increase of solvent acidity and unsaturation. The formation of emulsions and "cruds" in the process may be due to surface active agents and polymers produced by irradiation.

Question: What level of radioactivity is expected from fuel from normal pile operations ?

Answer: 0.25 watt-hour per liter in the 15-day cooled HRE material. The conditions of the laboratory extraction experiment were much higher. The results of our experiments indicate that we really do not have too much to worry about with the processing of HRE material, even if cooled only 15 days.

Question: What is the residence time used to establish the watt-hour figure ?

Answer: The same time cycle as the present Purex.

Question: Did you run some Hanford material cooled for different periods of time ?

Answer: Yes, we've run those materials at various cooling, but we didn't find any degradation effects. The Hanford material is quite a bit cooler than the HRE.

EXPERIENCE AT ORNL - E. D. Arnold, ORNL

Incident in 1944

In the early days of the bismuth phosphate process in the pilot plant at ORNL, it was necessary to neutralize the excess nitric acid after the metal was dissolved. This was first done by decomposing it with formic acid. The reactions of nitric acid with formic acid can take place in two different ways,

$$\text{(a)} \quad 2\ HNO_3 + 3\ HCOOH \longrightarrow 4\ H_2O + 2\ NO + 3\ CO_2$$

$$\text{(b)} \quad 2\ HNO_3 + 1\ HCOOH \longrightarrow 2\ H_2O + 2\ NO_2 + CO_2 \quad .$$

The pilot plant for the bismuth phosphate process used only one weigh tank to hold nitric acid for the dissolving step and to hold formic acid which was used to decompose the excess nitric acid. Of course, more nitric acid was involved in this process than was formic. This weigh tank was used several times per week to measure out nitric acid and only once or twice for formic.

The accident occurred on one of the few occasions in which formic acid was to be prepared. The weigh tank contained approximately 70 gallons of 70% nitric acid which the operator did not know anything about. The operator set the valve and the instruments for formic acid preparation and went to the next room to turn on the pump for 90% formic acid. When the formic acid entered the vessel, there was an explosion.

The immediate result of this explosion was to spray steam and water and air from the ruptured process lines of the tank. All process and service lines above and in the immediate vicinity of the tank were blown up and one or two instruments were destroyed. The windows were broken in the east end of the building. Fortunately, no one was hurt as a result of this explosion, as the operator was in the next room and the next operating board which had any attendant personnel was 50 to 100 feet away. There was one operating board 25 feet away which was slightly damaged, but no one was near it.

There were several reasons for using the reaction of formic and nitric acids in this bismuth phosphate process. On dissolving uranium metal in nitric acid, the amount of free acid which is left over depends upon several factors, one of which is time of reaction; but in any case the concentration will be approximately 0.2 molar to 0.4 molar at a concentration of 224 grams per liter of UNH. The precipitation of bismuth phosphate under these conditions is increased. This procedure, however, is not entirely satisfactory and, therefore, the removal of nitric acid by formic acid was employed. One of the advantages suggesting the use of formic acid for neutralization of the excess nitric acid was the fact that this reagent would not leave any foreign ions in solution; it would reduce the product from the oxidized state. Preliminary experiments showed that a more rapid decomposition of formic acid took place in 70% UNH solutions than in 20%. Reaction

in 20% UNH was very slow, with 1/5 of a mol of nitric acid removed in one hour using 1 mol of formic acid for 0.4 mol of nitric. The action in 70% UNH was very vigorous and at 40% UNH quite rapid. This suggested that the removal of nitric acid should be carried out in concentrations of UNH of 40% or better. If removal of nitric acid from the UNH solution was carried beyond a pH of 2.4, uranyl formate was precipitated. Neutralization of nitric acid in the UNH solution was carried out between 50 and 89% UNH in the pilot plant runs. The solutions were kept at the boiling temperature, and the acid was added below the surface over a period of one hour. This solution boiled for an additional hour.

Comment: There was a stainless steel weigh tank approximately 4.9 ft. in diameter and perhaps 4 feet high. It had a 1/4-inch stainless steel top which was held in place with bolts about 5/8 inch in diameter. They were sheared off with apparently no trouble at all during the explosion, giving some indication of the violence. There was one minor injury in the explosion - an operator who was running away from the weigh tank, as he had heard the initiation of the explosion. As described at the time, there was a sudden build-up of gas which threw acid over the immediate area. The operator that was running away had safety goggles on, but the acid sprayed him and unfortunately some splashed off one glass into an eye. He washed in a shower and no serious injury resulted.

Comment (Cole): I think it's probably a good thing to describe this simple little event. It reminds those who are a little younger in the game that this is a sure way of having an explosion. Mixing formic acid and nitric acid is a sure way of doing it, because one is a strong oxidizing agent and the other is a reducing agent. Now, it's true that this was a runaway chemical reaction because there wasn't good mixing in the tank, but this is only one of the number of typical operating "bulls" that happen in the organic chemical business. I think it's well to bring it up to remind us that in designing equipment you should so arrange your weigh tanks and your pipe lines and your pumps, etc. so that this kind of cross up just can't occur. If you're going to use formic acid and nitric acid around the same process, considerable thought has to be given to the design and layout of piping and proper controls of the process. In this case, everyone knew that you couldn't mix those materials and yet when the thing was set up, it wasn't recognized how easily this could be done by just forgetting to empty the nitric acid ahead of the charge.

