RFP-531

COMPATIBILITY STUDIES OF ANION EXCHANGE RESINS

PART I

THE COMPATIBILITY OF DOWEX 1x4 NITRATE FORM
ANION RESIN WITH NITRIC ACID AND OXIDES
OF NITROGEN

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G. F. Molen

THE DOW CHEMICAL COMPANY
ROCKY FLATS DIVISION
U.S. ATOMIC ENERGY COMMISSION
CONTRACT AT (29-1) -1106

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G. F. Molen

THE DOW CHEMICAL COMPANY
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Golden, Colorado

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ABSTRACT

The compatibility of Dowex lx4 nitrate form anion exchange resin with nitric acid, and the compatibility of several types of plastic tubing with nitric acid were investigated. Ignition properties of resin extract, treated resin and mixtures of tubing extract with either resin extract or treated resin were also investigated.

SUMMARY AND CONCLUSIONS

Dowex 1x4* nitrate form resin was treated with nitric acid at varying temperatures and for varying time periods. Mayon, Tygon, and thermoplastic tubing were similarly treated. The treated resin, and extracts from the treated resin and tubing were found to react exothermally at temperatures as low as 110°C. Some of these extracts ignited spontaneously at temperatures as low as 135°C. The smoke which evolved from these reactions would burn, and on occasion, explode, when ignited by a spark gun.

The possibility for forming ClF_3 was considered, however, a literature search indicated that reaction conditions are very rigorous. Lab analysis on the ion column effluent stream indicated only small quantities of chloride present.

Analysis of gases formed when resin is contacted with nitric acid in a pressure vessel indicates a C-C bond cleavage. This postulate is based on the excess of CO_2 found in the gas mixture.

Extraction of resin with nitric acid gave inconsistent results. The amount of insolubles found in the extract did not always increase with time and increased acid concentration. The extract was insoluble in carbon tetrachloride and soluble in water. Attempts to identify the extract by infrared analysis have not been successful. Concentrations of approximately 7N HNO_3 or greater were required to produce significant quantities of resin extract.

Reactions of NO_2 and N_2O with various glovebox materials produced nothing which would ignite spontaneously.

Others at Rocky Flats found the following:

1. Phthalic anhydride, o-phthalic acid, dioctylphthalate, and butylphthalylbutylglycolate were present in the tubing extracts.
2. Chloride could be leached from the tubing. The least amount was leached from Tygon tubing.
3. Although pressure buildup does occur in an ion column when not vented, no significant temperature rise was measured.

* Trade name Dow Chemical Company

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INTRODUCTION

This study was initiated to answer questions on why a fire occurred in an ion exchange column at the Rocky Flats Plant on July 14, 1963⁽¹⁾. Since this incident, a fire occurred in the Redox plant in Hanford⁽²⁾, which appears to be similar to the fire at Rocky Flats, both having taken place in an anion exchange facility.

As a result of the Rocky Flats fire, an investigation was undertaken to determine the compatibility of Dowex 1x4 nitrate form anion resin with nitric acid and with the various types of plastic tubing used in the recovery operation. The resin and tubing were leached with both 7N and 12N HNO₃ at 50°C and 100°C for periods up to two weeks. Ignition of the various residues was performed in a hot air ignition furnace conforming to ASTM specifications for determining self-ignition temperatures of plastics.

EXPERIMENTAL AND DISCUSSION

A. ANALYSIS OF FLUORIDE AND CHLORIDE IONS IN THE FILTRATE-RECOVERY COLUMN FEED STREAM

Since it is possible that both chloride and fluoride could have been present in the filtrate-recovery (FR) feed stream, it was thought that possibly a reactive interhalogen such as chlorine trifluoride could be formed according to the following equation:

A literature search indicated that ClF₃ is difficult to prepare, and that it decomposes in aqueous solutions. Furthermore, analysis of the FR stream for both fluoride and chloride indicated that chloride concentrations were very low. The fluoride concentrations varied from 0.2 to 3.9 grams/liter. Analyses for these ions are found in Table I. This information indicates that there probably was no reaction between chloride and fluoride.

- (1) Report of Investigation of Fire, Building 71, on July 14, 1963, The Dow Chemical Co., Rocky Flats Div., July 22, 1963, RFP-360.
 (2) "Incident in Plutonium-Processing Facility at Hanford," Reactor Fuel Processing, 7, No. 4, 297-303 (Fall 1964).

