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Hydrocarbons Tech Center Reactive Chemicals Handbook

INTRODUCTION

Following is the 1995 edition of the Hydrocarbons Tech Center Reactive Chemicals Handbook which has been compiled over recent years utilizing know-how based upon many years of Dow manufacturing experience. Every effort has been made to provide useful and accurate information so as to enhance training for new and experienced Hydrocarbons personnel. Both basic chemistry and incident summaries are included. Contributions of additional information to existing or new sections of the handbook are welcome and encouraged.

Reactive chemicals incidents occur many times due to operating outside of design conditions, other times due to inadequate design stemming from an inadequate knowledge of the process. This handbook is designed to eliminate reactive chemicals incidents through education so read on and remember.....

what you don't know CAN hurt you!

Brian Allison
Hydrocarbons Tech Center

5/26/95

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ACETYLENE/ACETYLIDES

Acetylene and numerous acetylenic compounds have a history of being able to decompose with explosive violence. As a group, these materials are known to be sensitive to heat, impact and electrical or frictional sparks. Pure Acetylene will decompose into its elements at a pressure on the order of one atmosphere. Compressing acetylene becomes a dangerous operations unless special techniques are used. When liquified or solidified, acetylene becomes an explosive of some commercial importance. They are one of the few commercial explosives which contain no oxygen or nitrogen.

The vapors of these acetylenic compounds are very flammable. Their vapor-air explosions can and do propogate from deflagrations to detonations over a wide range of compositions.

Acetylene reacts with copper to form the explosive copper acetylide. Please see the attached CRI report on this subject.

Incidents

Union Carbide - Texas City: A butadiene finishing column on total reflux exploded. It was concluded that vinylacetylene reached a concentration of approximately 60% between trays 10 and 15 because light fractions were leaking overhead. Temperature and pressure was sufficiently high enough to cause decomposition.

Precautions

Distillation columns containing acetylenic compounds should not be placed on total reflux. A bottoms draw-off must be maintained. These systems must be carefully studied to avoid unstable concentrations.

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FILE NUMBER

LABORATORY REPORT CODE: LAD 587

DATE ISSUED: December 31, 1980

DEPARTMENT: RESEARCH & DEVELOPMENT

LAD. NO. | PROBLEM NO.

POTENTIAL ACETYLIDE FORMATION IN COPPER SAMPLE LINES

4 PAGES IN FULL REPORT

Manuel Bonds

AUTHOR'S SIGNATURE

This report is: ☐ INTERIM ☒ FINAL and mainly: ☐ NEW ☒ REVIEW

DESCRIPTIVE SUMMARY OF CONCLUSIONS:

SUMMARY AND CONCLUSIONS

Explosive copper acetylides may form on copper and on brasses which contain 50% copper or more, when surfaces are exposed to acetylene under certain conditions. Clean metals require moisture for acetylide formation. None is formed in dry acetylene. Oxidizing agents, acidic conditions and nitrogen inhibit acetylide formation. Studies have shown that up to 300 ppm concentration of acetylene in contact with pure copper tubing over a period of 12 years does not produce a hazardous condition.

Also, a copper tubing sample line analysis indicated a low or safe amount of acetylides in a line containing on the average of 1000 ppm acetylene and in use for several years. These studies indicate that copper may be safely used in light hydrocarbon systems containing up to fractional percent concentrations of acetylenes.

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INTRODUCTION

It is known that acetylene forms explosive compounds with copper. These compounds are called copper acetylides, and are liable to decomposition under thermal or mechanical shock. Because of the interest in safety questions related to the use of copper and its alloys in sampling systems handling acetylene mixtures, a literature study has been done. The information needed is concerned with conditions under which acetylides may be formed on metallic copper and copper alloy surfaces. It is necessary to consider the possibility of such formation not only on the clean metal surfaces, but also when these surfaces have become corroded or contaminated by exposure to acid, alkali, moisture and atmospheric attack.

The Chemistry of Acetylides - Acetylene ($HC{\equiv}CH$), is unique among hydrocarbons in that the lone hydrogen attached to triply bound carbon is acidic and replaceable by metals. When acetylene gas is passed into a solution of cuprous ammonium hydroxide, a reddish brown precipitate of cuprous acetylide is produced. Both acetylenic hydrogens are replaceable by univalent copper atoms; an alkyne of the type $RC{\equiv}CH$ gives a monocopper derivative. Silver acetylides are similarly precipitated from an ammonical solution of ver nitrate.[2]

ylides are also prepared by the action of metals or metal compounds on c bon at high temperatures. Alkali and alkaline-earth acetylides are relatively stable, but most heavy metal derivatives are thermodynamically unstable and may explode when dry. They are readily decomposed by dilute acid and release acetylene under such conditions.[3]

Cuprous acetylide is an amorphous red powder which is an explosion hazard when shocked or exposed to heat. It reacts vigorously with Br_2, Cl_2, and $AgNO_3$.

Acetylides explode readily and are one of the few commercial explosives which contain no oxygen or nitrogen. Their explosion produces no gas but simply is an effect of the large amount of heat, instantaneously produced. They are in a class with the fulminates and the azides as primary detonants.

Because these materials are so sensitive to shock and temperature, they must be handled with extreme care. They must be kept cool and if they are to be stored, should be kept wet.[4]

Review of the Literature - Scheiber and Reckleben investigated the action of crude and purified acetylene on copper and a number of its alloys. They found that pure dry acetylene gave no action within a period of 20 months, t test specimens being unaltered in weight or appearance. Pure wet acet ne caused 1.6% increase in weight in the case of a copper specimen . Crude wet gas caused the copper to blacken and to increase in weight by 5.2% within 6 months. No explosive material was detected, however, nor was it possible to detect more than small amounts of acetylide.[5]

The occasional spontaneous decomposition of C_2H_2 in cylinders is initiated by Cu_2C_2 formed in the valve springs under the influence of soldering flux residue. Pressure-gage springs from acetylene cylinders (one from an exploded one) were investigated. By x-ray analysis or by electron diffraction the following corrosion products could be found in the bourdon springs: CuCl, $3\ Cu(OH)_2 \cdot CuCl_2$, Cu_2O, $4Zn(OH)_2 \cdot ZnCl$, and SiO_2. Elementary carbon and Fe_2O_3 could also be identified through color and chemical behavior.[6]

In a seven month study, the formation of Cu_2C_2 upon the surface of pure copper with both pure dry C_2H_2, and with moist acetylene was found to be extremely slow. The thickness of the acetylide layer reached 1.6 μ with moist acetylene and 0.16 to 0.4 μ with dry acetylene.[7] The basic problem with handling acetylene in copper sample tubing is the formation of copper acetylides on brass fittings, valves, lines, etc. The presence of NH_3, H_2O, and CO_2 further acetylide formation. It is probable that copper carbonate contributes to the formation also. Basic copper compounds are particularly reactive. Oxidizing, strong acid conditions, and nitrogen [illegible] bit formation.[8]

[illegible]er acetylides are only explosive when dry. The amount and explosiveness of the acetylides decrease with decreasing copper content of the alloys. If work has to be done on equipment known to have these deposits, the equipment should be thoroughly wetted down if it cannot be cleaned up immediately. The best material for wetting down equipment and keeping it wet is a calcium chloride brine. The best and most economical method for removal of copper acetylides from equipment is by cleaning with dilute hydrochloric acid. In-place acid cleaning will eliminate the hazard of copper acetylides explosions upon equipment dissassembly or removal.[9]

Experimental

It has been shown at the Texas Division Light Hydrocarbons I Plant that a ¼" copper sample line over 200' long and containing an average of 1000 ppm acetylene held a low or safe amount of acetylides after several years in service.[10]

In addition, laboratory data has been generated from a section of ¼" copper sample line from the Louisiana Division's Light Hydrocarbons I Plant which had been in service approximately 12 years. Highest concentrations of acetylene in the system ranged from 200 to 300 ppm. The concentrations of acetylides detected were extremely low and ranged from 0.06 ppm to 0.09

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* SUMMARY ONLY

Butadiene Explosion at Texas City—2

A company team representing the Operating, Engineering, and R&D Departments was assigned the job of finding out what happened, and what to do to prevent a recurrence.

R. H. Freeman, and M. P. McCready, Union Carbide Corp., South Charleston, W. Va.

THE FORCE OF THE EXPLOSION AT THE TEXAS CITY COMplex fragmented the lower portion of the column shell; that is, from the skirt-to-shell weld to the elevation of the 33rd tray, an overall height of 52 ft. Approximately 40 trays were torn apart and blown free of the column shell. The tray sections and pieces of the column shell were strewn over a wide area surrounding the center of the explosion. Most of the debris was located within 500 ft. of the refining column. The remaining portion of the refining column, approximately 100 lineal ft. of 90 in. ID shell and the associated trays, fell to the east. Hydrocarbons from the refining column, and from other operating equipment which had been ruptured by shrapnel, contributed to the ensuing fires.

Fortunately, there were no fatalities or serious injuries as a result of this explosion. However, the control building, the nearby residential area, the olefins unit itself and, of course, the butadiene refining facilities, sustained damage of varying severity.

A joint-effort investigation of the explosion has been conducted by Union Carbide's Operating, Engineering, and Research and Development Departments. The information gathered in the various phases of the investigation has been successfully correlated, and a plausible explanation of the cause and mechanism of the explosion has been formulated. In addition, this group worked with others to define a safe mode of operation for all butadiene refining facilities in the corporation. The overall conclusions and recommendations are contained in the third article in this series, based on information presented in all three articles.*

The Engineering Department has been involved both in the reconstruction effort at Texas City, and in the investigation to determine the cause of the explosion. This article describes the Engineering Department's contributions to the investigation, which include examination of the physical evidence, and calculation of the process conditions which existed at the time of the explosion. The conclusions derived from this phase of the overall investigation are stated, and they are reinforced by the results of the other phases of the investigation as reported in the other articles in this series.

Investigation of physical evidence

Refining column shell—After the explosion, some time was spent in collecting, marking, and identifying the debris. The column shell pieces were separated in a special area for further study. To aid in the identification of pieces, and to serve as a framework for the paper reconstruction of the column, a drawing, a projected view of the inside surface, was made of the lower 60 ft. of the refining column.

The pieces of column shell were physically examined to identify their location on the drawing. Characteristics such as shell thickness, clip type and location, shell weld seams, tray ring welds, downcomer welds, and insulation rings, allowed positive identification of all large fragments and many of the smaller pieces. Once identified, the shell pieces were measured, and

*See note on the bottom of page 51.

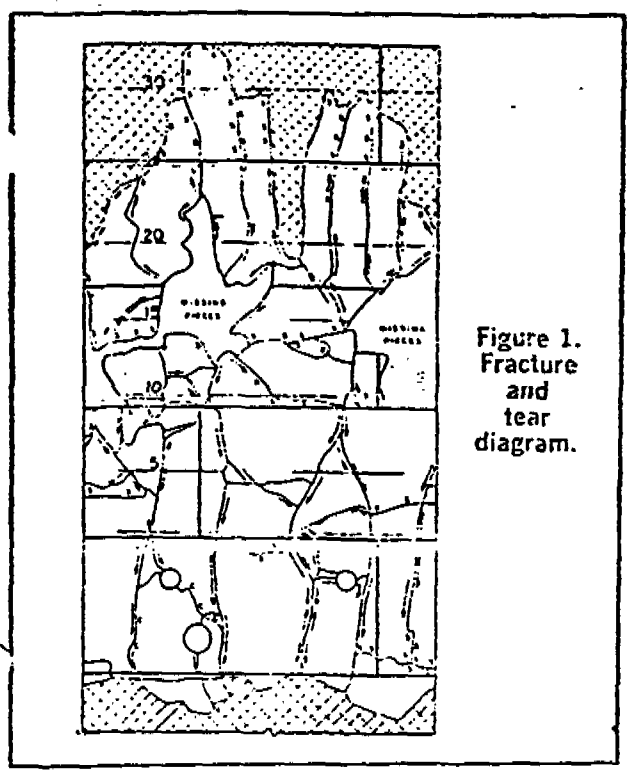

Figure 1. Fracture and tear diagram.