Statement: This particular weigh tank was equipped with a normal-sized breather large enough to take care of the liquid coming in and coming out. It wasn't designed, however, to take explosions, something that is important and is not generally taken care of in a number of places. Vents are properly designed for normal use, but when it comes to explosion considerations, they are not satisfactory.

EXPERIENCE AT Y-12 - R. G. Orrison (Y-12)

Experience at Y-12 is of interest in that it deals with a different extractant - dibutylcarbitol (dibutoxy diethylene glycol). The Y-12 plant has used dibutylcarbitol for a number of years, and most of the serious explosions occurred back in 1944, 1945, or 1946. There have been several non-explosive reactions occurring in adequately vented vessels such as extraction columns that were not closed at the top and 55-gallon drums that were without a top. The reaction in these open or well-vented containers seems to be a decomposition with copious liberation of nitrous fumes and quite a little liberation of heat.

The reactions have occurred at room temperature with nitric acid concentrations as low as about 3 molar. At lower acid concentrations in the order of 3/4 molar to 1 molar at elevated temperatures (temperatures up to the order of 80 to 100°C) there would definitely be a decomposition of dibutylcarbitol. In solutions with nitric acid, the ethylene radical is hydrolyzed into ether and oxidized on down to acid. Solutions that contain uranyl nitrate and traces of dibutylcarbitol show precipitates on standing. Those precipitates that have been analyzed turned out to be uranyl oxalate. So it is definitely indicated that the reactions in part go all the way down to butyric acid, oxalic acid, etc.

One of the first explosions we experienced back in 1945 was that of a 55-gallon drum of raffinate solution from the columns. It needed solvent stripping, as the organic content was too high for disposal. The drum had the top bolted down, and there was the regular standard type 55-gallon bung hole. The operator closed this up, and approximately 12 hours later, it was realized that an explosion had occurred. There was no doubt about it because the drum had left its bottom on the floor and started up like a rocket and went through several two-inch pipes and almost through the concrete floor above.

Another incident concerned a feed tank for an extraction system. This tank was normally used as a feed tank for extraction systems but had traces of organic carbitol in it from the storage of raffinate solutions. I believe the vent system was closed off after the tank was filled with adjusted feed material (the acidity had been adjusted to about half normal acid before extraction). This tank held about 100 to 125 gallons. Later an explosion occurred that blew the ends out of the tank and a hole in the wall and ripped out considerable amount of piping. It is fortunate that the operator was at the other end of the room when the tank exploded.

The recent explosion that we had was in a polyethylene safe bottle about 5 inches in diameter and 4 feet high; it contained an evaporated solution that had been drained into it while a repair was made on the evaporator.

These bottles had just been received at the plant, and they have very nicely-made caps that seal without a gasket because of the nature of the plastic. The evaporator was drained into one of these bottles, the cap screwed on, and the bottle placed at the far end of the room while work progressed. It was some 6 to 8 hours later that the bottom blew out of this polyethylene bottle. The rest of the bottle didn't raise very high off the floor as it did with the 55-gallon drum, so this could have been just a gas expansion.

There was one other instance that occurred in a pump. The pump was on a transfer line between two sets of columns, and it was used to transfer feed solutions or raffinate from one column to another. It had been shut down, the valves closed, isolating the pump and sealing solutions in the pump. Apparently the solvent was undergoing a slight decomposition all the time.

Question: Do these polyethylene containers contain predominantly organic solutions or merely neutral solutions with either dissolved organic or organic layers?

Answer: Well, these contained organic layers at the early operations that I'm speaking of. In a 55-gallon drum, the organic layer could be as high as an inch or two inches deep. So you not only have a solution that was saturated with organic, but you have a surplus of organic solution. Another thing is that the distribution coefficients of acid in the organic and in the solvent solutions brought the concentrations much higher than organic phase. So with 0.05 $\underline{M}$ acid in aqueous salted solution, the acid in the organic phase is of the order of 2 to 3 $\underline{M}$.

Comment (Alter): I believe it is generally true in a system where you have a raffinate containing a high molecular weight oxygenated solvent (such as butex or penta-ether) and you try to evaporate it, particularly at elevated temperatures, you will get this characteristic brown fumes reaction with more or less severity. The British are accustomed to this on a routine basis in the recovery of acids from their raffinates. We've also encountered it in some work we did some time back on the so-called penta-ether process in which concentration of the ICU uranium stream invariably resulted in copious quantities of nitrogen oxides coming off. The fuming could be prevented by simply stripping of the penta-ether from the aqueous phase by butyl alcohol. This is something you have got to live with if you are trying to concentrate systems which contain high molecular weight oxygenated diluents.

Statement (Orrison): There is fuming in the concentration stage between the primary and secondary extraction of uranium, the fumes appearing prior to evaporation of aqueous quantities. Dibutylcarbitol is soluble in this stream in the order of from 0.2 to 0.3 per cent. The temperature of the evaporator is something around 235 to 238°F. The solution is salted

with magnesium nitrate, the nitric acid in equilibrium from 1 to 1-1/2 normal. The dibutylcarbitol in the aqueous solution being fed to this evaporator very definitely flashes and decomposes as soon as it strikes the hot solution.

