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LIQUID BROMINE PENTAFLUORIDE RELEASE TESTS

AUTHOR:

K. E. Habiger

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE GASEOUS DIFFUSION PLANT

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**UNION
CARBIDE**

OAK RIDGE GASEOUS DIFFUSION PLANT
P. O. Box P
Oak Ridge, Tennessee 37830

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K. E. Habiger

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Liquid bromine pentafluoride has been considered for use as the uranium fluorinating agent in fluoride volatility processes for recovering values from irradiated fuel. Since bromine pentafluoride is extremely reactive, it was felt that a testing program should be undertaken to determine the resistance to attack and/or vigorousness of reaction when materials typical of those that might be present in a fluoride volatility plant are contacted with bromine pentafluoride. The tests were not intended to evaluate corrosion resistance of materials routinely exposed to bromine pentafluoride, however. The tests showed that, in general, almost all organic materials, including conventional protective clothing and equipment, react violently with liquid bromine pentafluoride. Residual explosive compounds may be formed as demonstrated in one test with a heat transfer cement. All of the metals tested were essentially inert to reaction with liquid bromine pentafluoride at room temperatures, as were metal fluorides, Transite, alumina, Teflon, and Kel-F. Foam type insulations, loose webbed materials, and fine powders or dusts appeared to be particularly susceptible to reaction with liquid bromine pentafluoride.

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LIQUID BROMINE PENTAFLUORIDE RELEASE TESTS

In cooperation with the national laboratories, the Oak Ridge Gaseous Diffusion Plant has been engaged in a variety of conceptual and hardware development studies aimed at the development of fluoride volatility processes for recovering values from irradiated nuclear fuel. In a study recently completed*, bromine pentafluoride was chosen as the uranium fluorinating agent. One of the reasons for its selection was that it can be used to convert uranium dioxide to the volatile hexafluoride, while leaving the plutonium in a nonvolatile form. Consequently, a basic separation of uranium from plutonium can be made at this fluorination step.

The use of bromine pentafluoride as the uranium fluorinating agent would necessitate handling large quantities of this material in the liquid phase. Thus, since bromine pentafluoride is extremely reactive, it was felt that a testing program should be undertaken to evaluate some of the hazards involved in dealing with this reagent. Accordingly, tests were conducted to determine the resistance to attack and/or vigorousness of reaction when various materials were contacted with liquid bromine pentafluoride. The materials included in the tests were those which might be found in the vicinity of volatility reprocessing operations. Liquid bromine pentafluoride could conceivably come in contact with these materials in the event of a spill or a break in a process line. The tests, it should be noted, were not intended to evaluate corrosion resistance of construction materials routinely exposed to bromine pentafluoride. Also, some items which were expected to be very reactive to bromine pentafluoride were tested as well, so that the importance of excluding these materials from plant operating areas could be emphasized. Following a brief description of the experimental apparatus and procedure, the test results are discussed.

SUMMARY

The objectives of the experimental work were, first, to deliver safely a controlled amount of bromine pentafluoride liquid to the test specimen and, then, to record and evaluate the results of the contact between the materials. In order to simulate a liquid bromine pentafluoride spill, a test volume of approximately 0.03 cubic feet (equivalent to about 5 pounds) was selected as the basic charge.

* Breton, D. L., Schappel, R. B., Merriman, J. R., Pashley, J. H., Littlefield, C. C., and Habiger, K. E., A Conceptual Study of a Fluoride Volatility Plant for Reprocessing Light Water Reactor Fuels, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, December 24, 1968 (K-1759).

The tests were conducted in the ORGDP hazardous gas disposal area. Samples were placed in a shallow nickel pan, and a small amount of liquid bromine pentafluoride was drained into the pan via pipeline from a valving station located 150 feet upwind. Upon completion of each test, the pan was tilted, and the contents were dumped by the use of a sling and a long rope.

A variety of materials were tested. For convenience, these materials can be categorized as (1) fabrication and construction materials; (2) lubricants and oils; (3) wearing apparel; (4) animal flesh; (5) insulation, coatings, and gaskets; and (6) miscellaneous items.

