National Transportation Safety Board
Washington, D.C. 20594

Hazardous Materials Accident Brief

Accident Number:	DCA-97-SZ-001
Transportation Mode:	Rail
Type of Accident:	Tank car failure and release of corrosive and poisonous liquid
Location:	Illinois Central Railroad yard, Memphis, Tennessee
Date and Time:	April 2, 1997, about 12:05 p.m.
Carrier:	Illinois Central Railroad
Shipper:	Allied-Signal, Inc.
Tank Car Number:	ACAX 80010
Tank Car Specification:	DOT 112S400W
Tank Car Manufacturer:	ACF Industries Incorporated
Injured:	None
Evacuated:	Approximately 150 people
Material Released:	Hydrogen fluoride, anhydrous (corrosive and poisonous)
Type of Failure:	Hydrogen-assisted crack in repair weld

Description of the Accident

At 4:30 a.m., on April 2, 1997, tank car ACAX 80010 arrived at the Illinois Central Railroad yard in Memphis, Tennessee, on Illinois Central train No. GEME 01. At 12:05 p.m., a railroad inspector noticed leakage from the tank car during switching operations. The tank car was filled with anhydrous hydrogen fluoride, a corrosive and poisonous liquid. Vapor appeared to be leaking from a weld at a 2- by 3-foot patch in the tank wall. About 150 people (26 residences) were evacuated from a ½-mile radius around the yard for about 17 hours while the leak was controlled and the material was transferred to another tank car. No injuries were reported.

The tank car had been loaded at Allied-Signal, Inc., (the tank car owner and shipper) in Geismar, Louisiana, on March 17, 1997, and shipped on March 31, 1997, destined for Cameco in Port Hope, Ontario, Canada. The tank car had been removed from service for repairs in February 1997; the repairs included cutting out a 2- by 3-foot section of the tank wall and welding a patch into the wall. This shipment was the tank car's first after being returned to service.

Tank Car

Tank car ACAX 80010 was built in 1971 by ACF Industries Incorporated (ACF) as a U.S. Department of Transportation (DOT) specification 112A400W tank car.[1] The tank was constructed of steel that met the Association of American Railroads (AAR) classification for TC 128 Grade "B" steel, with a minimum thickness of 0.7317 inch. According to the AAR Certificate of Construction, ACAX 80010 was one of six cars originally built by ACF for transporting anhydrous hydrogen fluoride.

Allied-Signal, Inc., purchased tank car ACAX 80010 and used it in the company's Amherstburg plant fleet in Canada from the early 1970s until 1994 (when the Amherstburg plant shut down). The tank cars at that plant were transferred to Allied-Signal, Inc., Geismar, Louisiana. ACAX 80010 was 1 of 26 tank cars transferred that were made of TC 128 steel.

On December 4, 1996, during a visual inspection of ACAX 80010, Allied-Signal, Inc., discovered two hydrogen blisters[2] in the inside of the tank car; one on the bottom of the tank shell near the tank middle and the other on the side of the tank shell near the "B" end. The tank car was sent to Texana Tank Car & Manufacturing, Inc., (Texana) in Nash, Texas, for repair. On February 24, 1997, the two blisters and the adjacent steel were cut out, and 1-inch-thick American Society for Testing and Materials (ASTM) A516, grade 70 steel patches were butt-welded in the openings.

After the patches were welded into the tank wall, Texana stress-relieved the welds and the heat-affected zones in the material on each side of the welds at temperatures above 1100° F (about 1150° F) for about 1 hour. After the heat treatment, the weld material on each patch was tested for hardness at two locations: one on the interior and one on the exterior of the tank. The hardness readings for the patch near the middle of the tank, where the leak occurred, were Rockwell C 15 (exterior) and C 17 (interior).[3] Texana also radiographed the repair welds, and no defects were observed that caused the welds to be rejected. (During the investigation, the radiographs taken by Texana after the repair were examined at the National Transportation Safety Board's metallurgical laboratories; the examination did not reveal any evidence of cracking.) The tank car was hydrostatically tested to the required test pressure of 400 psig, and no leaks were reported. The tank car was then returned to Allied-Signal, Inc., where an additional hydrostatic test was performed without evidence of leakage being found.