Comment: If my organic chemistry doesn't let me down, dibutylcarbitol is a secondary alcohol. We can conclude that secondary alcohols are more sensitive to nitric acid than primary alcohols and tertiary alcohols are still more sensitive and that the resulting nitrated products are less stable in the same order. The very technique that Mr. Orrison described in that evaporation is the proper technique, because you don't allow any energy to build up; you burn it up. But, on the other hand, it is the kind of technique that has to have careful operating control or sometimes it will build up.

Question: Have you found that the rate of this reaction between nitric and dibutylcarbitol is increased by the presence of the impurities?

Answer: We found it occurring in both primary extraction systems and secondary systems. In the primary extraction systems where there are higher concentrations of other contaminants, the reaction liberating nitrogen oxides appeared to be quite a bit more vigorous than in the secondary system. The secondary system seems to lead to a formation which is perhaps carbon dioxide or maybe carbon monoxide.

EXPERIENCE AT THE ST. LOUIS PLANT - E. I. Miller (Mallinckrodt)

We have been using diethyl ether as an extracting agent for about 11 years, and during this time we have had three explosions, one of which was of a relatively minor character. The first explosion occurred very early during the war and happened after a product solution of uranyl nitrate was pumped into the pot room where the uranyl nitrate was regularly decomposed into orange oxide. The solution was regularly heated to an elevated temperature to boil off the ether, but the boil-off was not made in this particular incident. As a result ether vapors were liberated in the pot room and were ignited. Fortunately, it was a very minor explosion in the tank with little damage. There were a few windows broken and no one was injured.

More interesting to this group are the two explosions that we have had as a result of the reaction of nitric acid and ether. The first one occurred on May 4, 1946. That occurred in the startup operation at the then new refinery at St. Louis. The original production of uranyl nitrate was done on a batch operation using ether as extracting agent. In 1946, the new refinery was started to use the principal of countercurrent continuous extraction in a packed column. A one normal solution of nitric acid in ether was used as the extracting agent. There was a 150-gallon tank in the building which was used for the storage of nitric acid. The acid was pumped from this tank through a flow ratio controller and check valves into a pipe line mixer to mix with ether to make a one normal solution. During one of the shutdowns for checking equipment, a small amount of ether leaked back through the check valve into the tank. It reacted with the nitric acid and there was a very rapid pressure rise in the tank. The tank ruptured with a boiler-type explosion, causing considerable amount of damage to the transite walls of the building.

Subsequent to this, we changed the equipment. We installed an outside tank of about 400 gallons capacity for the mixing operation, and we introduced the nitric acid to the ether through a funnel that was guarded by an air break so that the back flow of ether into the acid storage tanks couldn't occur. We put a number of engineering safeguards on the tank, such as temperature alarms and controls. On the tank there were also two 14-inch vents that had light sheet metal walls brazed on to blow off in case some reaction did occur. In addition we felt that we had some safeguard in the new equipment, because we had a relatively large volume of ether and we had data to show that it takes very large concentrations of ether to get a violent reaction. After we made these changes, we operated the refinery using one normal acid-ether solution from June of 1946 until about October of 1951, at which time we stopped using acid in ether. We had found that without packing the column and by using a jet mixer apparatus neutral ether could be used instead.

After the explosion, we did some experimental work on the type of reaction that occurs on mixing nitric acid and ether. The literature reported studies of the reaction of nitric acid and ether with a view to producing ethyl nitrate. It reported that when nitric acid and ether were mixed at room temperature a violent reaction with the evolution of NO_2 resulted; no detonation but a very heavy release of NO_2 fumes. If the reaction is carried out at a reduced temperature like -15°C, ethyl nitrate can be produced by this method. When sulfuric acid was added along with the nitric acid to take away any water that might be a product of the reaction, there was a detonation at room temperature.

In view of the fact that we planned to use the one normal acid solution, we performed a series of laboratory experiments by mixing various ratios of ether to nitric acid. We started with a ratio of 1 part of ether to 100 parts of nitric acid, and we got a minor decompositon with evolution of nitric acid fumes. As the ether was increased, the amount of fumes qualitatively increased. The apparent maximum was one part of ether to 8 parts of nitric acid, which gave the most violent reaction. As the ratio approached unity of volume of nitric acid to ether, the reaction rate decreased until finally at two parts of ether to one of acid there was no good visible reaction. The plant operating conditions were about 13 parts of ether to one part of HNO_3.

We also tried to reproduce the conditions of the explosion. In an Erlenmeyer glass flask with a closed neck, ether and acid were mixed in 1:8 ratio. The flask ruptured with a fairly violent explosion due to pressure build-up from the reaction. This reaction of nitric acid with ether is quite characteristic of the other reactions that have been described today in that there seems to be an incubation period. After the nitric and ether are mixed, the first indication of reaction is the appearance of a light green color. This color darkens and finally turns to a dark emerald green; NO_2 starts to evolve accompanied by a high temperature increase (in some cases we got temperature increases as high as 50 degrees). Then the solution darkens to dark brown, and there is a vigorous evolution of NO_2 fumes. We tried the effect of temperature here, and we found that cooling the reaction mixture down below the test point (about 30°C) retarded the reaction. We found that by adding water, the reaction could be stopped (quenched).