With the exception of asphalt, wood, poly(methyl-methacrylate), and electrical wiring, the materials tested under the fabrication and construction materials category were quite resistant to attack from liquid bromine pentafluoride. Included in the tests were selected metals, Transite, concrete, glass, and the four aforementioned materials. In general, most of the lubricants and oils tested reacted violently with bromine pentafluoride and were completely consumed. An exception was fluorocarbon oil, which reacted vigorously, but without evidence of open flames or explosions. All of the wearing apparel tested, including conventional safety equipment, were quite reactive with bromine pentafluoride. An explosion occurred when animal flesh contacted the reagent. The reaction of liquid bromine pentafluoride with materials listed under insulation, coatings, and gaskets ranged from no visible reaction with Teflon and Kel-F to quite vigorous reactions with some of the insulation materials. Materials with the largest surface-to-volume ratios reacted the most violently. A heat transfer cement exploded when subjected to mechanical shock several minutes after the test. Gasoline, water, and soda ash, listed under the miscellaneous category, reacted vigorously with bromine pentafluoride, while alumina, potassium hydroxide, sodium fluoride, and magnesium fluoride exhibited little or no reaction tendency.

EXPERIMENTAL PROCEDURE AND APPARATUS

The bromine pentafluoride release tests were performed at a gas cylinder disposal site west of the ORGDP buildings, an area remote enough so that the vapors resulting from the tests did not constitute a hazard in the operating areas. The entire test area was roped off and posted at a minimum distance of about 300 yards from the point of release before, during, and after the tests.

The test apparatus consisted of a fixed-volume chamber with attendant equipment and instrumentation designed to (1) purge the chamber with nitrogen, (2) evacuate the hold volume, (3) fill the volume with bromine pentafluoride liquid, (4) sample the liquid, (5) drain or force the liquid through a length of tubing and onto the test specimen placed in an open pan, (6) remotely apply mechanical shock to the residual ingredients in the pan and also dump it, and (7) again purge the system.

The hold volume consisted of a 17-inch length of 2-inch-diameter schedule-40 Monel pipe, with weld caps and 1/2-inch-diameter outlets on each end. When filled to capacity, this chamber contained approximately 5 pounds of liquid bromine pentafluoride. The bromine pentafluoride was discharged through a Monel bellows seal valve and was then drained or forced through a 150-foot length of 1/4-inch copper tubing and was released into the nickel pan containing the test specimen. The charging and metering station was at an elevation which was approximately 20 feet above the level of the test site.

Mounted in a rack and inclined with its valve downward, a 250-pound bromine pentafluoride cylinder served as the supply for the tests. A laboratory vacuum pump was connected to the hold volume through a soda-lime trap to aid in charging and sampling. The soda-lime material, intended to prevent bromine pentafluoride vapors from contacting the vacuum pump oil, was changed frequently. A cylinder of nitrogen was also connected to the hold volume to permit purging and to allow a pressurized discharge of bromine pentafluoride, if desired. A schematic diagram of the test apparatus is shown in figure 1 for better visualization.

To record the reaction results for future reference, 16 mm silent motion pictures were taken of selected tests. The films were edited and spliced to make a continuous 17-minute show of these tests.

TEST RESULTS

The ambient temperature at the times the tests were conducted varied from about 75 to 85°F, with high humidity conditions prevailing. No attempt was made to control or alter the sample or bromine pentafluoride temperatures during any of the experiments.

The materials tested can be listed, for convenience, under six main categories. These are (1) fabrication and construction materials; (2) lubricants and oils; (3) wearing apparel; (4) animal flesh; (5) inculation, coatings, and gaskets; and (6) miscellaneous items. The reaction of liquid bromine pentafluoride with materials in each of these categories is discussed below.

Fabrication and Construction Materials

The materials tested under this category are listed, with observed reactions, in table I.