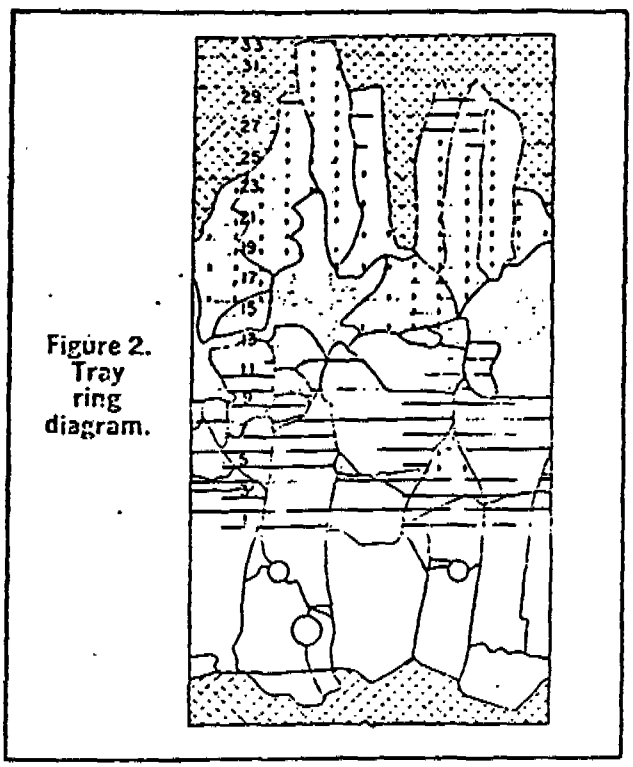

Figure 2. Tray ring diagram.

their shapes reproduced to scale on the drawing. The result is the fracture and tear diagram, Figure 1.

Approximately 90% of the separated shell pieces were found and located on the drawing. The low recovery of pieces in the ⅜ in. thick shell ring No. 3, and the relatively small size of the pieces found suggest that the most intense force prevailed in this area. The crosshatched areas at the bottom and top of Figure 1 represent shell plate not fragmented. The bottom section consisted of 8- to 10 ft. of the skirt that had remained attached to the column foundation. The upper crosshatched area represents a portion of the upper 100 ft. of column shell which remained intact.

Further examination of the shell fragments confirmed the location of the explosion. The torn edges of many of the fragments exhibited chevron marks, while other edges were smooth and in a few places showed evidence of a slight thinning by drawing. The appearance of the edges of the fragments is an indication of the speed and direction of fracture. A rapid crack propagation in the range of 2,000 ft. sec. and above is termed cleavage. Cleavage fractures leave chevron markings on the edge surface which point back to the origin of the crack. Conversely, a low rate of crack propagation is termed shear. Shear failures occur at rates less than 500 ft.. sec., and may show thinning of the material adjacent to the edge. Fractures that propagate at rates between 100% shear and 100% cleavage may exhibit characteristics of both (*1*).

The results of the examination of the fragment edges are shown in Figure 1. The arrows indicate the direction of shell fracture as evidenced by chevron markings. The letter "S" refers to fractures that appeared to have undergone shear failure. The letter "C" indicates chevrons that did not positively show the direction of tear. The few edges that showed no indication of either the type or direction of failure had been severely damaged by hitting other objects.

The fact that the shell tore both up and down from shell ring No. 3 centers the maximum intensity of the blast between the 10th and the 18th trays. The high incidence of shear between the 25th and the 33rd trays is explained by the fact that the fracture stopped in this region.

Trays and tray rings—During the initial cleanup of the area, many tray sections from the refining column were collected and removed to the salvage area for further examination. The examination comprised a count by section type, and an evaluation of the direction of the explosive force on each section (*2*).

Severe distortion of many of the sections made it impractical to distinguish among all section types, but many pieces could be identified with either a side downcomer deck (odd numbered trays) or a center downcomer deck (even numbered trays). In all, 39 trays were accounted for, out of the 43 blown free of the column, with 85 percent recovery of the sections.

Tray sections which had constituted the bubbling area were examined in detail to determine whether they had been deformed by an upward or downward force. Of the sections examined, 95% appeared to have been subjected to an upward force. This points to an origin of the blast below the bottom tray.

Tray support rings had been attached to the inside of the column shell at 12 in. spacing throughout most of the fractured area. Each shell piece was examined to determine 1) if tray rings remained or 2) if missing, whether the weld metal remaining showed which way the tray ring broke off.

The results of the tray ring examination are shown in Figure 2. The wide bands superimposed on the lighter tray ring outlines represent ring segments that remained attached to the shell. All other tray rings were missing, and in many cases the direction of tear could be determined. The arrows on Figure 2 show the direction of tear as evidenced by a shear lip produced by drawing of the material.

In the lower part of the remaining column section

(tray Nos. 23 to 26), the trays had been torn from the rings, and the rings bent inward. The shearing of ring A between tray Nos. 11 and 12 probably was caused by a pressure surge that caused the trays to move up the column like a piston. A "stack" of tray sections in the remaining column is shown in Figure 3. It is significant that the rings remained attached to the shell pieces below the lower tray. This and other evidence is evaluated later in this article.

Reboiler and manway cover—The butadiene refining column was provided with two, vertical, natural circulation reboilers heated with 15 lb./sq. in. gauge steam on the shell side. Only one reboiler was in service at the time of the explosion; the other was isolated by shutoff valves.

The force of the explosion ripped both reboilers from the column, and the mitered heads on both reboilers broke free of the shells.

The operating reboiler (tube sheet to tube sheet) appeared to be in good condition externally. When the shell was cut away, however, five ruptured tubes were discovered, one of which is shown in Figure 4. The tube wall at the ruptured edge was thinned, indicating that the reaction causing the rupture was slow enough to permit yielding. The vapor return mitered head from the operating reboiler is shown in Figure 5. The head showed little damage, but the flange that mated with the tube sheet flange had been deformed as though by a severe overpressure.

Deformation of the manway cover from the base of the column is additional evidence of an overpressure [illegible].

Calculations were made to estimate the pressures which were attained in the system (3). The minimum burst pressure for the reboiler tubes was calculated to be from 6,500 lb./sq. in. gauge at 120° C to 2,300 lb./sq. in. gauge at 600° C. The minimum yield pressures of the mitered head flange and the manway cover were estimated to be 2,000 lb./sq. in. gauge at 120° C. The shell plate which fractured would have had a minimum burst pressure of about 1,650 lb./sq. in. gauge at 120° C.

The butadiene refinery column was fractured by a high-energy reaction between tray Nos. 10 and 18. Two physical observations substantiate this statement:

1. Chevron markings on the fractured edges establish that the shell tore away from this region.

2. This area is characterized by a high proportion of missing pieces, and by fracture into comparatively small and severely damaged pieces.

The location of the intense blast, however, does not pinpoint the overall mechanism. It is theorized that a reaction originated in the tubes of the operating reboiler. This reaction had sufficient energy to rupture the tubes, and resulted in a pressure and temperature surge in the base of the refining column. The pressure surge was sufficiently slow to permit deformation of the reboiler mitered head and the column manway cover. The lower trays were lifted off their rings sequentially. Between tray Nos. 10 and 18, the combination of pressure, temperature, and composition led to a detonation. The data and physical evidence support the theory. In particular:

1. The theory explains why tray rings were left attached to shell pieces from the lower column (see Figure 2). Unless the lower trays were out of the way, a detonation at tray Nos. 10 to 18 would wipe out the lower tray rings by the same piston action that was evident above the detonation area. In addition, there [illegible] evidence of downward deformation of tray sections.

2. The yielding of the reboiler tubes indicates relatively slow shear failure. Conversely, the column above was fractured by fast cleavage failure with little evidence of yielding. Two separate events are indicated: one slow, the other fast.

3. The yielding of the manway cover and the reboiler mitered head flange indicates initial pressures above 400 lb./sq. in. gauge, but because the shell did [illegible] pressure was less than 1,000 lb./sq. in. gauge prior to detonation.

Calculation of process conditions

Analysis of operating data—Following the explosion, operating data were made available by the Texas City Operating Department. These data, which were used in this portion of the investigation, are as follows:

1. Information extracted from the process computer for October 23 (1)

2. Charts recovered from the trend recorders for October 23 (1, 2, 6)

3. Instrumentation, instrument readings, and hand-valve positions at 7:27 p.m. on October 23 (7)

4. Typical refining column system operating conditions and analyses (5)

These data indicate that the refining column system

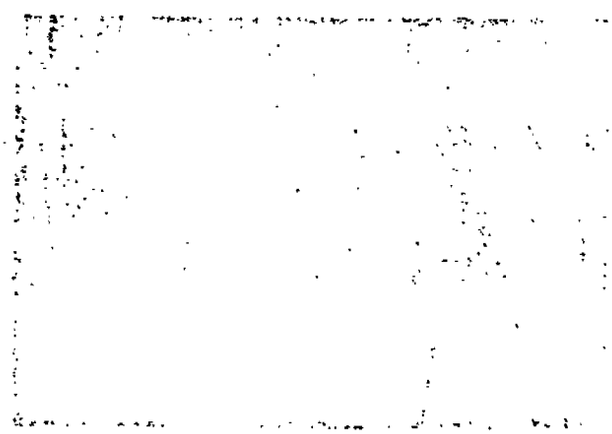

Figure 3.
Stacked trays in the remaining column.

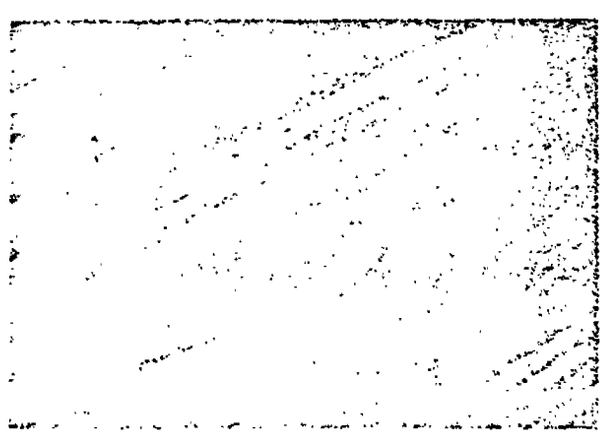

Figure 4. One of the ruptured tubes in the reboiler operating at the time of the explosion.

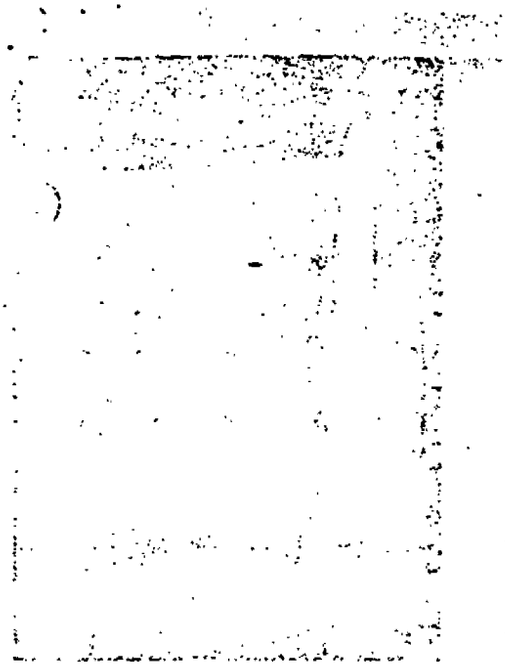

Figure 5. The mitered head flange from the operating reboiler.