The second explosion that occurred at Mallinckrodt was on February 1, 1951. The reaction again took place between nitric acid and ether. We had just started processing some new feeds which had given us considerable difficulty in our second extraction step in that we had gotten precipitation of uranyl vanadate. In order to get rid of the solids in the system, we'd employed a small quantity of dilute nitric acid after the system had been de-etherized. Unfortunately, one of the cleanouts was conducted using a concentrated nitric acid mixture without adequate de-etherization. This resulted again in a pressure-type explosion, which caused considerable damage to the building.

We shut down the St. Louis refinery for a period of about 10 days while repairs were made on the system. After that incident, we developed a different method for cleaning out.

Comment: I think there were a couple of incidents other than this that occurred at Mallinckrodt.

Answer: In no case did we have any other except fires. These explosions were purely a pressure-type relief - the vessel would virtually open up to vent itself, but we had no indication of any fire or any kind of ignition or flame. In each case we were able to determine that there was relatively little ether and higher quantities of acid.

Question: In the investigation of the incident, was there consideration given to the previous history of the ether, say check the peroxide content?

Answer: I'm glad you mentioned that. We have always been seriously worried about the possibility of peroxide build-up in the ether systems, and we have made a number of checks throughout the system several times. In no case have we been able to detect any peroxide concentrations that were more than 2 parts per million. For some reason, apparently contacts with nitric acid destroys the peroxide.

Comment: It was conceivable that the vapor phase did shoot; you never see that plainly. I think it is interesting to note the period of time before NO_2 appears. I don't know if that's a result of the reaction or whether it is a contributing factor.

Answer: Well, apparently the NO_2 is both a product of the reaction and necessary in the reaction. In the literature it was indicated that if precautions were taken to try to remove the dissolved NO_2 from the solution, the reaction was retarded quite markedly.

Question: I wonder in that case if the bulk of the energy comes from the vapor phase NO_2-ether reaction?

Answer: Well, I don't know. The experimental results that we found in our Erlenmeyer flask experiments were that we got a simply terrific evolution from the liquid phase of NO_2 gas, and we postulate the reaction as a complete oxidization of the ether to H_2O and CO_2 with the acid going to NO_2. The pressure of the products of the reaction simply ruptured the vessel.

Question: You didn't find that nitric acid was coming off at that stage?

Answer: No, because for one thing when this stage was reached we had a fairly high temperature and I guess we had ether boiling off. We didn't try to find HNO_3, but it's an interesting suggestion.

Question: When you speak of nitric acid, what concentrations are you talking about ?

Answer: 38° commercial acid.

Comment (M. Wahl): I think one point might be brought out that I mentioned - diluents; water is a pretty good diluent, and frequently the nitric acid concentrations can be adjusted to keep plenty of water vapor in the vapor phase to repress the explosive limits.

Comment (R. G. Orrison): Mr. Miller described the color stages that these solutions go through as the reaction progresses, like turning green and dark green and NO_2 appearing. This same thing occurs with dibutylcarbitol. In concentrated acids, this has been observed in glass piping used for introducing concentrated acids to the bottom of an extraction column through a check valve. In one of our systems, the check valve sometimes pumps dibutylcarbitol which is rising in the column back into the nitric acid line. This only occurs when the acid flow has been cut off; as long as we have a very slight acid flow, we have no leakage of carbitol into the concentrated nitric acid introduction line. When leakage does occur, this is where we get the reactions that have been described.

Comment (Pittman): I believe that I'm right in saying that the Mallinckrodt plant is the only plant that is now using ether in the AEC program. In the early days out at Los Alamos in plutonium purification, they did use ether; fortunately, we have never had one of those things blow and spread plutonium all over. We did have an ether explosion out there, but this was because somebody was boiling some pure ether; unfortunately, it was over an open flame.

Comment: At one time, if I remember correctly, Harshaw was using ether extraction.

Comment (Fernelius): We have had one explosion. A little puff came from a maintenance man who was repairing a leak in the tank and didn't watch his explosion meter while he was getting his reading. We followed the system of flooding with water and CO_2.

Comment (Orrison): I was going to say that the Y-12 plant in the early days did have some ether extraction. It was batch extraction, and it was conducted in a room that was protected by a Davis gas alarm system and a very extensive CO_2 system. But it is difficult to work in a room that is normally closed all the time: this was one impetus to changing over to another extractant (dibutylcarbitol). There were no ether explosions.

SAVANNAH RIVER PLANT EXPERIENCE AND SUBSEQUENT
EXPERIMENTAL STUDIES - R. M. Girdler (du Pont)

Editor's Note: Mr. Girdler described an explosion which occurred in an evaporator during the concentration of uranyl nitrate solutions. His talk is not included here because the same information is presented in report DP 25; May 15, 1953; Cohen, Nichols and Siddall; Interim Technical Report TNX Evaporator Incident January 12, 1953.

However, a brief summary of the incident is included for purposes of continuity.

Dummy Purex ICU solutions containing uranyl nitrate and nitric acid after contact with Amsco-TBP were being concentrated in an evaporator when the evaporator exploded. Laboratory studies showed that TBP reacts vigorously with uranyl nitrate or nitric acid at temperatures above 130°C at atmospheric pressure, and this reaction is hypothesized as the cause of the explosion.

REVIEW OF HANFORD EXPERIENCES - E. T. Merrill (G.E., Hanford)

I was asked to make some comments on the explosion in our pilot plant, building 321, at Hanford on January 23, 1949. The extent of the damage and a detailed description of the incident has been reported in documents HW-12873, HW-13812 and HW-12374.