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SCHEMATIC DIAGRAM OF EQUIPMENT USED IN
LIQUID BROMINE PENTAFLUORIDE RELEASE TESTS

Figure 1

TABLE I

REACTION OF FABRICATION AND CONSTRUCTION MATERIALS
WITH LIQUID BROMINE PENTAFLUORIDE

<u>Material</u>	<u>Observed Reaction with Liquid Bromine Pentafluoride</u>
Selected Metals*	None
Transite	None
Concrete	No damage to sample
Glass	Etched
Poly(methyl-methacrylate)	Burned, completely consumed
Asphalt	Burned, possibly exploded
Wood	Partially burned
Electrical Wiring	Completely burned

* The metals included stainless steel-304, stainless steel-316, Inconel, nickel, brass, copper, steel, zirconium, and Monel.

Two types of tests were performed with the metals listed in table I. The first of these consisted of carefully cleaning the metal samples with acetone and then contacting them with liquid bromine pentafluoride. The second test consisted of covering each sample with grease, followed by exposure to bromine pentafluoride.

The results of the first test indicated that none of the metals reacted appreciably with liquid bromine pentafluoride. In fact, there was no observed violent reaction, such as an explosion, flame, smoldering, etc. After the test, each sample was observed to be coated slightly, presumably by a metal fluoride, which indicated that a slight surface reaction had taken place, as expected. The surface coating probably prevented any further reaction from taking place.

In the second test, the grease covering the metal samples exploded and burned vigorously when contacted with liquid bromine pentafluoride; however, the metals remained unscathed. None of the samples was ignited by the burning grease, a possibility considered prior to the test. The results of these tests do not rule out, however, the possibility that metals might ignite under conditions of prolonged exposure to grease and liquid bromine pentafluoride. The actual exposure time of the metals to

liquid bromine pentafluoride in this test was fairly short, probably on the order of 15 to 30 seconds.

It seems reasonable to conclude from the results of these tests that all of the metals tested can be used safely in applications that might result in their contacting liquid bromine pentafluoride at room temperature. To minimize any reaction that might occur, the metal surfaces should be free from grease, scale, or other foreign material.

As indicated in table I, there was no observed reaction with Transite. In fact, there was no visible change in the appearance of the sample tested. Thus, this material should be suitable for construction applications in areas that might inadvertently be exposed to liquid bromine pentafluoride.

Concrete also exhibited good resistance to reaction with liquid bromine pentafluoride in that there was no visible damage to the sample tested; however, since it was simultaneously tested with other samples, it was impossible to determine if any surface reactions occurred. It is probable that there could have been a reaction with a dust coating that may have been present. It was observed that, whenever liquid bromine pentafluoride spilled onto limestone material below the sample pan, an immediate reaction occurred which was of short duration. Presumably, the reaction was with a layer of high surface area dust on the limestone; when the dust was totally consumed, the reaction stopped. This same situation probably occurred with the concrete sample.

Poly(methyl-methacrylate) was completely consumed in the reaction with liquid bromine pentafluoride, while glass, asphalt, wood, and electrical wiring were all partially consumed. Glass was etched, but otherwise undamaged, while the electrical wiring was almost totally consumed, and the wood sample was badly charred. Asphalt exploded upon contacting liquid bromine pentafluoride and then burned until it was almost completely consumed.

Lubricants and Oils

The materials tested under this category are listed in table II with the observed reaction for each.

Greases, hydrocarbon oils, and silicon oil exploded when contacted with liquid bromine pentafluoride. Each burned in a very hot fire until totally consumed. Fluorocarbon oil reacted less violently, releasing copious amounts of orange-white vapors. No explosions or visible flames occurred, however, and the sample was only partially consumed.

TABLE II

REACTION OF LUBRICANTS AND OILS
WITH LIQUID BROMINE PENTAFLUORIDE

<u>Material</u>	<u>Observed Reaction With Liquid Bromine Pentafluoride</u>
Greases	Succession of explosions, fire
Hydrocarbon Oils	Explosion, fire
Fluorocarbon Oil	Reaction gave off orange-white smoke, but no flames or explosion; partially consumed
Silicon Oil	Exploded and burned vigorously

Wearing Apparel

The materials tested under this category and the test observations are listed in table III.