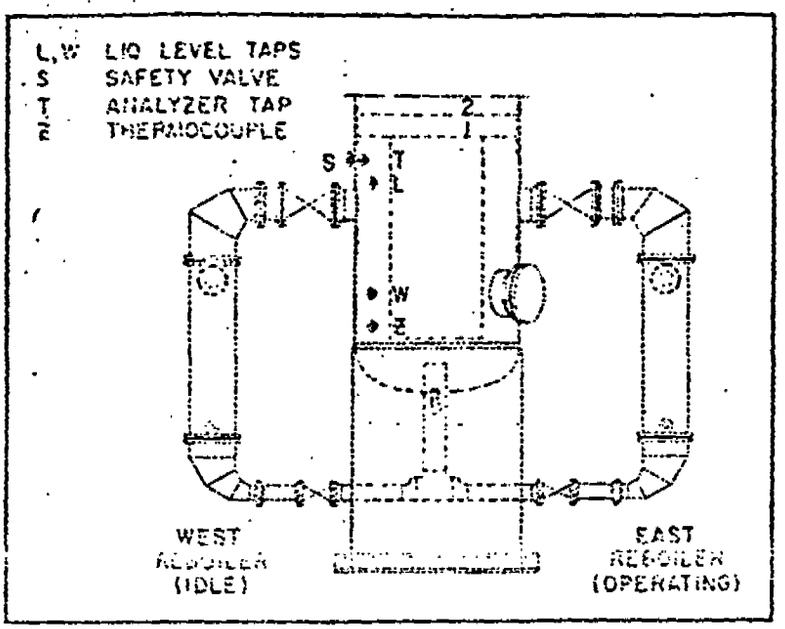

Figure 6.
Refining column base elevation.

operated normally until 11 a.m. on the day of the explosion. At that time, the refining system was placed in a standby condition, with reflux on the column, in order to perform maintenance elsewhere in the unit. The feeds to the forecolumn and the refining column were hand-valved off, the overhead product motor valves on both columns were closed, and the residue product from the refining column was hand-valved off. The standby operation of the refining column from 11 a.m. to 7:23 p.m. was erratic. A small amount of overhead product continued to flow through the closed motor valve; this caused depletion of the material in the system, and continual reduction of the steam and reflux flows during the eight hours prior to the explosion.

The standby operation of the refining column prior to the explosion was intended to be a total reflux situation, that is, a steady-state condition as follows:

1. No process flows into or out of the system

2. Constant operating parameters, viz., temperatures, pressures, and flows

3. Constant composition at any point in the system, following the transient period immediately after cessation of normal, continuous operation

Examination of the data, however, together with a consideration of the system geometry, would define the operation as follows:

1. Unsteady-state, batch distillation of a relatively pure butadiene fraction

2. Generally decreasing system pressures, temperatures, and flows, but high and generally increasing reflux ratio

3. Large hold-up of material in the system; tray and reflux receiver hold-up large compared to column base capacity

Initial observation of the operating data indicated that a determination of the process conditions at the time of the explosion would require three steps: First, the column base, tray, and reflux receiver holdups as a function of time would have to be calculated, because they affect the outcome of a batch distillation. Second, a computerized model, employing proper relative volatilities and tray efficiency, would have to be constructed to represent the steady-state operation prior to 11 a.m. And finally, the abnormal operation of the system, or the unsteady-state batch distillation, would have to be simulated by a computerized model and the calculations made. The final result, then, would be a representation of what existed in the refining column system at the time of the explosion. The information developed is used to help explain the mechanism of the explosion and to define operating conditions to prevent any re-occurrence.

System holdup—During the eight hours and 23 minutes from 11 a.m. to 7:23 p.m., the base level in the refining column decreased. The chart on base liquid level recovered from the trend recorder indicated that the level had dropped to the elevation of the high side instrument tap, nozzle "W", by 2:30 p.m. (see Figure 6). Extrapolation of the decrease in liquid level predicted a level in the vicinity of the weld between the shell and bottom head at 7:23 p.m. This is just above the elevation of the riser which supplied liquid to the east reboiler (see Figure 6), but below that required to maintain natural circulation through the tubes. The calculated overall decrease in the amount of liquid in the column base is from 1,900 gal. at 11 a.m. to 540 gal. at 7:23 p.m.

The operating data indicated generally decreasing head pressure, reflux flow, and steam flow during the eight hours and 23 minutes prior to the explosion. Therefore, the tray and downcomer holdups had to be calculated for various times prior to the explosion, because changes in these holdups were taken into account in the final unsteady-state calculations. Holdup calculations were made for hourly intervals, taking into account the system geometry and the applicable process conditions (3). During the eight hours and 23 minutes, the total of all tray and downcomer holdups decreased by 4.6% (1,370 lb.).

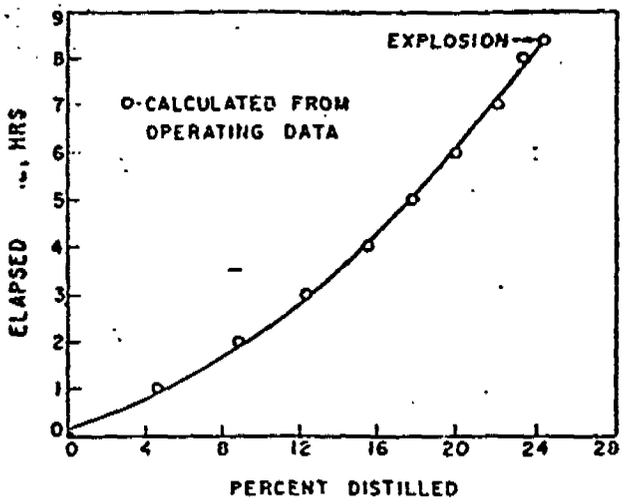

Figure 7. Passage of time prior to the explosion as a function of the per cent distilled from the system.

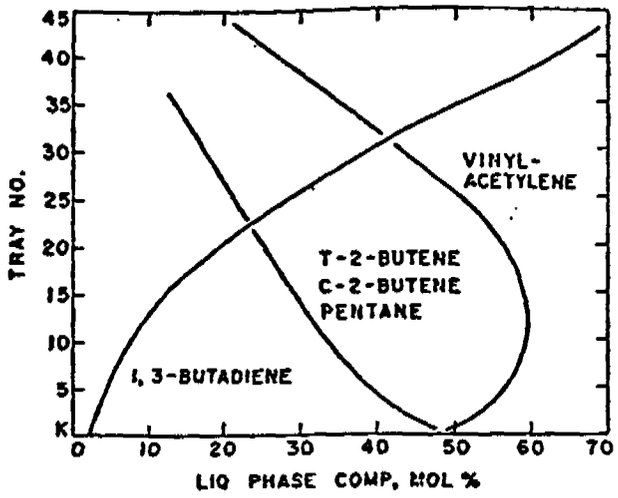

Figure 8. Final liquid-phase composition profiles as predicted by the unsteady-state model.

The reflux receiver holdup also decreased during the period of abnormal operation prior to the explosion. The chart recovered from the trend recorder indicated that the level fell from 582 gal. at 11 a.m. to 140 gal. at 7:23 p.m.

During the period of abnormal operation of the system prior to the explosion, a total of 10,309 lb. of overhead product was removed from the system. This is 24.4% of the material present originally in the system at 11 a.m. Figure 7 comprises the results of all holdup calculations, and indicates the passage of time from 11 a.m. as a function of the percent distilled from the system. This form of presentation is explained in the section of this article on unsteady-state operation.

Steady-state operation—A computerized, multicomponent, tray-by-tray calculation was utilized to simulate steady-state operation of the refining column system (*9*). The relative volatilities and tray efficiency utilized were available from laboratory and plant data within Union Carbide. The model derived was tested against the historical operation of the Texas City system under normal conditions, and the model predictions were found to be in close agreement with actual operation.

The steady-state model was "loaded" with a crude feed composition representative of the operation on the day of the explosion. In addition to processing crude butadiene, the unit had been re-refining some off-specification product. This resulted in a crude feed higher in butadiene content, and lower in residue content than normal.

The crude butadiene feed composition for October 23 was calculated by completing a component material balance around the system for the ten hours prior to 11 a.m. Data from the process computer log sheets (*4*) and analyses of the product and residue tanks (*10*) were utilized in the calculation. The feed composition, together with other operating data on the refining column, then was used in the steady-state model to determine the process conditions which existed prior to 11 o'clock. The component compositions which were predicted for the reflux receiver, each tray, and the column base were combined with the system holdup calculations to arrive at the system holdup for each component immediately prior to the period of unsteady-state operation.

Unsteady-state operation—A computerized, finite-difference solution of the differential equations (which describe the multistage, batch distillation of a multicomponent mixture with stage holdup) was utilized to simulate unsteady-state operation of the refining column system (*11*). The relative volatilities and tray efficiency utilized in this model were the same as those utilized in the steady-state model.

Because the unsteady-state model applies during the eight hours and 23 minutes prior to the explosion, all the time variable operating conditions had to be taken into account. The tray and downcomer holdups, which decreased generally, and the reflux ratio, which increased generally, were related to time through the use of second-degree polynomials and a least-squares technique (*12*). The reflux receiver holdup was related to time by a linear function. The material initially in the system at 11 a.m. was taken from the steady-state model, and material was "distilled" from the system in accordance with Figure 7. As each increment of product was distilled, the program calculated a new elapsed time. This time was then used to adjust each of the

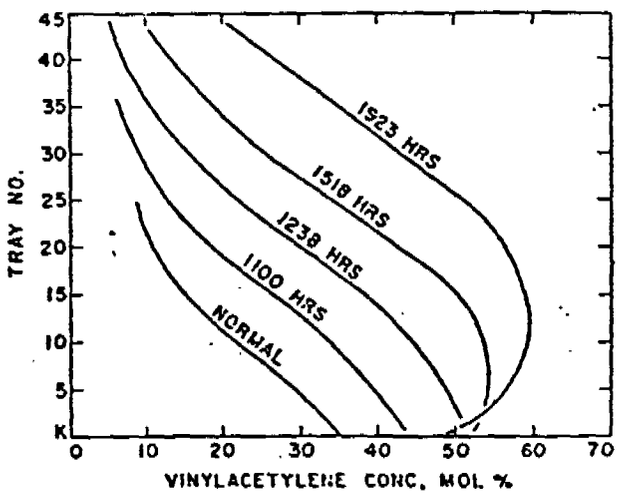

Figure 9.
The development of the vinylacetylene profile.

time variable operating conditions, and the process was repeated. The inventory in the column base was calculated by difference each time, so no correlation of this variable was required.

The batch distillation calculation was carried out until 24.4% of the material originally in the system had been withdrawn as product. At this point, the material left in the system was representative of the process conditions at the time of the explosion. In Figure 8, final liquid-phase composition profiles are reproduced as predicted by the unsteady-state model. Mole percentages of 1,3-butadiene, vinylacetylene, and the other major components present are given for the column base (K), and for the bottom 45 actual trays. The 1,3-butadiene content of the column base has been stripped down to about 2 mole %, while the concentration rises with increasing tray number from the bottom. The vinylacetylene content of the column base is 18%, and a maximum vinylacetylene concentration of 59 mole % has built up in the vicinity of tray Nos. 10 to 15, caused by the depletion of butadiene and the subsequent partial separation of vinylacetylene from the butenes. Above tray No. 15 the vinylacetylene concentration decreases. Damage to the column extended from the base section to an elevation corresponding to the 33rd tray; the liquid-phase vinylacetylene concentration throughout this volume is predicted to have been upwards of 40 mole %. The area of maximum fragmentation of the column shell centered around tray Nos. 19 to 18; the vinylacetylene concentration in this volume is predicted to have been in the range of 57- to 59%.

A discussion of the results of this study naturally centers around the concentrations and quantity of vinylacetylene, because of its inherent thermodynamic instability and because of the tremendous release of energy which occurred. Referring again to Figure 8, the quantity of vinylacetylene present in the liquid phase, between the column base and the 33rd tray, was 4,800 lb.

The development of the vinylacetylene profile is detailed in Figure 9. For comparison, a curve labeled "normal" is presented. Such a concentration profile would exist when the refining column operates in a steady-state, continuous manner, with sufficient residue flow to hold 35 mole % vinylacetylene in the base. The curve labeled 1100 hr. is the result of steady-state, continuous operation on October 23. It has the same shape as the "normal" curve, but it originates at a base concentration of 44%. At 1100 hr., the column was put on standby, and the remaining three curves show the development of the final profile. The curve labeled 1923 hr., reproduced from Figure 8, represents the conditions at the time of the explosion. The curves labeled 1238- and 1518 hr. represent intermediate profiles resulting from the distillation of 8- and 16% of the material in the system, respectively.