A pump was pumping hexone as part of an equipment testing program. The pump was in a torque tube purged by air. The torque tube and pump assembly was inserted in a 55-gallon stainless steel drum and used to pump a solution of 0.5 molar nitric acid in hexone. Hexone was preferentially evaporated from the system during the first run. Not realizing this, the volume was made up again with more of the original hexone-acid solution. The second run concentrated the solution further until the acid was about 3 molar in about 14 gallons of solution. The color changes of this hexone had been proceeding for a number of days, from the original water white color through straw color, light amber, dark amber until the solution was quite dark on the observations made by the swing shift on the 22nd and the first few hours of the shift on January 23rd. The explosion ruptured the drum, tossed the pump-torque tube assembly over a wall into the adjacent cell and the 14 gallons of hexone were ignited.

Mr. Schwennesen, who was then working at Hanford, was assigned the problem of duplicating the explosion on an experimental scale. He succeeded in exploding several drums under pressure. I believe that he was unsuccessful in exploding any drums at atmospheric pressures. He also made tests with bearings and found that if hexone vapors were permitted to reach bearings, the vapors removed hexone-soluble grease eventually causing the bearing to bind with sufficient heat developed to ignite the vapors. He also found that there was a reaction which occurred at approximately the pertinent concentration in the nitric acid-hexone system and that the air purge which was passing through the solution removed the reaction products. When the air purge failed, reaction was rapidly increased until an explosion followed.

Another incident occurred in the Redox building on February 5, 1953, in the 2D column waste sample pot. Fumes of nitrogen oxides were observed coming from the waste receiver, and the 2D column operation was interrupted. The lead caps were blown off all the samplers (1A, 2D, 3B, 2A, 3A) leading to this waste header. The caps weigh about 4 pounds and the lines are 1/2 inch pipe. Investigation showed probability of the accidental presence of hexone and 2-3$\underline{M}$ nitric acid in the sample pot. The fumes of nitrogen oxides were interpreted as indicating a reaction between hexone and nitric acid.

SEPARATIONS PROCESSES ASSESSED IN THE LIGHT OF
EXPLOSIVE RISKS - J. E. Cole (du Pont)

As an organic chemist, and several of us I believe are unfortunate enough to have had that background, whenever we deal with solvents and organic materials in general we are accustomed to a certain amount of hazard with regard to explosion and fire. This is true of producing organic chemicals in general. We expect to take a certain amount of risk with respect to fire or to something that approaches explosions. I don't think there's any major organic manufacturer in this country who hasn't had to deal with that in planning his plant. And if he has run it any length of time he has had to deal with some consequences of taking those risks.

When the Atomic Energy business started back during the war, the mystery of handling radioactive materials and the respect with which they were held made those concerned with plant design at the time plan the best they could to at least avoid that hazard. The assumption was made that if you were to use solvents and organic chemicals, generally you would be certain to have some kind of a dispersal type of fire or explosion and that this would very probably make it impossible to use the plant, at least for long periods of time.

This was certainly sound thinking at the time. If it were possible to apply that philosophy indefinitely I think it could still be a sound principle. The problem, of course, at that time was to get the minimum amount of plutonium for Army considerations and to be sure of getting it on time. Consequently, this sort of delay or shutdown type of risk which we had to take with solvents just seemed to be out of the question. We even considered it to have been poor judgment to fool around with that formic acid and immediately got rid of it after having had the experience which was mentioned at Oak Ridge. Therefore, any of the processes which were seriously considered early in those days were the precipitation type - such as bismuth phosphate process which was handled at Hanford and the lanthanum fluoride process.

But to be perfectly frank about it, these were not complete processes, and after the war the necessity for continuing this business made the problem of uranium recovery become more important. The chemistry of uranium and the historical methods of separating and purifying it led one to turn immediately to solvent extraction processes.

In the studies which were made during that time, I believe that there was only one precipitation-type process which was seriously applied to uranium recovery and that was the so called UAP process worked out by Carbide at K-25. If one were to link that with the bismuth phosphate process, it is possible to recover both plutonium and uranium without resort to solvents in the highly irradiated state. You would still have to resort to solvents

after you get rid of bulk fission products, I believe, in order to get a real good feed for K-25. I simply mention that as a matter of record to point out that there is at least one way of dealing with this problem without having to go through the solvent systems. However, there are some disadvantages to that. One of which is that I believe it was pretty well demonstrated it can only be done on cold waste, that is, based on an inventory hold-up as storage of uranium waste which would probably be three to four years. Secondly, it has an extremely high-volume in terms of solids - a waste producer. I believe the third one, perhaps minor, is that the yield of uranium is somewhat low.

Now, of course, the other solvent processes which were studied at various places since the war - they all depend on the ability to complex both uranium and plutonium; and of course there are different separation characteristics under oxidation or reduction conditions to separate them; so far as the plant man is concerned, operation-wise they're all about the same. The so-called Redox formulation which involves hexone and the Purex process employing TBP are typical examples.