TABLE III

REACTION OF WEARING APPAREL
WITH LIQUID BROMINE PENTAFLUORIDE

<u>Material</u>	<u>Observed Reaction With Liquid Bromine Pentafluoride</u>
Leather, Neoprene Gloves	Completely consumed
Safety Glasses	Frames destroyed, lenses etched
Assault Mask	Burned vigorously, completely consumed
Paper and Cloth	Burned, completely consumed
Vinyl Coat	Burned, completely consumed
Asbestos Mitten (tight weave)	Partially consumed

In general, all of the wearing apparel tested was quite reactive with liquid bromine pentafluoride. It was apparent from the tests that conventional protective apparel, such as that fabricated from rubber, leather, or vinyl (polyvinyl chloride), offers little or no protection to the wearer in the event of direct contact with liquid bromine pentafluoride.

In-line air filters or chemical cartridges containing carbon reacted vigorously and sometimes explosively when contacted with liquid bromine pentafluoride. Carbon-impregnated chemical cartridges are frequently used in assault masks. The asbestos mitten tested appeared to offer more resistance to attack in that it was only partially consumed; however, it too would have probably been totally consumed under prolonged exposure to liquid bromine pentafluoride.

Thus, of the materials tested, asbestos was the only one in which some degree of protection from direct contact with liquid bromine pentafluoride would be obtained. Even this material would be of little value if its porosity was high. (A loose web sample of asbestos was completely pulverized by its reaction with liquid bromine pentafluoride [see table IV]).

Animal Flesh

The reaction of bromine pentafluoride with animal flesh, which consisted of sow's ears and bone material, was violent. Immediately upon contacting liquid bromine pentafluoride, a sharp explosion occurred which blew the test materials out of the sample pan and, thus, prevented any further reaction. The test materials were slightly scorched, but otherwise intact. The explosion was not surprising, since the animal flesh probably consisted of a high percentage of unsaturated fats which would be expected to react violently with liquid bromine pentafluoride, just as the oils and greases mentioned above.

Insulation, Coatings, and Gaskets

A list of these materials is shown in table IV, along with the observed reactions with liquid bromine pentafluoride.

All of the insulation materials listed in table IV reacted, at least partially, with liquid bromine pentafluoride, polyurethane being the most reactive and felt the least reactive. Of the foam-type materials tested, polyurethane was the most reactive, followed by the low-temperature foam and then the phenolic foam. There were several small explosions as soon as bromine pentafluoride contacted the polyurethane, followed by a very vigorous self-sustaining fire that almost completely consumed the sample. The low-temperature foam was also completely consumed, while the phenolic foam was only partially consumed by a fire that extinguished itself after all of the bromine pentafluoride had reacted.

The reactivity of the remaining insulation materials was probably related to the surface area available to reaction. For example, two samples of asbestos were tested, one a loose web material and the other

TABLE IV

REACTION OF INSULATION, COATINGS, AND GASKETS
WITH LIQUID BROMINE PENTAFLUORIDE

<u>Material</u>	<u>Observed Reaction With Liquid Bromine Pentafluoride</u>
Teflon	None
Rubber	Melted and burned
Cork	Burned, almost totally consumed
Yellow Tape and Plastic	Burned, completely consumed
Kel-F	None
Rubber Weather Stripping	Burned, almost completely consumed
Fire Retardant Coating (Gray)	Almost completely consumed
Heat Transfer Cement	Burned, residue exploded in two out of four tests
Reinforced Phenolic Foam Insulation	Partially burned and charred, discolored
Glass Wool Insulation	Burned, completely consumed in contacted areas
Urethane Insulation	Burned vigorously, almost completely consumed
Magnesium Oxide Insulation	Partially burned and charred, discolored
Foamed Plastic Insulation (low temperature)	Reacted vigorously, totally consumed
Felt Insulation	Remained intact but partially consumed
Asbestos Strip (loose web)	Almost totally consumed
Asbestos Strip (tight weave)	Remained intact but partially consumed

in the form of a protective mitten. The first sample was completely disintegrated, while the other, as noted previously, remained intact, although it was partially reacted. The high surface area of glass wool made it particularly susceptible to reaction with liquid bromine pentafluoride. Thus, it was not surprising to find it completely consumed in areas that had come in contact with bromine pentafluoride, although the reaction was smooth, with no evidence of explosions or splattering.