In summary

1. During the eight hours and 23 minutes preceding the explosion, the Texas City butadiene refining column was operated in a standby mode defined as follows: an unsteady-state, batch distillation of a relatively pure butadiene fraction.

2. a. In this mode of operation, the absence of feed and residue flows, the depletion of material from the system, and the high reflux ratio brought about abnormal, liquid-phase concentration profiles within the refining column.

b. In particular, vinylacetylene reached concentrations of 18- and 40 mole % in the column base and on the 33rd tray, respectively, and a maximum concentration of 59 mole % in the vicinity of tray Nos. 10-15.

c. The system volume bounded by the description in 2.b. above contained 4,800 lb. of liquid vinylacetylene at the time of the explosion.

3. The liquid in the base of the refining column fell to a level above that required to maintain flow to the reboiler, but below that required to maintain natural circulation through the tubes.

4. At this point, a reaction occurred in the reboiler tubes. Five of the tubes yielded to an internal pressure and burst.

5. The reaction propagated to the base section of the column, deforming the mitered head on the reboiler and the cover on the column manway, and lifting the lower trays off the support rings.

6. When the high pressure-high temperature front became exposed to a sufficiently high concentration of vinylacetylene, in the vicinity of tray Nos. 10 to 15, the liquid vinylacetylene detonated.

7. The column shell was demolished in this area and tore from this point both up and down into relatively large fragments; ultimately, the lower 42 ft. of the vessel shell was destroyed.

8. Additional, widespread damage resulted from the shrapnel and from subsequent fires, caused by the release of hydrocarbons from the fallen refining column and from other, punctured vessels. #

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M. P. McCready was responsible for the physical investigation of the incident. He is a senior process engineer in the Engineering Department at Union Carbide's Technical Center, South Charleston, W. Va. He has a Bachelor of Science Degree in Mechanical Engineering from the University of Maine. He is a Registered Engineer in West Virginia, and a member of ASME.

Butadiene Explosion at Texas City - 3

Along with other findings, investigation of this incident determined that the maximum temperature for butadiene refining systems should be no higher than 105°C.

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part of the investigation into the butadiene unit osion at Union Carbide's Texas City plant on October 1969, a laboratory investigation into the stability of vinylacetylene-butadiene mixtures was initiated. Union Carbide's data and the literature indicated that vinylacetylene in the diluents normally present in butadiene refining systems would be stable up to 48 mol %. An operating experience of over 28 years and the lack of documented incidents in the six operating unit owned by Union Carbide confirmed the validity of these data.

ompanion articles by other Union Carbide personnel *(1, 2)* describe the operating conditions at the time of the explosion, the calculations on concentration profile, and the results of the physical investigation. This investigation, in essence, revealed that the butadiene refining column had leaked butadiene overhead while on total reflux, and generated high concentrations of vinylacetylene in the column and low inventories in the base. The physical evidence indicated the initiation was in the reboiler and the deflagration propagated to the fourteenth tray where the detonation occurred.

The objectives of the experimental work were to support the physical investigation into the cause of the explosion, and to establish the operating conditions that would prevent a reoccurrence. This article defines a ·aximum heating-medium temperature, identifies a sible initiator, and more thoroughly defines the miting concentration level at which vinylacetylene apors will support a deflagration.

The following paragraphs on the individual phases of the experimental work discuss the thermal stability tests and the evaluation of initiators, define the upper limit for heating mediums in butadiene systems, and comment on the positive ignition tests that specify concentration limitations.

Thermal stability tests

The initial goal was to define the conditions which would lead to an explosive decomposition of a liquid-phase mixture of 1,3-butadiene (BD) and vinylacetylene (VA). Of particular concern was the *temperature at which the mixture became self-heating*. A thermal stability test which has had wide acceptance within Union Carbide was chosen to provide the base data.

The test vessel, shown in F-1, used has a capacity of 106 cc. of liquid. Its main body, constructed of 304 stainless steel, is a nominal 1 in. (the same size as the Texas City reboiler tubes) Schedule 80 pipe having an inside diameter of 0.956 in., and an outer diameter of 1.315 in. The bottom is closed with a 304 stainless steel, 3,000 lb./sq.in. pipe cap, and the top with a Black, Sivalls and Bryson 3,000 lb./sq.in., Type-1S, 1/2 in. screw-type safety head containing a 347 stainless steel rupture diaphram rated at approximately 7,500 lb./sq.in. at a temperature of 72°F.

Measuring appurtenances for determining temperatures

and pressures inside the test vessel consit of two 1/16 in. dia. shielded, grounded-tip, chromelalumel thermocouples (time constant 0.1 sec. in boiling water) and one 10,000 lb./sq.in. air-cooled pressure transducer which had a response of 6,000 to 8,000 cycles/sec. One of the thermocouples is axially located approximately 1/2 in. from the bottom of the test vessel for measuring material temperature, and the second is placed against the wall of the test vessel approximately 7 in. from the bottom of the vessel for measuring test-vessel skin temperatures. The pressure transducer is attached to the test vessel via a 1/4 in. OD high pressure tube approximately 11 in. long to thermally isolate it from the system. The pressure transducer line has a high pressure cross in it to allow insertion of the thermocouple measuring skin temperature of the test vessel.

Both the pressure transducer and the thermocouples are connected to a high-speed Offner Dynograph recording potentiometer capable of a response of 100 cyles/second/cm. of deflection. Liquid chemical solutions are charged to the test vessel as follows:

1. The vessel is evacuated to less than 1/2 mm. mercury and then pressurized to atmospheric pressure with high-purity nitrogen.

2. After repeating the above procedure twice, the system is evacuated to less than 1/2 mm. Hg pressure.

3. The test vessel is cooled with dry ice, and the liquids to be tested are allowed to drain into the evacuated test vessel. Care is taken to prevent nitrogen from entering.

After being filled to the desired level, the vessel is placed in a furnace consisting of a coiled 3,000 W, Calrod heater contained in an insulated, 1 gal. can. The temperature of the sample and container is increased at the desired rate by applying a fixed voltage to the heater. Usually 106 V. a. c. will produce a temperature rise of 5 to 10°C/min. Initially, the temperature rise will lag until the radiant heaters reach their normal temperature. In the latter stages of a test, if it spans 200 to 300°C, heat loss to the surroundings, and also the lessening of the temperature difference between the heater and the vessel, may result in a reduction of the heating rate. The voltage is gradually increased during this period to attempt to hold the heating rate steady.

Deviations from the normal time-temperature curve (which is slightly S-shaped) indicate chemical or physical changes such as fusion, reaction, polymerization, or changes in heat capacity taking place within the test vessel. These phenomena are used to recognize the differences in the materials tested.

Heating rate

With test vessel fills of 50%, a series of experiments was carried out to determine the temperatures and pressures at which various mixtures of BD and VA reacted, or exploded. A test of pure BD, slightly inhibited with nitrosophenylhydroxyl-amine (NPH), carried out at a rate of temperature increase of 5-to 10°C/min. resulted in an exothermic reaction, probably polymerization, beginning at a temperature of 160°C, and a pressure of 750 lb./sq.in. gauge. The vessel temperature rose to 285°C in 16 min. due to the reaction, whereas without a reaction, the temperature would have risen only to approximately 200°C in this period of time. Further increases in temperature to 360°C caused no detectable reaction. No quantitative energy release data are given inasmuch as the system was not calibrated to yield such information. A vapor pressure type plot showed that at a temperature of 170°C enough BD had reacted (probably polymerized) so that the rate of pressure rise with temperature was no

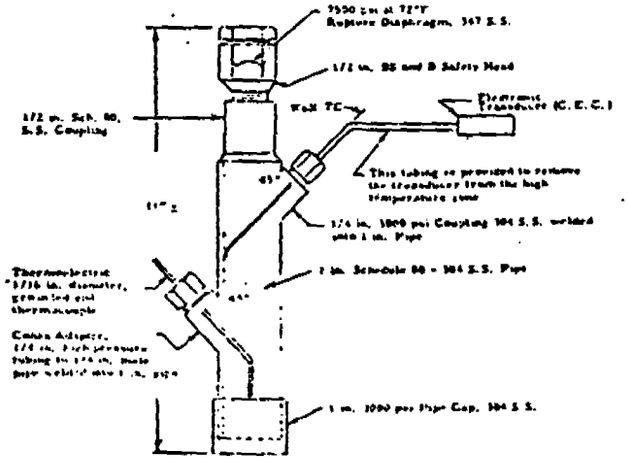


Figure ermal stability test vessel.

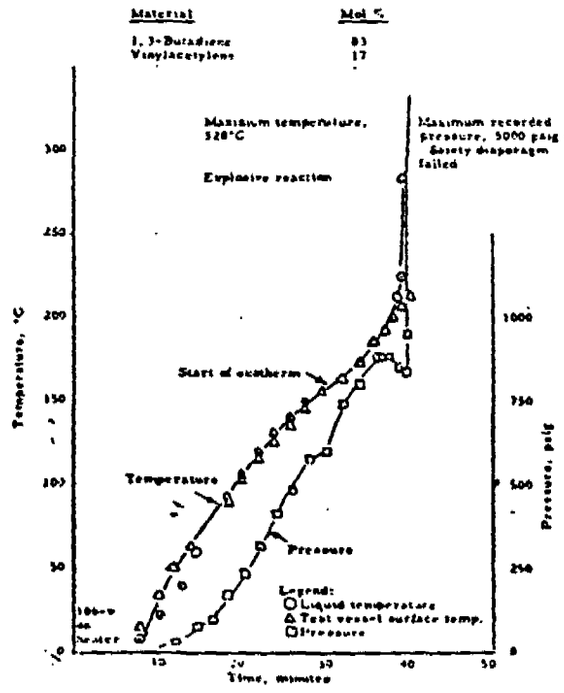


Figure 2. Thermal stability test of a vinylacetylene-butadiene mixture.

longer maintained. Thus, with pure BD at this heating rate an exothermic reaction is indicated, but no explosion is observed. It is shown later that by increasing the heating rate both an exotherm temperature and an explosion temperature can be generated.

An illustration of the type of data obtained with a mixture containing 83 mol % BD in VA is shown in F-2. This material was heated at a rate of 5- to 10°C/min. exhibiting an exothermic reaction at a temperature of 158°C, and a pressure of 590 lb./sq.in. gauge. The temperature rose to 285°C at which point the reaction mixture explosively decomposed, and increased the pressure in the test vessel to failure of a safety diaphragm rated at 7,500 lb./sq.in. gauge at 72°F. From exotherm temperature to explosion temperature required about 10 min. elapsed time.

Test results of mixture of BD and VA are summarized in F-3. All samples of material, except those labeled

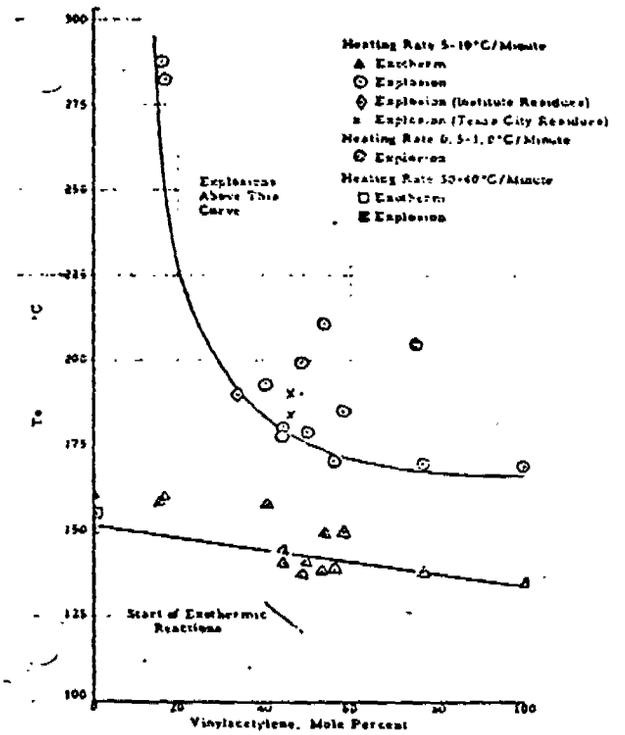


Figure 3. Thermal stability of vinylacetylene-butadiene mixtures.

specifically as being from the plant residue, were mixed in the laboratory from relatively pure BD, VA, n-pentane (n-P), cis-2-butene, and trans-2-butene. The major portion of the results shown in Figure 3, however, represent mixtures of refined BD and VA. Most samples exhibited an exothermic reaction beginning at a temperature of 135- to 145°C, with reaction being observed at a slightly lower temperature with increasing VA concentration. Explosions occurred at lower temperatures and pressures the VA composition was increased.