At the time we came back into business in '50, we were reconciled to the proposition that a solvent extraction process, with the knowledge available at the time, was the best technique in the separations business. When we made that decision we made it recognizing that there were certain risks with a solvent process that did not exist with a precipitation type process, but that the advantages offset the safety disadvantage. Fundamentally, when we made that decision we had to reconcile ourselves to the fact that we could deal with a process of this sort by methods of remote maintenance and still keep an operating plant and at the same time the process would not be prohibitively dangerous with respect to the surrounding community.

Now let's review that just a minute. When you build a reactor installation there are certain community hazards which have to be taken into account. To offset them you buy land. This doesn't apply so much to an experimental installation, but for a production installation you buy land. Now you accept the hazards with respect to the reactors, and these hazards are much greater than one sudden flash of 90-day old material of one charge through the separation plant. The controlling factors depend on the reactors and not the separation plant. So all you face is a shutdown time long enough to clean up. This can be accepted with very strong confidence that you are not exposing the community outside the boundaries to a situation which can become intolerable. So it's purely a matter of operating expense. It is fortunate in one respect dealing with this type of plant that you always have to have a heavy enough gamma shield so that your personnel could not be particularly exposed to the risks which one takes in the organic chemistry industry all the time.

The decision first (on the part of Hanford, I believe) to go to a solvent process, I think represents the maturity of their thinking with respect to their ability to deal on our remote maintenance basis with problems of this sort.

I'm quite certain it does not represent their fundamental belief that they would never have an accident. Because while, it's possible to assess the areas where you can stay out of trouble, it's impossible having once put together nitric acid and organic compounds in the same plant to guarantee somebody won't make one or more mistakes so as to pile those things together in an incompatible way. I do not know of any chemistry or a change in process chemistry which is going to remove that risk as long as we stick to extraction processes. The type of thing that Ward Alter talked about, for example, is the type of thing which can set routine operation techniques farther and farther from the borderline of danger, and there are other things which equipment-wise can be done to put into the distance and make more improbable an error, but I think in this business we might as well face the fact that we are in the organic chemical business to a degree and be prepared to accept incidents of this kind and to provide for them by doing two things - first of all, protect plant personnel and second minimize the down time of the plant. I'd also add a third, to protect outside personnel.

Statement: I'd like to add one thing to your point about the possibility of using precipitation methods for both uranium and plutonium recovery. You indicated several objections. There's one additional objection that you did not mention and that is the rather large cost differential between both construction and operation of the solvent extraction type as it has turned out versus the precipitation.

Answer: I deliberately didn't talk economics, but limited myself to talk about safety here.

Statement: There's another fact there: we're faced with quite valuable material that can be scattered around. The cost per unit weight really gets pretty high, which might affect the economics.

EFFECTS OF EXPLOSION HAZARDS ON SRP PROCESS
AND PLANT DESIGN - J. E. Cole (du Pont)

Editor's Note: Dr. A. J. Hill, du Pont, was scheduled to speak on
this subject. He was unable to attend the symposium and Dr. Cole
offered to present the information.

I'm sure that I can't give this in as much detail as Dr. Hill would,
but I think I can give some of the high spots of it. In the basic planning for
the separations plant at Savannah River we took into our original design
planning certain safety features and plans because we were using a solvent
process. After our experience at TNX and the subsequent study of the prob-
able mechanism of that difficulty, we have made some further plant changes
both in design and process. So I will give you some of the things which were
in the original plant design and then go to the changes.

First we selected a kerosene (diluent) with as high a flash point as we
could get, and I believe that we have selected a pretty good one. We had re-
quirements for transfer of liquor from one place to another with minimum
temperature rise. We have found that while it's possible in all cases to use
steam jets, they sometimes give too much temperature rise to be comfortable;
so we've made provisions to hold that down. We have installed a high capacity
ventilating system for the building as a whole, so that the ambient temperature
in the process area would not go higher than about $100°F$. We have provided
off-canyon air filtration very much like Hanford has. The tanks are individu-
ally and separately ventilated to a separate header so we would not expect to
carry a very large increment of radioactives into the main ventilating air
stream; hence, we might have done without the off-gas filtration. We didn't
do without it, for we felt that even one flash fire might put such a load of par-
ticulate matter carrying plutonium or fission products that it would cause a
serious off-site trouble or at least contaminate the area. We would like to
have built our process area without cell construction, that is, isolation be-
tween one area and another. We could have done it so far as shielding was
concerned, but in view of keeping down the over-all process equipment risks
we have isolated the process area in cells. It is not exactly cell type con-
struction because the partition walls are not meant for gamma shielding, but
at least they are strong enough for fire shielding. Then, in case we do have
a fire, it would be isolated in a relatively small process area. We provided
sprinklers throughout the process area. We have two types of control, one
the so-called "Fire Eye," which we believe is a very satisfactory type of
automatic sprinkler. It will take hold in case of just seeing a fire rather
than waiting until the heat melts out a plug. We have manual control over
some of the sprinklers too. Then process-wise (and I won't go into this in
detail) we have tried to do a good thorough job of instrumentation on all our
process equipment.