Postaccident examination of the tank car revealed a vertical through-wall crack in the upper horizontal leg of one of the butt welds made during the February 1997 repair. The

[1] In 1990, head shields were added to the tank car, and it was converted to a specification 112S400W car.

[2] A hydrogen blister in steel is a bulge caused by molecular hydrogen trapped at an internal flaw within the steel.

[3] The Rockwell C hardness scale is used for rating the hardness of steels. Higher values indicate higher hardness.

fracture surface had a "river pattern,"[4] indicating that the fracture initiated from multiple locations along the weld crown on the interior surface of the tank car (adjacent to the anhydrous hydrogen fluoride). The crack propagated through the entire weld fusion zone, except for one exterior weld bead. The crack also propagated through portions of the heat-affected zones on both sides of the weld. In the heat-affected zones, areas of flat circular fractures were centered around cavities containing inclusions typical of a form of hydrogen-assisted cracking called "stress-oriented hydrogen-induced cracking." Postaccident testing revealed that the hardness of the weld material near the crack site ranged from Rockwell C 26 to C 32 and averaged Rockwell C 29.

Anhydrous Hydrogen Fluoride and Tank Car Compatibility

Anhydrous hydrogen fluoride is a colorless liquid that fumes in air and has a sharp, pungent odor. The DOT defines anhydrous hydrogen fluoride as a Class 8 (corrosive) [5] with a poison-inhalation hazard and assigns it to Packing Group I, which contains materials that represent the greatest hazard in transportation within that class and therefore require the strongest packaging. According to the material safety data sheet,[6] both the liquid and its vapors can cause severe burns that may not be immediately painful or visible; the symptoms may be delayed for hours. Anhydrous hydrogen fluoride will penetrate the skin and attack underlying tissues and bone. Severe inhalation exposure can cause nose and throat burns, lung inflammation, and pulmonary edema. The toxic effects can result in death if not promptly treated.

E.I. DuPont de Nemours (DuPont) has studied the effect of anhydrous hydrogen fluoride on carbon steel vessels. One DuPont study[7] documented three types of damage caused by atomic hydrogen involved in corrosion: hydrogen-assisted stress corrosion cracking, blistering, and stress-oriented hydrogen-induced cracking. In each of these processes, anhydrous hydrogen fluoride reacts with the surface of carbon steel and releases atomic hydrogen. When released, atomic hydrogen can diffuse into the steel and pass through it. When, however, a single hydrogen atom encounters an internal void space or a flaw (an inclusion) in the steel, it will combine with other atoms to form molecular hydrogen. Molecular hydrogen cannot pass through the steel and becomes trapped in the flaw.

According to DuPont, hydrogen-assisted stress corrosion cracking normally occurs in welds and associated heat-affected zones that have a material hardness exceeding Rockwell C

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[4] A river pattern is a series of radiating lines on the fracture surface. The lines indicate the direction of crack propagation.

[5] "Class" or "Hazard Class" refers to the hazard category to which the DOT assigns a particular hazardous material under the definitional criteria provided in 49 *Code of Federal Regulations* (CFR) Part 173 and the provisions of the associated hazard table (172.101).

[6] A material safety data sheet is developed by the producer of a chemical product and contains general information about it, including its chemical and physical properties, the health and environmental hazards it poses, and guidelines for responding to product releases.

[7] Schuyler, Roy L., III, Ph.D., *Hydrogen Blistering of Steel in Anhydrous Hydrofluoric Acid*, National Association of Corrosion Engineers, Houston, Texas, March 1979.