The two threshold-temperature curves were drawn through the minimum points in each set, primarily to indicate the potential exotherm and explosion temperatures. In more complex mixtures, like plant residues, the initiation of an exotherm was more difficult to distinguish on the heating curve. The explosion temperatures, however, did occur at predictable values and are included in Figure 3. It is presumed that the presence of more thermodynamically stable compounds than BD masked the inflection in the curve.

The influence of heating rate on the data can be shown in a run containing a mixture of 71 mol % BD and 29 mol % VA. This mixture was heated at the slower rate of 0.5- to 1°C/ min. exhibiting an exothermic reaction at a temperature of 156- to 158°C (similar to the faster heating rate) and a pressure of 480- to 520 lb./sq. in. gauge. Heating rate had a substantial effect on the temperature at which explosions took place, with the temperature of explosion increasing as the heating rate is decreased. It is believed that this phenomenon occurs because substantial amounts of VA and BD are consumed during the initital polymerizations. If too much VA and BD were consumed in the initial polymerization, the critical pressure, temperature, and composition requirements to obtain an explosive decomposition are never met coincidentally if the rate of rise of temperature is too slow. If the rate of temperature rise was increased 30- to 40°C/ min, even BD exploded provided the critical temperature, 200- to 340°C, and pressure of 1,450- to 1,800 lb./sq.in. gauge are met coincidentally. This effect of heating rate has been noticed by other experimenters studying the explosibility of the peroxides of BD *(3)*. Maximum rate of pressure rise for a laboratory prepared sample containing 55 mol % VA in BD was approximately 180,000 lb./sq.in./sec., while it was 60,000 lb./sq.in./sec. for a similar-prepared mixture representing the calculated composition in the base of the Texas City refining column just prior to the explosion.

In samples which exploded, yellowish, black polymers occured. In samples which did not explode, yellowish liquid and tacky, yellow polymers remained. A 50/50 mixture of bd/VA produced polymers in laboratory explosive decompositions which were very similar in nature to the polymers obtained from the Texas City explosion site. Such decompositions produced classic "ladder" polymers with a bicyclic and fused ring structure. Polymers produced via controlled thermal polymerizations in thermal stability tests were distinctly different from those found at Texas City. These were generally low molecular weight species with minimum crosslinking.

Contaminants and additives results

As was seen in the thermal stability study, any mixture of BD and VA can be considered explosive. When the composition of the mixture is 50 mol % VA and 50 mol % BD, the composition of material has little effect on explosibility at a heating rate of 5- to 10°C/ min. For this reason, the above mixture and heating rate were selected

in an effort to determine the effect of contaminants and additives which may be found in the BD processes. Test results employing a 50/50 mixture with various additives or contaminants are shown in T-1.

Materials which were considered possible additives in the BD proces were paratertiarybutylcatechol (TBC), sodium nitrite, and nitrosophenylhydroxylamine (NPH). TBC is generally added to the refined BD in concentrations of approximately 100- to 200 ppm to prevent polymerization. Sodium nitrite solutions (12 wt. % aqueous) or NPH (5 wt. % aqueous) are generally added to the distillation columns to prevent the formation of butadiene polyperoxide, polybutadiene, and "popcorn" polymer formation by scavenging oxygen from the system.

Sodium nitrate, copper vinylacetylene, oxygen, and residue solids gathered from the reboiler of the exploded distillation column were considered as possible contaminants that could sensitize the reactivity of the mixture. The residue solids were analyzed to contain 80% organic polymer with a sodium nitrite to nitrate ratio of approximately 1:2. From the results shown in Table 1, only the addition of a 12% aqueous solution of sodium nitrate apparently lowered the explosion temperature. All other tested materials considered as additives or contaminants did not alter the results.

Literature indicates that the use of over 4% concentrations of aqueous sodium nitrite solutions may be hazardous. The Phillips Chemicals Co. found organic nitrites, which when dry, decomposed explosively when heated above 150°C even in the absence of air. These compounds were not found when more dilute nitrite solutions are utilized and when the pH of the system is maintained above 8 *(4)*. Phillips maintains aqueous solutions of sodium nitrite of not over 0.5%. Because they used reboiler steam at 287°C, a dried polymer which fires at 150°C was considered dangerous.

The initiation of reactions shown in Table 1 began at

Table 1. Effect of additives and contaminants.*

Additives or Contaminants	Added as wt % Aqueous Solution	Weight Added % of Mixture	Conditions at Start of Exotherm		Temperature at (**) Start of Explosive Decomposition, °C
			Temp., °C	Pressure, lb./sq.in. gauge	
None (control)	—	—	141	520	185
Para Tertiarybutyl Catechol	—	9 ppm	138	500	175
	—	70 ppm	143	560	178
Sodium Nitrite	0.5	5.0	142†	510	186
	12.0	5.0	146	590	175
Sodium Nitrite	0.5	5.0	140	520	180
	12.0	5.0	143	590	166
Replicate	12.0	5.0	140	590	160
Nitrosophenylhydrazine	5.0	0.1	147	535	190
Coppervinylacetylene	—	0.1	140	490	186
Oxygen	—	50 ppm	139	545	173
Solid Residue Gathered From Calandria Tubes of Texas City Butadiene Column After Explosion	—	22	138	500	230
	—	74	150	350	210

* Base mixture 50/50 mol % vinylacetylene and butadiene.

** Ruptured diaphragms rated at 6,000- to 7,500 lb./sq.in. gauge at 72°F failed in all cases except test 62 where a partial charge of material was used. All samples tested exploded.

† In 2 out of 4 tests no exotherm was observed before explosive decomposition occurred.

temperatures ranging from 138- to 150°C, and pressures ranging from 480- to 620 lb./sq.in. gauge approximately 50% full. Explosions took place at temperatures ranging from 160- to 230°C, and pressures ranging from 650- to 0 lb./sq.in. gauge. The lowest temperature (160°C) for e explosion was in the presence of sodium nitrate.

All explosions led to yellowish, black polymers (black probably because of imbedded carbon). In the case where a smaller than usual charge was used, with just-wet polymer residue from the Texas City BD column calandria, the decomposition was contained and the test vessel was full of carbon. The polymers produced in explosive decompositions of mixtures containing additives were similar to those previously observed in explosive decompositions.

Pressure

Pressures occurring in thermal stability tests just prior to explosions were in the range of 600- to 1,800 lb./sq.in. uge, considerably higher than the pressure in the base of the Texas City refining column at the time of the explosion. To determine the effect of pressure on test results, the charge to the test vessel was decreased and the normal test procedure was followed. To minimize the reaction occurring during the heating, all tests were performed using a rate of temperature increase of 30- to 40°C/ min. As the charge to the test vessel was decreased, the temperature and pressure required for decompositon generally increased and decreased respectively. The ratio f maximum explosion pressure to the pressure just prior to the decomposition, P_2P_1, decreased with a decreasing sample charge. It is thought that this decrease was due to energy losses in the laboratory equipment becoming substantial, compared to the energy released, as the charge to the test vessel was decreased. This ratio should be fairly constant because all of the material tested was probably in a single phase when explosive decompositons occurred since critical temperatures were exceeded in essentially all ases. Although BD was extremely difficult to initiate, it readily contributed to the explosion while a true diluent such as n-P, a thermodynamically stable compound, did not contribute.

Thermal stability test results of laboratory mixtures of BD-VA, and plant BD residues showed that all mixtures will decompose explosively at temperatures ranging from 170- to 400°C. All laboratory mixtures exhibited an exothermic reaction, probably a polymerization, starting at a temperature of 135- to 145°C. This polymerization could lead to an explosion if the heat removal capacity of the system is exceeded, and the necessary temperatures and pressures are realized. With BD alone in the system, heat must be applied at a rate of 30- to 40°C/ min. to cause an explosive decomposition. With 50/50 mixture of BD and VA, a thermal initiation of a reaction is adequate to result in an explosion at predictable temperatures with the polymerization reaction generating the heat. As the VA concentration is increased in the system, generally lower temperatures and pressures are required for initiation of explosive decompositions. Although BD is considerably more stable than VA, it can contribute energy once an explosion occurs. Tests generally have shown that higher decomposition initiation temperatures are required as the pressure in the system decreases.

Heat soaking tests

Although the thermal stability series of tests indicated that all materials present in BD systems can generate an exothermic reaction that can culminate in an explosion, the time at temperature was not considered. Relating these tests to systems that operate at temperatures considerably below those indicated for initiation of an exotherm must include the time variable. Two series of tests were made to follow the time-temperature relationship. The first to find the effect of temperature on the stability, and the second to provide the basis for a recommendation of the maximum allowable temperature limit.

In these first tests, a 50/50 mixture of BD and VA was maintained at temperature of 100- to 135°C for various periods of time. The outside of the test vessel was generally maintained at the designated temperature and the inside of the test vessel was allowed to vary and to respond to the chemical reactions taking place. The thermal stability apparatus, previously described, was modified to include a thermocouple strapped to the outside of the vessel approximately 4 in. from the bottom. This temperature was controlled by using an on-off controller; the inside temperature and pressure were continuously monitored. The vessel was charged approximately 50% full as in the thermal stability tests.

A sample was held at approximately 100°C for 9.5 hr., cooled to ambient temperature, and then run through the standard thermal stability test procedure. At 180°C and 600 lb./sq. in. gauge an explosion occurred which compared well with the thermal stability results of a similar mixture which had not been aged (140°C and 520 lb./sq.in. gauge). A second sample held at 100°C for 16 hr. required 240°C and 700 lb./sq.in. gauge to cause an explosive decomposition in the stability test. The increase in temperature required for autodecomposition probably stemmed from substantial amounts of monomer polymerizing during the aging. In a third test, conducted for seven days at 100°C, the test vessel was found to be filled with a yellowish, soft, tacky polymer, and no liquid remained. Relating this to the operation of a system, a reboiler with a maximum of 100°C steam would only polymerize a 50/50 mixture of vinylacetylene and butadiene, not explode it.

In a similar test, a 50/50 mixture maintained at 120°C did not explode after one week's aging. Repeating this experiment at 125°C, an exotherm and an explosion occurred after 3.5 hr. At 135°C, the explosion occurred after 1.9 hr. Although the test vessel was held at the

indicated temperatures, the material inside the vessel increased in temperature and finally exploded. The inside walls of the test vessel and the thermocouple in the liquid phase were found to be heavily coated with polymer. In ormal thermal stability tests conducted at a 5- to 10°C e of temperature rise per minute, only small quantities f polymer were found in the test vessel. In previous tests where pure butadiene was decomposed explosively, quantities of polymer found were even smaller and were located primarily on the failed rupture diaphragms. This work suggested that the maximum calandria steam temperature should be in the range of 100- to 110°C.

To develop a maximum temperature recommendation, a series of 20 tests was made using a 1 in. dia., 3,000 lb./sq.in. pipe cap as a test vessel. The cap was sealed with a pipe coupling and a high-pressure valve. The cap was charged with 1 cu. in. of liquid (approximately two-thirds full) and placed in an oven controlled at 110°C for one week. After cooling the caps and opening them, samples of the residual polymer were examined visually and with a Time-of-Flight Mass Spectrometer to determine whether an explosion had taken place during the aging. All samples had polymerized in controlled reactions to form a yellow polymer typical of nonviolent reactions. The 20 no-go results at 110°C resulted in a probability of explosion that had a statistical 95% confidence range from 0- to 5%. Based on this work, a maximum calandria steam temperature of 105°C was recommended and has been implemented in Union Carbide plants.