The studies which were made after the TNX incident brought out to us one very practical thing that we could do which would eliminate the chance of that kind of an incident - limit the steam pressure on our heating coils. This we are doing and it's a relatively small design change. We, therefore, can continue on about the same flowsheet, and as far as that particular problem is concerned we can be pretty confident that no matter what the operator does he can't get enough steam (about 30 lbs.) to give him a temperature high enough to initiate this type of reaction. This change involves a little more evaporative capacity - I believe we're putting in one more evaporator. In reviewing the evaporation problem we changed location of one or two evaporators and took them out of the high level canyon. This was because they were essentially evaporating uranium nitrate and with low enough concentrations of fission products that our problem was not any worse than anyone's who denitrates uranium. This is the case only for interstage evaporation. Denitration in our case, and I think it's generally true in industry, will only come after the uranium is well decontaminated. We propose to do that outside the canyon, of course, with some (essentially structural) shielding and open to the air rather than enclosed.

Now there's one point where at the moment we have made a process change: to run the plant without evaporating acid, taking the penalty of increased waste volumes. I hope that the change is only a temporary one. The incident at TNX only served to wake us up on this point, although it does not apply exactly since we're pretty well convinced that the incident was caused by evaporation of uranium nitrate in the presence of TBP. However, the whole question of evaporating nitric acid in the presence of phospho-organics makes us want more carefully to study the possible conditions we might have in the evaporation of acid wastes. As a hedge against that, we have the process that Alter's talking about, and KAPL has done a very nice job on that. I believe that our further work on the characteristics of this system coupled with possibly some changes in process along the line Alter's talking about will enable us to carry out some evaporation or at least to reduce the volume of waste in line with our original intent. This change sounds rather simple, but if you were to ask our design engineers they would say it was an enormous one. But then you can't change a valve from 2 inches to 1/2 inch now without its being a major matter; so we are planning to build on our present flowsheet before we make any other changes.

Comment (Alter): There's another step which has been eliminated and that's the concentration coupling of plutonium. One of the alternate processes that was considered for concentrating dilute plutonium to a final product suitable for peroxide precipitation was simply taking the dilute product (which was also dilute in acid) and evaporating it by as much as 500 fold to constant boiling nitric acid, driving to a final concentration of about 1 mol plutonium in 10 molar nitric acid. This solution, of course, would have solvent phase in it. We did quite a bit of laboratory work on this reaction and noticed that if it was only soluble TBP in the stream that we we're evaporating, it flashed

off at the start of the evaporation and we got no trouble; but if there was en-trained TBP in this material, it could run into trouble. We didn't have any explosions, but we did notice that in a semi-continuous or pot type of evap-orator with a constant heel that every time we fed in a charge of dilute ma-terial from a run in which there had been entrained organics we got consid-erable foaming. It is my belief that this was due to a nitric acid-organic reaction which was controlled only by virtue of the fact that we were feeding in small quantities at a time. This step has very logically been removed from the canyon.

Answer (Cole): I didn't mention that because we removed that for other reasons before the incident.

Question: When you (Alter) were doing that, did you find that if you were to stop a continuous run and continue as a batch that the foaming would subside?

Answer: Put in a shot of material, it foams, then it subsides. Put in another shot and it foams again.

Comment (Feder): In your reference to so-called general assessments, you pointed out that in the organic-nitrate systems one is taking calculated risks which essentially you feel will pay off. We have been, at Argonne, doing some thinking along the lines as to what sort of insurance we really need in case the calculated risks do not pay off. We have followed this reasoning by going to the Halex type process where carbon tetrachloride substitutes for the hy-drocarbon diluent; one can reasonably have assurance that the fire hazards from solvent alone can be eliminated. One is still left with the fact that the nitrate is the oxidizing agent capable of setting carbon detonations or "pop" type explosions. The alternative it seemed to us was to look at non-nitrate systems. This gets a long way off, of course, from anything you can do in present day equipment, so we're putting some effort looking at the chloride systems with a flowsheet very similar to the Purex. The separation works in a chloride system. There aren't too many major changes that one has to make, as the chemistry is fairly straightforward. A chloride system Halex process would be reasonably safe from the standpoints of the possible risks. Whether engineering-wise this would pay off is another question, but we felt that it was at this point not worthless to put in some effort to have that in-surance behind us.

Answer (Cole): Facts were given me and I have a note here on it. I don't think I said anything about it, but I ignored the volatility process altogether.

Statement: This is still solvent extraction -

Answer (Cole): I understand that, but I should have mentioned the volatility process because after all they don't suffer from the same fundamental difficulty - they have some others, which eliminate the system at least as

far as our consideration was concerned and so I just skipped it on the notes entirely.

Statement: I think it's interesting to point out that historically the choice of nitrate medium versus chloride mediums for various separations processes was based on not too large difference in corrosion rates on common materials of construction. This is a factor which nowadays we aren't inclined to give as much emphasis. We're not thinking of building tanks that last a thousand years subject to corrosion you'll encounter. So historically this might have gone to entirely different routes except that the very early decision to go to nitrate.

Comment: I would like to add as we are required to go into installations processing large quantities of plutonium, for example, the risks that Dr. Cole mentioned are greatly increased. Also, changes in fuel element composition can dictate starting with something other than nitric acid too. It is not too early to consider alternative aqueous compositions.