22. The hardness in the weld and the heat-affected zone directly relates to unrelieved residual stress from welding. When the atomic hydrogen diffuses into the weld material, it forms molecular hydrogen at microvoids in the material, thus increasing the stress and the potential for cracking. DuPont determined that hydrogen-assisted stress corrosion cracking propagates with relative rapidity in materials of high hardness and will not readily propagate from the harder material into an area of lower hardness. DuPont studied a through-wall crack caused by hydrogen-assisted stress corrosion cracking in a weld on a vessel transporting anhydrous hydrogen fluoride. The weld failed after 26 days of exposure to anhydrous hydrogen fluoride. DuPont determined that the weld material had a hardness exceeding Rockwell C 22 from the inside surface to the outside surface of the vessel. The crack affected only the material in the weld and the nearby heat-affected zone; the adjacent material, with hardness below Rockwell C 22, was not affected.

Blistering, according to DuPont, primarily affects low-carbon steels and occurs when atomic hydrogen combines to form molecular hydrogen along well-developed planes of impurities in the steel. These planes of impurities usually run parallel to the surface near the mid-plane of the steel plate. As molecular hydrogen forms along the planes of impurities, the pressure increases, eventually becoming sufficient to expand the flaw and separate a localized area in the steel into two thinner plates, distorting one of the exterior surfaces. The distortion is called a “blister.”

DuPont stated that stress-oriented hydrogen-induced cracking is associated with blistering; however, it affects steel that has a soft microstructure but does not contain large planes of impurities. Molecular hydrogen collects at small inclusions within the steel and forms microblisters. Stress-oriented hydrogen-induced cracking is characterized by cracking between the microblisters. It occurs in areas of the steel that have residual stress and is frequently discovered in the heat-affected zones adjacent to welds.

Since the early 1970s, the DOT and the AAR have recognized compatibility problems between anhydrous hydrogen fluoride and certain carbon steels. The DOT provided limits in 49 CFR Part 179.102-13 that included a requirement that all valves and appurtenances be made of metal not subject to rapid deterioration by anhydrous hydrogen fluoride.[8]

In 1972, the AAR began studying the compatibility of materials used to construct tank car shells and heads for anhydrous hydrogen fluoride service. On February 18, 1977, in response to information provided by the National Association of Corrosion Engineers (now NACE International) and the Chemical Manufacturers Association (CMA), the AAR petitioned the Materials Transportation Bureau, (now the Office of Hazardous Materials Safety in the Research and Special Programs Administration [RSPA]) to amend 49 CFR Part 179.102-13 to further regulate the manufacture of tank cars used in the transportation of

[8] In 1990, as part of a comprehensive revision of the hazardous materials regulations to make them parallel the United Nations Standards (HM-181), 49 CFR Part 179.102-13 was removed. Parts 173.24(e), 179.15, and 179.100-13(a) have general product compatibility requirements similar to those removed.

anhydrous hydrogen fluoride. In part, the petition proposed limiting steels used in tank shell construction to specification ASTM A516-71, grade 70 normalized steel and ASTM A537-69, class 1 (normalized) steel. The petition also proposed that welding or welded repairs on tank cars should be subjected, after the initial heat treatment, to a localized postweld heat treatment that would reduce the maximum hardness of the weld and heat-affected zone to Rockwell C 22. In 1980, the AAR resubmitted its petition for regulatory changes. This petition was not acted on until June 3, 1986, when RSPA issued a Notice of Proposed Rulemaking (NPRM), Docket No. HM-166U,[9] that proposed amending 49 CFR Part 179.102-13 to incorporate the AAR's changes as submitted.

In 1979, after the AAR petition was submitted and before RSPA issued the NPRM, DuPont provided new information to the AAR, which included the material concerning the effect of anhydrous hydrogen fluoride on carbon steel noted earlier. The information provided by DuPont indicated that hydrogen blistering was a problem in some, but not all, tank car steels, and that certain steels, other than those cited in the petition, might be acceptable in anhydrous hydrogen fluoride service.