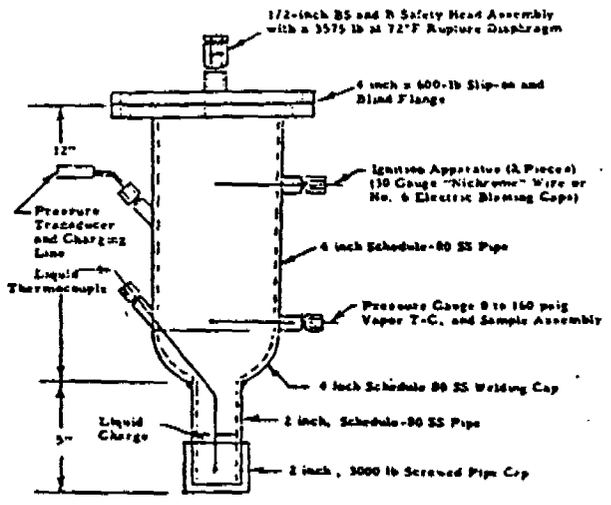
itive-ignition tests

Mixtures of BD and VA have been shown to be capable of being decomposed explosively in all proportions in thermal stability tests. Because of the nature of the tests, pressure control was not achieved during the testing, and the bulk of the tests were carried out at pressures ranging from 700- to 1,500 lb./sq.in. gauge to achieve explosions. These pressures are far in excess of those occurring in BD fining columns which operate at approximately 50 b./sq.in. gauge. Although the thermal stability test was useful for determining unsafe temperatures, it was believed to be too severe to be used to predict unsafe compositions. Hence, a series of tests was devised to determine maximum safe VA concentrations as a function of refining column operating pressure. Throughout these tests the liquid and vapor phases were essentially in equilibrium with each other.

This series of tests was carried out in a 4 in. dia. (2,410 cc. volume) test vessel shown in F-4. A 4 in. dia. vessel is suitable for predicting safe pressures in acetylene deflagration tests, and hence was deemed suitable for this study based on Union Carbide experience. In addition to the accessories described for the thermal stability test ssel, the system was equipped with a pressure gauge and ee firing devices. The charging procedure was similar to it described previously. Normally 100 cc. of the mixture were charged, providing a ratio of vapor to liquid equivalent to that present in the Texas City refining column. The liquid in the test vessel was heated for about 2 hr. until the pressure was lined out at the desired level. A vapor sample was then collected into an evacuated 3 cc. stainless steel sample tube. The pressure gauge was then isolated to protect it, and the first igniter was fired. Results were monitored using a Beckman Type R Dynograph Recorder. The first igniter was discharged at the lowest pressure in the series, and if this failed to initiate a vapor-phase deflagration, the pressure was raised 10 lb./sq.in. gauge (by increasing the temperature) to the next, and the second igniter discharged.

The ignition sources were either the fusion of Nichrome wire or the discharge of a No. 6 high-temperature electric blasting cap. The fused-wire igniter consisted of two strands of 30 gauge Nichrome wire in parallel, 0.6 in. long, fused by the discharge of a 17,000, farad condenser charged to 150 V. d.c. This ignition system has been found to produce slightly more than 3.2 joules of energy. The No. 6 blasting cap liberated approximately 2,000 joules and created an instantaneous pressure of approximately 200,000 atmospheres *(5)* and had a propagation velocity of 6,000- to 7,000/m./sec. Both sources have been used successfully by Union Carbide's Fire Research Group to predict the explosiveness of various materials and to determine safe compositions. Explosions have never occurred in Union Carbide plants which operated within safe limits predicted using the above ignition sources.

Vapor-phase testing was done in preference to liquid-phase testing because it was believed that for propagation to be continuous in a distillation column of the type which exploded in Texas City, it had to continue through the vapor phase. Secondly, a large number of liquid-phase ignitions had already been completed in terms of thermal stability tests, and conditions for initiation of the liquid had been established.



The liquid in this container was refluxed to maintain the proper test pressure by placing the 2" diameter section into a furnace consisting of a coiled 1000-Watt Calrod heater. The spiral-wound heating core was contained in an insulated 1-gallon paint can.

Figure 4. Positive-ignition test apparatus.

The tests were made in the vapor phase with mixtures of BD and VA, mixtures of BD, VA, and n-P and plant BD column residue fortified with VA. Pressures were varied from 65- to 85 lb./sq.in. absolute in 10 lb./sq.in. increments.

Test results and conclusions

Pure VA exploded from a starting pressure of 85 lb./sq.in. absolute, using a No. 6 high temperature electric blasting cap in the vapor phase to yield a final maximum pressure of 4,800 lb./sq.in. absolute in 0.02 sec. The vapor-phase deflagration initiated the liquid explosion in approximately 0.01 sec. when the system pressure was 500 lb./sq.in. gauge, and the vapor temperature approximately 100°C. These conditions were in good agreement with the thermal stability test results which indicated that VA explosively decomposed at a pressure of 450 lb./sq.in. gauge, and a temperature of 137°C. In other words, temperatures and pressures had to be equivalent to those existing on the upper curve of Figure 3 before a decomposition of the liquid phase would occur. This equivalency reconciled the thermal stability test data with the vapor-phase positive-ignition data, despite the disparity of the operating pressure (60) versus the test decomposition pressure (<500 lb./sq.in. of the operating pressure (60 lb./sq.in. absolute) versus the test decomposition pressure (<500 lb./sq.in. absolute).

In laboratory mixture of BD-VA, vapor samples containing 53- to 55 mol % VA deflagrated in the vapor phase at 65 lb./sq.in. absolute pressure using the Nichrome-wire ignition source. A typical time delay to

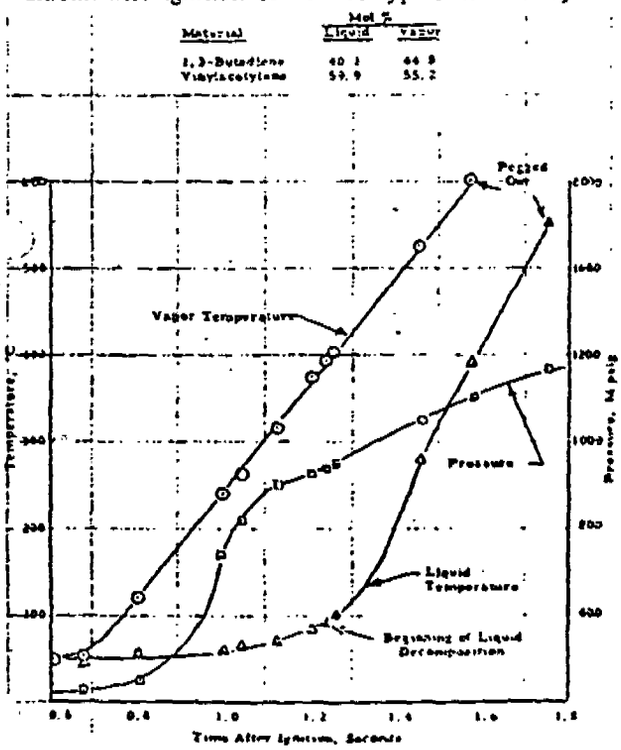


Figure 5. Typical positive-ignition test.

develop the pressure and temperature required for decomposition of the liquid is illustrated in F-5. Again they are in fair agreement with those recorded in the thermal stability tests; an accurate reading is handicapped by the different time responses of the pressure transducer and the thermocouples.

At 75 lb./sq.in. absolute, a vapor-phase concentration of 51% VA in BD resulted in an ignition, while at 85 lb./sq.in. absolute pressure, 41 wt. % VA was unstable. In the above two cases, ignitions were attempted at 65-and/or 65-and 75 lb./sq.in. absolute, respectively, without a vapor-phase deflagration. As in all cases for BD-VA mixtures, a deflagration in the vapor initiated an explosive decomposition of the liquid. The vapor composition was measured at the lowest ignition pressure; the actual VA vapor composition may have been somewhat higher because increased pressure was developed by vaporizing additional liquid.

At 85-lb./sq.in. gauge with a vapor composition of 41- to 44 mol % VA in BD, there was one explosion in seven tests using a fused wire igniter, none in two tests using a blasting cap in the vapor, and none in one test using a blasting cap in the liquid. The blasting cap was *not* a more effective ignition source than the Nichrome wire despite the greater energy released.

In one test, a 50% overcharge was used. Although the system was ignited by a blasting cap, propagation was slow and, hence, there was no measurable contribution of pressure developed due to the cap which develops its pressure almost instantaneously and only contributes about 1- to 2 lb./sq.in. detectable with measuring instrumentation. The normal charge (100 cc. volume) yielded an explosion pressure of approximately 1,400 lb./sq.in. absolute, and the 150% overcharge yielded 150% of the pressure of a normal charge, or 2200 lb./sq.in. absolute. The final pressure developed in a partially filled system was a function of the quantity of explodable charge, therefore, the vessel was large enough that the wall effects were insignificant. The reasons for the delay in the explosion after the blasting cap ignition are not known.

In the tricomponent BD-VA-n-P system, 30 mol % n-P replaced part of the BD in the charge liquid. The vapor phase deflagrated with 70 mol % VA (23 mol % n-P) at 65 lb./sq.in. absolute, and with 63 mol % VA (17 mol % n-P) at 75 lb./sq.in. absolute. This latter test was the only test in which the vapor phase did not decompose the liquid. A vapor composition of 60 mol % VA (13 mol % n-P) did not deflagrate even at 85 lb.sq.in. absolute.

A sample of residue (kettle liquid) from a Plant BD refining column (36% VA) was found to be stable even at 85 lb./sq.in. Absolute. This material was fortified with pure VA to produce mixtures up to 61% VA. This composition exploded at 75 lb./sq.in. absolute, while samples containing from 55- to 58% VA were unstable at 85 lb./sq.in. absolute, but stable at 75 lb./sq.in. absolute. Mixtures containing from 53- to 54% VA exploded once in eight tests at 85 lb./sq.in. absolute using both ignition sources.

The positive-ignition tests show that with vapor-phase VA-BD mixture, 40 mol % VA will not deflagrate at 85 lb./sq.in. absolute, nor will 50 mol % VA at 65 lb./sq.in. absolute. Adding the components normally present in butadiene column residues varies the allowable concentration at 85 lb./sq.in. absolute to 53 mol % VA, and at 65 lb./sq.in. absolute to 60 mol %. Adding an inert component such as n-pentane to a VA-BD mixture raises the allowable VA concentration to higher levels. These data are shown in F-6. In this work, in which the liquid and vapor phases were in equilibrium, the vapor-phase deflagration generated the necessary conditions to initiate the liquid-phase decomposition in all cases except one of the tests using pentane.

Based on the above, if plant BD refining distillation columns are treated as though they were mixtures of BD and VA, there is a built-in safety factor of about 10% in VA concentration. An additional safety factor may be built in if the column is operated at a pressure less than that for which the safe concentration of VA was developed. It is the authors' opinion that 45- to 50 mol % VA could be considered safe in a column operating at maximum pressure of 65 lb./sq.in. absolute, if there are no excursions above 50% VA. The degree to which the VA concentration can be controlled is a factor in establishing the safe operation limit. Since the data are available to adjust for operating pressure and experience is required to determine control variability, a maximum of 40 mol % VA was chosen for systems operating at 65 lb./sq.in. absolute.

The experimental work on the stability of vinylacetylene-butadiene systems generated the following conclusions:

1. All mixtures of vinylacetylene and butadiene are thermally unstable, and will generate exotherms and explosions at predictable temperatures and pressures.

2. Sodium nitrite, converted to sodium nitrate, can make butadiene-vinylacetylene mixtures less stable.

3. The maximum temperature for butadiene refining systems should be no higher than 105°C.

4. Concentrations of vinylacetylene up to 40 mol % will not support a vapor-phase deflagration at 65 lb./sq.in. absolute.