Of the three insulation materials remaining to be discussed, magnesium oxide was the most reactive, its reaction being similar to the one for phenolic foam. Cork reacted partially with liquid bromine pentafluoride resulting in a smoothly burning fire that continued to burn after all bromine pentafluoride was consumed. Felt remained essentially intact and was only partially consumed by its reaction with bromine pentafluoride.

As can be seen from table IV, all of the remaining materials were quite reactive with liquid bromine pentafluoride, with the exception of Teflon and Kel-F. Teflon and Kel-F did not appear to react to any significant degree. The reactions of liquid bromine pentafluoride with rubber, with weather stripping, with yellow tape, with plastic, and with fire retardant paint were similar in that each of these materials was completely consumed. While the former materials were consumed in a flame, no flame was evident in the case of the fire retardant coating which had been painted on metals. A vigorous reaction with the fire retardant did take place, however, as evidenced by the copious amounts of orange-red vapors given off.

The heat transfer cement tested burned after being exposed to bromine pentafluoride, with no evidence of an initial explosion. Several minutes after the test, the nickel sample pan was moved to prepare for the next experiment. At this point, the greenish-black powder residue began to slide down the pan and exploded violently. Apparently, the reaction of bromine pentafluoride with heat transfer cement had created a highly unstable compound, possibly an interstitial carbon-fluorine compound, which was detonated by mechanical shock as the pan was moved. The test with heat transfer cement was repeated three times in attempts to reproduce the earlier results. In all three tests, the samples burned in a manner similar to the above case; however, on only one occasion was another explosion obtained when the sample pan was moved, and this explosion was quite small in magnitude compared to the previous case. Apparently, in the last three tests, conditions were less favorable for the formation of the explosive compound. An important point to remember, however, is that a violent explosion did occur once, which suggests the possibility of reoccurrence with heat transfer cement or with similar materials.

Miscellaneous Items

These materials and the reaction of each with liquid bromine pentafluoride are shown in table V.

TABLE V

REACTION OF LIQUID BROMINE PENTAFLUORIDE
WITH MISCELLANEOUS ITEMS

Material	Observed Reaction
Gasoline	Explosion
Water, Soda Ash	Reaction gave off orange smoke with appreciable splattering
Alumina, Potassium Hydroxide, Sodium Fluoride, and Magnesium Fluoride	Gave off orange-brown smoke, no apparent damage to materials

As shown in table V, gasoline exploded and burned when contacted with liquid bromine pentafluoride. The reactions with water and soda ash were similar. There was considerable splattering in each case and copious amounts of vapor were evolved, ranging in color from orange to red-orange for soda ash and water, respectively. Neither material reacted explosively with liquid bromine pentafluoride, and no flames were evident. Each was partially consumed.

The remaining materials reacted to give off small amounts of orange-brown smoke, but no noticeable damage occurred to the samples.

CONCLUSIONS

The tests showed that, in general, almost all organic materials, including conventional protective clothing and equipment can be expected to react violently with liquid bromine pentafluoride at room temperatures. Greases and oils tend to react explosively, while other organics tend to burn without exploding. Extreme caution should be taken in handling partially consumed organic materials or residues after they have been exposed to liquid bromine pentafluoride. There is a possibility that explosive compounds may be formed that may detonate when exposed to vibrations or other mechanical shocks.

The degree of reactivity of liquid bromine pentafluoride with many materials is probably related to the surface area available for reaction. Foam type insulations, loose webbed materials, and fine powders or dusts appear to be particularly susceptible to reaction with liquid bromine pentafluoride.

All of the metals tested were essentially inert to reaction with liquid bromine pentafluoride at room temperatures, as were metal fluorides, Transite, alumina, Teflon, and Kel-F. Of course, a reaction would be expected to occur with any surface contamination; such as grease, oil, or dust on the samples.

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