Because of the information provided by DuPont, the AAR, with the help of the CMA, began collecting information about hydrogen blistering in tank cars in anhydrous hydrogen fluoride service. A March 13, 1985, letter from the CMA to the AAR stated that 132 of the 212 tank cars in anhydrous hydrogen fluoride service had been inspected and that the inspections indicated that hydrogen blisters developed slowly in most tank car materials. The letter stated that blisters could be identified during the required periodic visual inspections and repaired before they threatened tank car integrity. The letter also stated, however, that tank cars manufactured of TC 128 steel were the exception to this rule because 22 of the 29 TC 128 steel tank cars inspected had developed hydrogen blisters after only 3 years in anhydrous hydrogen fluoride service. The CMA letter further stated that only one tank car made of TC 128 steel was still in anhydrous hydrogen fluoride service and that the industry had no intention of placing additional cars made of TC 128 steel in this service.[10]

In 1987, before RSPA amended its regulations, the AAR amended its *Manual of Standards and Recommended Practices* (M-1002), incorporating the changes it had proposed to RSPA. (The limit on the post-heat treatment hardness of the material in the heat-affected zone was lowered from Rockwell C 22 to Rockwell C 20.)[11] In addition, the AAR forbade the use of TC 128 steel for repair patches on tank cars in anhydrous hydrogen fluoride service and forbade the conversion of tank cars made of TC 128 steel to anhydrous hydrogen fluoride service. The AAR standards did not limit the use of tank cars made of TC 128 steel that were already in anhydrous hydrogen fluoride service. The AAR

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[9] *Federal Register*, Vol. 51, No. 106, dated June 3, 1986, page 19666.

[10] Twenty-six tank cars made of TC 128 steel, including ACAX 80010, were in Canada at this time.

[11] AAR standards restrict the material hardness of the weld material on repairs to tank cars in any service to Rockwell C 20 (M-1002, R10.00).

withdrew its petition for rulemaking, and RSPA dropped the provisions concerning tank cars in anhydrous hydrogen fluoride service from the amendments in HM-166U.[12]

Postaccident Actions

After the April 1997 leak in Memphis, Allied-Signal, Inc., and Texana jointly performed experiments to determine what changes to their procedures for repairing anhydrous hydrogen fluoride tank cars were necessary to ensure that the material hardness of the repair welds and heat-affected zones would be below Rockwell C 20. As a result of these experiments, Texana modified its weld repair procedures for anhydrous hydrogen fluoride tank cars. The procedures now require the use of filler metal with a carbon equivalent of less than 0.42 percent, and the repair heat treatment was increased to 2 hours at a temperature of about 1225° F. In addition, hardness tests will be performed on the entire perimeter of the inside weld surface (the side exposed to the anhydrous hydrogen fluoride) in ½-inch intervals. Each interval will include at least three tests; one each on the material in the heat-affected zones on each side of the weld and one on the weld material. Random hardness tests will also be performed on the exterior of the weld.

The two February 1997 patch repairs on tank car ACAX 80010 were inspected and tested in accordance with these new procedures, and the repair patch that failed was completely removed and replaced, and the replacement patch was heat-treated. The patch that did not fail was tested and was determined to be in compliance with AAR standards; therefore, it was not replaced. In the process of inspecting the tank car, four additional hydrogen blisters were identified in the tank shell; these were removed and repaired using the revised procedures.

Also, the AAR Tank Car Committee formed a subcommittee that will investigate the Memphis, Tennessee, accident and review the prohibition of TC 128 steel from tank car manufacture (M-1002, section 2.1.7); the intermixing of TC 128 and A516 steels in repairs and the required hardness tests (M-1002, R5.02); and the requirements for "rise-time, hold-time, and sink-time [cooling period]" in postweld heat treatment (M-1002, R21.00).

Probable Cause

The National Transportation Safety Board determines that the probable cause of the failure of tank car ACAX 80010 was inadequate heat treatment to reduce the hardness of the weld material used in the repair of the tank to a level that would retard or prevent hydrogen-assisted cracking and inadequate testing to determine whether the weld material hardness exceeded established limits.

Adopted: November 17, 1998

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[12] *Federal Register*, Vol. 52, No. 75, dated April 20, 1987, page 13034.