5. The temperature and pressure developed from a vapor-phase deflagration is sufficient to initiate an explosive decomposition in the liquid phase.

As a result of the investigation into the explosion in the Texas City No. 3 butadiene refining column and the subsequent experimental work, the cause can be attributed to the following sequence of events:

1. The butadiene refining still was placed on standby, as was the usual practice, to perform maintenance on equipment in the system.

2. Under near-total reflux conditions, the overhead product valve continuously leaked butadiene from the distillation system.

3. The column fractionated, over 8.38 hr., the light components overhead and concentrated the heavier components in the lower section. The trays between 10 and 15 from the bottom developed a maximum concentration of 60 mol % vinylacetylene.

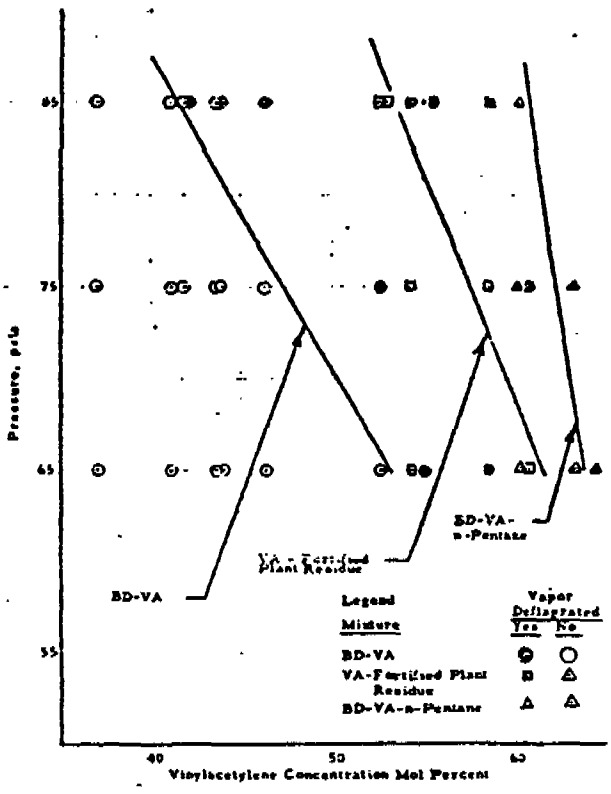


Figure 6. Positive-ignition test of vinylacetylene mixtures.

4. The base liquid level fell to a level above that required to circulate the organic liquid, but below that required to maintain all the tubes covered in the natural circulation reboiler.

5. At this point, a reaction occurred in the reboiler tubes. The exact initiator is not known, but a thermal polymerization sensitized by the presence of sodium nitrate, is a possibility. Since the 15 lb./sq.in. gauge superheated steam has a maximum temperature of 157°C, the reboiler level was low, and the condensate temperature was rising, the conditions for a thermal polymerization were present.

6. Five of the tubes yielded to the internal pressure and temperature and burst.

7. The shock and heat generated by this event decomposed the highly concentrated vinylacetylene vapor in the reboiler causing a deflagration wave to proceed up the column.

8. The pressure and heat from the wave over-pressured the reboiler vapor outlet, the bottom of the column, and displaced or tipped, the bottom ten distillation trays.

9. On or about tray number 14, the temperature and pressure were sufficiently high to decompose the liquid containing about 60% vinylacetylene.

10. The column tore from this point up and down at velocities over 2,000ft./sec. destroying the bottom 42 ft. of the column and causing it to fall.

11. The release of the large amount of hydrocarbon from the system surrounding the column ignited.

Union Carbide, as a result of this investigation, has implemented the conclusions of this report and required their other units to comply with the following recommendations:

1. Avoid total reflux to prevent the concentration of any component in any part of the column.

2. As long as there is heat on the reboiler maintain a residue flow from the system at all times.

3. Do not exceed 40 mol % vinylacetylene in the vapor phase at any point in the system.

4. Provide continuous monitoring of the kettle vapor phase and approximately the sixth tray vapor phase for vinylacetylene concentration. The column concentration should always be less than the base concentration.

5. Reduce all heating systems for all butadiene refining columns to a maximum temperature of 105°C.

6. Do not use sodium nitrite in the refining system. For polymer and peroxide control, use 10 ppm nitrosophenyl-hydroxylamine (NPH) in the reflux loop, based on the reflux flow.

Acknowledgement

The content of this article represents the combined efforts of a number of people from all levels of Union Carbide. Advice and assistance from Dr. W. B. Howard of the Monsanto Co. and Dr. R. A. Schultz of Du Pont is sincerely appreciated. Dr. Paul Johnson, also of Du Pont, provided the vinylacetylene for the experimental work. The cooperation of the industry, in general, was gratifying and it is hoped that this report repays, in part, for their contributions.

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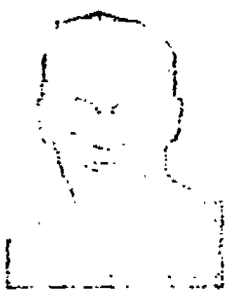

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PLANT SAFETY &
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Butadiene Explosion at Texas City—1

The force of the Texas City explosion scattered large fragments to a radius of 1,500 ft., and blew one 800 lb. section 3,000 ft.

H. C. Jarvis, Union Carbide Corp., Texas City, Tex.

AN EXPLOSION OCCURRED ON OCTOBER 23, 1969, IN THE year-old butadiene refining unit at Union Carbide's Texas City plant. Much of the butadiene unit was destroyed and the adjacent 1.2 billion lb./yr. ethylene unit suffered major damage. The explosion, which occurred in the lower [illegible] refining column, littered the area within 600 ft. of the column with shell and tray fragments, and tray valves varying from a few ounces to several hundred pounds in weight. Large shell fragments were scattered to a radius of 1,500 ft. One 800 lb. section landed 2,000 ft. away. Grass fires were set at a distance of 750 ft.

Damage was not confined to the plant site. Numerous houses in a residential area starting 750 ft. away were damaged by flying materials and windows were broken 1¼ mi. away. Fortunately, no disabling injuries occurred, and injuries outside the plant area were confined to minor cuts and abrasions and mental anguish.

The butadiene refining unit recovers byproduct butadiene from a crude C_4 stream originating in the olefins unit. Similar units have been operated by Union Carbide for almost 30 years. The primary separation of butadiene is by absorption. Recently built units, including the one at Texas City, differ from the earlier units in that a new absorbent, dimethylacetamide (DMAC), is used. The stripped gases from the saturated solvent are compressed for recycling to the base of the absorber as a heat medium and as feed to the refining section of the unit. Light components of the stripped gas are removed in a forecolumn. The high purity butadiene product is produced as the overhead of the refining column. The heavy components of the feed stream, including vinylacetylene, are removed as refining column kettle product.

Vinylacetylene in the kettle product is normally maintained at a concentration of about 35% by supplementing the heavy ends in the feed stream with butadiene. Explosibility tests had indicated that concentrations of vinylacetylene under 50% in the kettle product were stable at column operating conditions. Some 80 column years of refining column operation under column conditions similar to those in the Texas City unit had been accumulated without incident.

Status prior to the explosion

The butadiene refining unit was operating normally, and all other pieces of equipment were in good working order when the unit was shut down for repairs to the stripper make compressor. Reduction of feed flow to the absorber began about 9:00 a.m. and all feed flow was discontinued by 11:00 a.m. Circulation of DMAC was continued until all dissolved gases were stripped out and flared. The absorber and stripper were valved in under methane pressure in a standby condition, and the stripper make compressor was purged with inert gas and prepared for maintenance.

The forecolumn and refining column were placed on total reflux when the stripper make compressor was removed from service. The columns were shut in with hand valves in the feed and kettle product lines and by motor valves in the overhead lines. Both columns continued to operate under total reflux conditions—the normal practice for these columns when the absorption section is shut down for short periods of time.

The forecolumn operated smoothly under total reflux at near normal end conditions. The only change in conditions, a reduction in vapor gravity at the top of the column, was probably caused by an accumulation of light ends during the total reflux process.

Operation of the refining column appeared normal to the operator on duty even though operation was erratic. This column normally operates under a very high reflux ratio and erratic operation on total reflux was common. Operator attention was required in maintaining a balance between the liquid in the base of the column available for kettle vapor generation and liquid in the accumulator available for reflux. Reflux flow was controlled on manual while steam flow to the calandria was controlled automatically by the liquid level at the base of the column.

This article, and the one that follows, are two of three articles written on the Texas City explosion and its aftermath. All three articles will be published shortly in a CEP technical manual; "Loss Prevention," volume 5.

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Although operation of the column appeared normal at the time, examination of the records after the explosion showed that the column was slowly losing material through the closed, but leaking, motor valve in the overhead line. Column pressure and pressure drop stabilized at 75- to 80% of normal showing reasonable tray loading following a rapid decrease when feed was shut off. Reflux and steam flow continued to fall slowly throughout the shutdown period, indicating a loss of material from the column. The make flow meter showed a continuous flow; however, the operator assumed that the meter was off calibration since the make motor valve was closed and the tracing on the chart was a continuous straight line near the base of the chart. The column base level indicator showed a low level in the base of the column, but ample kettle vapor was being generated.

Loss of butadiene from the system through the leaking overhead line motor valve resulted in substantial changes in tray composition in the lower section of the column. The concentration of vinylacetylene in the tray liquid in the vicinity of the tenth tray approximately more than doubled to an estimated 60 mole %. The loss of liquid in the base of the column uncovered the calandria tubes, allowing the tube wall temperature to approach the temperature of the heat supply. The increased vinylacetylene concentration and high tube wall temperatures set the stage for the explosion which followed.

The explosion

The explosion in the refining column occurred some 11 hours after reduction in feed flow began and 9 hours after the refining section was placed on total reflux. The explosion occurred without warning other than as covered in the paragraphs above. It was so sudden that none of the pressure and temperature changes which accompanied it were recorded on any of the instruments in the unit. Two loud noises were produced. The first was probably caused by the disintegration of the column in which the lower 40 ft. was fragmented and scattered around the area. The second, which occurred almost immediately thereafter, was probably caused by the ignition of the large quantity of gas released from the ruptured lines and equipment.

The extent of physical damage to the butadiene unit is shown in Figure 1. One distillation column was replaced and several others received major repairs for deformed shells, shrapnel holes, and distorted or missing nozzles. A major part of the auxiliary equipment was repaired or replaced. The piperack, including piping, instrument and electrical cable, and most of the instruments, was replaced. Damage was similar but not as extensive in the adjoining olefins unit, although evaluation and repairs were more complex and costly because of the special metals and insulation required for cold temperature service in this unit. Rebuilding costs exceeded $6 million.

Determining the absence of damage was of major importance for economic and safety reasons. The thousands of pieces of flying metal, some very small, cut holes and gashes in insulation and equipment. Heat effects caused stresses and metal distortion which, in turn, caused mechanical strain in attached equipment. Temperatures over 1,350 F caused grain growth in cold temperature steel rendering it brittle when cold and unsuitable for reuse.

All piping and equipment affected by the explosion and fire were inspected for damage. Carbon steel piping for warm temperature service was considered metallurgically sound unless visual inspection showed severe scaling or distortion. Stress relief was required for cold temperature steels heated above 375°F. Grain growth was assumed in steels heated over 1,100°F. The color changes below were used as indicators of the temperatures reached. The validity of this approach was established by field and laboratory testing.

1. Foam glass cement melts at 280°F
2. Polyurethane insulation turns dark at 250°F, and chars at 300°F
3. Phenolic resin in the fiber glass blankets turns brown at 375°F
4. The insulation weather barrier chars and becomes chalky at 400°F
5. Dimetcote No. 4 turns brown at 1,000°F
6. Foam glass melts at 1,800°F

Effect on personnel

Thirteen people were in the immediate area when the explosion occurred; 6 in the control building and 7 in the equipment area. Three maintenance men working on the compressor 100 ft. away from the refining column were shielded by small items of equipment and thrown to the ground by the blast. One suffered a ruptured ear drum and the other two were uninjured. One operator, approximately 200 ft. away and relatively unprotected, was thrown to the ground but uninjured. The main fireball was over his head, but he crawled out of the fire area and immediately took steps that limited the amount of flammable material entering the fire zone. He also activated the emergency relief valves on the distillation equipment. His quick action was instrumental in limiting the extent of the fire.