ENGINEERING DESIGN CONCEPTS OF THE REDOX AND PUREX PLANTS
AS RELATED TO EXPLOSION HAZARDS - E. T. Merrill (G. E., Hanford)

The special features of the Redox plant were primarily designed for the complete removal of solvent ignition hazards by going to explosion-proof motors and the use of equipment that would not create sparking or ignition, eliminating as much as possible moving parts in solvent systems. We do, however, have one hot zone organic pump and one cold zone organic pump because the head requirements preclude using jets. All concentration steps where there is a possibility of the existence of hexone are preceded by a stripping operation which removes well in excess of 99 per cent of the dissolved hexone plus of course any second phase. The instrumentation is adequate to follow these stripping operations, and in addition the design rates are such that the instrumentation isn't essential. The temperature in the evaporators falls very rapidly if azeotropic conditions in the vapor are approached, which would mean that the aqueous phase is approaching the condition of saturation with respect to the organic. We always operate in the region where this azeotrope is not present - we have a large excess of steam.

The Purex plant will also include steam stripping prior to final uranium concentration. Intermediate concentration steps do not use a steam strip; however, steam jets used to lift the solution up into the stripping section of the concentrators have the same effect to some extent. The concentrators for the final step and the intermediate steps are identical, but the stripping sections are used for de-entrainment in intermediate stages.

In the acid recovery portion of the plant, the stripping is not readily possible because the waste is stripped in the reflux. The entering solution travels down against the vapor flow, and this will reflux acid into the bottoms and raise the acid concentration. In this case, we depend upon adequate second phase removal and the flashing-off phenomenon that (Wagner) described when the waste is introduced into the evaporator. The uranium solution will be concentrated only to 60 per cent, rather than to incipient calcination, and this solution will be transported to our present calcination building where the final steps will be taken. In the event that stripping does not work and organic is carried over into the final receiver, our method of transferring the solution out of the building acts as a decanting mechanism and leaves the organic in the Purex building, where it is intermittantly cycled back through the solvent system for recovery. The calcination building is also equipped for decanting if necessary. It should never be necessary but in their present location adjacent to the metal recovery process they are required to make a decantation for the metal recovery building in case solvent is inadvertently sent through.

Question: You say that you have a more or less automatic decanting when you're transferring 60 per cent material to calcination. If you should get a third phase, it seems to me you could be in trouble.

Answer: Possibly.

Question: Is the third phase normally material with specific gravity of 1.67?

Reply: You would expect it to be from 1.3 to 1.45.

Answer: Then I think we might be able to separate it.

Question: Have you given any consideration to lowering steam pressure to the evaporators and hot canyons?

Answer: The steam is reduced to 100 lbs. in the building mains. We intend to use 100 lbs. steam; but if sufficient need be shown, why it's just a twist of the wrist to reduce it to lower pressure.

Comment: Well, we feel that this is pretty strong insurance against the type of thing that happened at Savannah River, and I don't believe that you will be penalized too much heat transfer-wise.

Answer: The concentrators are sp.g. controlled and we cannot visualize any steam demand that would bring the temperature to above that necessary for explosion. The solutions boil at 105°, and it is difficult to visualize these high temperatures because the sp.g. would cut off the steam. We also have such instruments on the steam lines which are to be watched by the operators.

Question: I realize the Redox plant is blanketed with nitrogen because of the low-flash point of the solvent. Is this considered necessary for the Purex plant?

Answer: No.

Question: Would you say your decision to steam strip the uranyl nitrate was motivated more by the foaming problems than by fear of possible explosion hazards?

Answer: Almost entirely by the foaming.

Question: You have not had any incidents with TBP in denitration, regardless of how minor they might have appeared to be?

Answer: We had one that I know very little about. We tried almost every conceivable way to eliminate this foaming problem. One of the things we tried was water injection into the pot - sprayed on top of the foam and this met with some success. I never was sure whether it was cooling which just slowed things down or whether it actually had an action in breaking the foam. On one occasion we had a pot that was foaming quite badly; the foam began coming out around the lid onto the floor. An operator couldn't get up to manipulate the valve, so he grabbed a water hose on the wall and squirted it on the pot. The

temperature of the pot was about 165 C, and there was a little poof. It was completely contained. I don't know whether it was a chemical reaction or whether it was the flashing of the water when it hit the moderately warm melt in the pot.

Question: Did this happen after you put in your steam stripper?

Answer: I don't know when it happened.

Question: From your observations on this foaming problem would you say it is possible that foaming and explosions can be caused by different degrees of the same thing - concentration of material?

Answer: It's possible - it never occurred to me until (Alter) mentioned it. Foaming can be caused with as low as 200 ppm of dibutyl phosphate. It doesn't seem to me that can be the same type of thing as an explosion. This seems to be more of a surface action.

Question: And that's the reason you always took this as a surface action?

Answer: Yes.

Comment: We can strip the TBP, but the DBP will not strip.

Comment: There's something else. In the early days of metal recovery when we were getting foaming, I understand that there were several charges which actually contained at least a second phase of TBP and I also understand that there was no particular explosion hazard connected with the denitration of this material. I was wondering if that tied in with (Wagner's) observation that the minimum percentage ratio of TBP to UNH was necessary before there is this temperature rise? It was a relatively small quantity compared to the uranium itself.

Comment: You realize that we have a relatively small charge and when this foaming - when we were working on this foaming problem, we were really having trouble, I mean it was strictly a baby-feed proposition. The operator was right there and as soon as the charge started to come up, he cut the heat and played with it until he could work his way past. This foaming occurred in the range of 140 to 155 degrees.

Question: There is a point beyond that at which time you can pick up your heat again?

Answer: Yes, once we got past this temperature, we were still in the melt phase and then we would get into the calcination proper.