Six men were in the central control building 200 ft. from the refining column. Although this building took the full brunt of the blast, no serious injuries occurred to those inside. One man seated in an office downstairs near the wall facing the explosion was shaken up and suffered head bruises, but he was able to clear the building and the area between the initial blast and explosive burning of the released gases. The four men on the control room floor made their way out among falling light fixtures and ceiling parts, and escaped from the area. One of these men suffered a broken heel which was probably cracked when he jumped to the sidewalk from the intermediate level of an outside stairway. The remaining men in the area were far enough away that they were not affected by the blast.

The fire was brought under control by unit personnel and the plant fire squad. Employees living in surrounding areas who were familiar with the unit responded immediately to the emergency and assisted personnel on duty in bringing the fire under control. The fire fighting effort was impeded by the terrific noise created by high pressure steam and gas escaping from ruptured lines which made communication almost impossible. Conversation was difficult 800 ft. away from the blast area, and the noise was discomforting even with ear muffs.

Fire protection is provided by a water spray system, stationary fire monitors, and hose hydrants. Total fire water pumping capability is 37,500 gal. min. Six of eight 6 in. water spray system supply headers passing through the blast area were destroyed. These lines supplied water to portions of the adjacent olefins area, as well as to systems in the immediate blast area. Loss of these lines was of primary concern in the fire fighting effort. Fire protection to structural steel in the immediate blast area was lost, and the reduced pressure limited the supply of water to sprinkler systems pro-

the columns decreased as the pressure was relieved. A hazardous condition could have occurred without this anti-vacuum feature since air might easily have been sucked into the columns. Some of the shutoff valves were inaccessible due to the fire and maintaining a purge on all of this equipment would have been most difficult, even though nitrogen purge gas was available.

Metal-covered steel-framed buildings are good construction in areas where explosions can occur. The control and office building was of this type. Although the exterior and first floor office area suffered extensive damage, the instrument consoles and computer located on the second floor escaped major damage. The exterior walls, being of light metal construction, easily deformed and, thus, absorbed energy and reduced damage to the interior of the building as well as to the building frame. The interface cabinets, which are constructed of medium weight steel sheet, formed a shield protecting the instrument consoles. Although extensive instrument checkout was necessary, the main damage to the consoles resulted from the tremendous quantity of dust, dirt, and small particles blown inside. The principal damage to the computer occurred when the shock wave caused some heads to drag on the drum.

A number of hardware problems occurred after the computer was returned to service. The explosion no doubt contributed to these problems, but some of them could well have been problems not yet identified and corrected prior to the blast. Information recovered from the computer gave a complete picture of operation of the unit up to the time of the explosion, and made possible the subsequent studies which established the cause of the explosion.

One deficiency in building construction could have caused serious personnel injury. The light fixtures in the building were supported by the suspended ceiling. The entire ceiling fell, leaving all the light fixtures hanging from flexible electrical conduit. Surprisingly, none of the six men in the building were injured by the falling fixtures, or by running into them when escaping from the building. All light fixtures are now suspended from the building frame.

Many of the fire monitors in the area were too far removed from the high steel structures to play water on the upper steel where it was needed. The monitors have been relocated to provide better water coverage, although, in many cases the shutoff valve was retained at the original location for better access in the event of a fire.

Block valves, located outside the area but close enough for operation by unit personnel, are required in all process lines entering the area. All these lines had valves at other locations outside the unit and could theoretically be closed when required. In practice, the severe emergency that occurred in the rest of the plant as a result of this fire and explosion was such that persons in other areas who normally would have closed the valves were not always available or could not be reached.

Problem areas

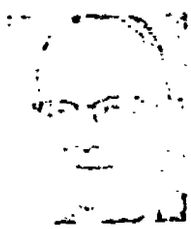
Communications both inside and outside the plant area provided very serious problems. Voice communication was almost impossible near the blast area because of the noise generated by escaping gas and steam. The telephone system in the immediate area was destroyed and communication with the rest of the plant was limited to radio. The difficulty in communicating with the rest of the plant was particularly important when the remotely located shutoff valves in many of the ruptured lines had to be closed.

Communication with the outside world was almost impossible. The deluge of telephone calls from people in the surrounding areas completely tied up the telephone system for miles around. Calls both into and out of the plant could not be completed, making communication with personnel needed to deal with the emergency extremely difficult. Obviously, public communication systems have extreme limitations in emergencies such as this one.

Communication with the news media was made difficult by the reporter's unfamiliarity with technical terms. Emergency press headquarters with direct outside lines was open at 7:30 p.m., 17 min. after the explosion occurred. Assistant plant managers were available for questioning. Press information booklets were passed out so that all corporation personnel present were properly identified. Questions were answered as factually and accurately as possible. A formal news release, including names and addresses of employees involved in the fire and a picture of the fire, was made available at 9:00 p.m. Four more news releases were made as additional information became available. In spite of the special efforts made to accommodate the press and provide accurate information, much that was printed was inaccurate or misleading. Information packets on each operating unit in the plant that will help bridge the gap between the technical and nontechnical world are being prepared, should their use ever be required again.

Three persons known to be in the area at the time of the explosion could not be accounted for several hours later, although a preliminary count had established that there were no serious injuries. These men escaped from the blast area by scaling the plant fence. Two were taken to a hospital by a passing motorist, while a third walked around the plant and reentered at the front gate. All these men knew the importance of reporting to the plant that they were safe, but those in the hospital were unsuccessful in their attempts to do so. Word of their safety finally reached the plant through a news reporter. Unfortunately, this information was not passed to the blast site and rescue personnel were exposed needlessly to additional danger as they searched for the missing men.

The streets leading to the plant site were immediately choked with vehicles and people. Some who remembered the Texas City explosion in April, 1947 were rushing to get out of the vicinity but others, much greater in number, were rushing in to watch the fire. The traffic jam seriously impeded those plant personnel needed at the plant site. Fortunately, local police arrived at the scene in minutes and blocked off the public highway adjacent to the blast area, greatly reducing the probability of injury to the curious if additional explosions had occurred. #



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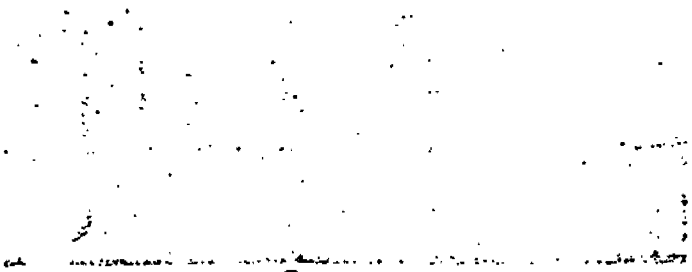
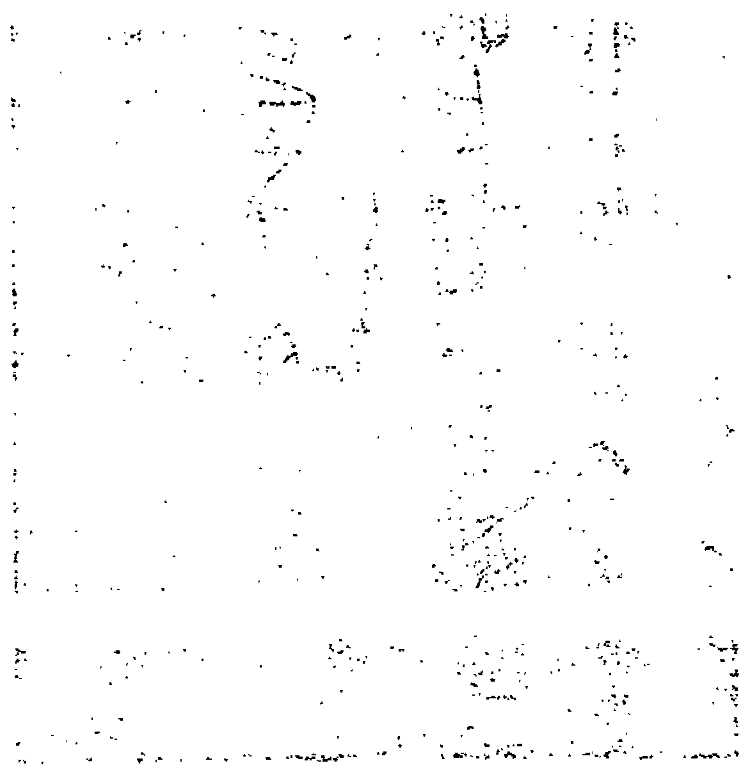


Butadiene unit just prior to completion of construction. The explosion occurred in third column from the left.



The remains of the butadiene column after the explosion.

tecting areas adjacent to the fire. Stemming the flow of water from the broken lines was complicated by the absence of shutoff valves [illegible]. [illegible] area to close the shutoff valves, exposing them to additional hazard. Some hose lines were carried into the [illegible] structures adjacent to the fire to supplement the damaged sprinkler systems.

The stationary fire monitors were a very important part of the fire fighting system. These were used principally to cool steel in or near the fire area, and some were kept in service until the fire burned out. In spite of damage to the fire protection system, sufficient water [illegible] out of the immediate blast area.

Although the fire was under control in three hours, [illegible] was allowed to burn itself out after some 57 hours. [illegible] fire was not extinguished because of the danger [illegible] secondary explosions in many of the ruptured lines near the scene of the blast. Much of the hydrocarbons in the process lines and equipment was vented outside the immediate fire area through the emergency vent system. Each system was liquid freed, reduced in pressure, and purged with nitrogen. The fires extinguished themselves as the purged lines and equipment ran out of fuel. The slight pressure supplied by the nitrogen purge gas prevented the flames from entering the fractured lines, and no secondary explosions occurred.

Community effects

A residential area which reached to within 750 ft. of the refining column received damage from flying metal and concussion. The damage area was about four blocks wide and extended $1\frac{1}{4}$ mi. from the plant. Over 600 claims totalling over $600,000 were paid. Fortunately, injuries were limited to minor cuts and abrasions.

The immediate reaction of nearby residents included panic and hostility. The April, 1947 Texas City explosion with its great loss of life and property was still vivid in many memories. Telephone complaints were received by the plant's Insurance and Employee Relations Divisions for handling, where applicable, or transmittal to the insurance carrier's office in Texas City. The complaints indicated residential damage was much greater than originally estimated, and plant carpenters were sent to the area to help in making emergency repairs. The insurance carrier used due haste in [illegible]ing claims and employed independent appraisers when necessary.

Community relations would have been much improved if:

1. An emergency [illegible], staffed by the Corporation Public Relations Division and insurance adjustors, had been set up immediately in the damaged area so that both groups were easily accessible to the residents.
2. The public relations men had been authorized to make emergency relief funds available on the spot.
3. All complainant's first contacts had been made through corporation personnel rather than through the insurance adjustors.

Lessons learned

The necessity for an adequate inert purge gas supply was demonstrated by this fire. Since the main piperack intersection was near the scene of the blast, a large number of hydrocarbon lines were ruptured. These lines were up to 18 in. in size and, in some cases, were connected to large vessels with no shutoff valves. Nitrogen trucks were brought to the area as soon as the fire was under control for use in purging equipment and ruptured lines. Purge gas was obtained from plant sources as soon as temporary piping bypassing the blast area could be installed. The purge gas was introduced as soon as equipment was liquid free and reduced to low gas pressure. As the quantity of hydrocarbons in the system diminished, purge gas was increased so that eventually the fire burning at the end of open lines was extinguished. The absence of secondary explosions during the emergency and cleanup effort testified to the effectiveness of this approach.

Anti-vacuum type emergency blowdown valves which close at 1- to 2 lb. pressure provided an important safety feature. The blowdown valves on the major distillation columns were opened immediately after the explosion to reduce pressure on equipment near the fire. Since much of this equipment contained light hydrocarbon liquids under pressure, the temperature of

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