TABLE I

RANDOM FLUORIDE AND CHLORIDE ANALYSES IN THE FR FEED
STREAMS FROM AUGUST 1 THROUGH OCTOBER 31, 1963

Req. No.	F ⁻ (g/l)	Cl ⁻ (g/l)	Req. No.	F ⁻ (g/l)	Cl ⁻ (g/l)
63992	0.7	---	64307	3.2	0.2
67636	1.5	<1	64588	3.9	0.3
67648	1.7	0.3	64594	2.6	0.2
64059	1.8	0.3	64755	0.9	---
64075	2.1	0.4	64837	2.8	0.3
64081	2.2	0.4	64848	1.9	---
64089	1.5	0.1	64340	0.4	0.3
64137	---	<1	64986	2.5	0.2
5-0229	0.2	0.6	65028	1.4	0.2
5-0230	0.2	0.6	65062	1.4	---
64228	1.2	0.8	65076	---	<1
64234	1.5	0.6			

B. CLOSED VESSEL TESTS:

Approximately 300 gm of the Dowex resin were mixed with 800 ml. of 16N HNO₃ in a polyethylene bottle. The bottle was sealed in a steel pressure vessel equipped with a 100 psi gage. The vessel was then placed in an oven at 50°C. After 19 days, the vessel was removed and the pressure was found to be 49 psig. A sample of the gas was taken. Both mass spectrometric and infrared analysis indicate a high CO₂ content. At the same time, an identical experiment was performed using 7N HNO₃. After 19 days, there was negligible pressure buildup. The vessel was then placed in the oven at 100°C. After 7 days, it was removed, and the pressure was found to be 92 psig. A gas analysis indicated a composition similar to the previous sample. Results of these analyses are found in Table II.

These tests indicate that a reaction between nitric acid and resin takes place. A possible explanation is a C-C bond cleavage as evidenced by a high CO₂ content in the gas samples.

TABLE II
CLOSED VESSEL TEST RESULTS¹

Component	Volume%	
	7N HNO ₃ at 100° for 7 days	15N HNO ₃ at 50° for 19 days
NO	0.1	8.2
N ₂ O	26.0	14.7
H ₂ O	0.4	0.1
CO	9.7	---
N ₂	20.5	46.6
A	<0.1	0.2
CO ₂	43.1	30.2

¹ Volume-percent values are from Mass Spectrometric analysis.

C. NITRIC ACID LEACHING:

Samples of Dowex 1x4 nitrate form resin were mixed with both 7N and 12N HNO₃ at 50°C and 100°C for up to 2 weeks. The solutions were then filtered, and the filtrates carefully evaporated to dryness on a hot plate. The quantity of dissolved resin in the filtrate fluctuated widely for no apparent reason. Results of these experiments are found in Table III. The extracts were then carefully evaporated to dryness for use in the ignition tests.

Samples of Tygon, Mayon, and thermoplastic tubing were mixed with both 7N and 12N HNO₃ at 50°C and 100°C for 2 weeks. These solutions were then treated in the same manner as described for the resin.

The extracts and the treated plastic and resin appeared to be stable at room temperature. However, during one of the evaporations of resin extract, a portion was spilled on the hot plate which resulted in an instantaneous reaction. The product was a large black fluffy material which was many times the volume of the extract being evaporated.

TABLE III
 INFRARED ANALYSES OF REACTION PRODUCTS FROM NITRIC ACID
 LEACHING OF DOWEX 1x4 NITRATE FORM RESIN

<u>Reaction Conditions</u>	<u>Time Days</u>	<u>Dissolved Solids CCl₄ Phase (g/l)</u>	<u>Dissolved Solids Aqueous Phase (g/l)</u>
12N HNO ₃ at 100°C	1	0.03	3.4
	2	0.0116	76.8
	5	<0.001	9.4
	17	0.005	43.06
7N HNO ₃ at 100°C	1	0.03	4.1
	5	--	65.9
	17	0.003	11.03
12N HNO ₃ at 50°C	1	<0.002	1.9
	5	<0.003	5.6
	17	<0.005	206.22
7N HNO ₃ at 50°C	5	0.007	3.4
	17	0.002	70.90

D. IGNITION TESTS:

A hot air ignition furnace, conforming to ASTM designation D 1929-62T was used for the ignition tests. Samples of the treated resin, resin extract, and mixtures of tubing extract with either treated resin or resin extract were ignited in the furnace. The mixtures were prepared by taking approximately two parts treated resin or resin extract and one part tubing extract and carefully blending them into a homogeneous sample. At the time of either ignition or the start of an exothermic reaction, power to the furnace was shut off. The temperatures of the sample, and the furnace atmosphere were then recorded. When smoke evolved from the furnace (this was usually accompanied by a heat spike) a spark gun was used to ignite the smoke.

The minimum spontaneous ignition temperature was found to be 135°C. This was attained with an extract mixture of resin and Mayon tubing, each of which were treated with 12N HNO₃ at 100°C.

The minimum temperature for initiating an exothermic reaction was 110°C. This was attained with an extract mixture from the resin and thermoplastic tubing, each of which were treated with 12N HNO₃ at 50°C.

In most instances, either spontaneous ignition or exothermic reaction occurred at temperatures <200°C. The resin did not have to be dry in order for a reaction to take place. The maximum temperature increase for the exothermic reactions was 310°C. Upon ignition of the smoke in the exothermic reactions, an explosion would sometimes occur. However, explosions could not always be duplicated when the experiments were repeated. Data for the various conditions are found in Table IV and Table V.

In general, the various extracts were found to ignite at lower temperatures than the treated resin. Identification of the various residues from reacting nitric acid with the resin is not complete, and the mechanism for the reaction is not fully understood.

TABLE IV
IGNITION TESTS ON RESIN AND RESIN EXTRACT AFTER 2 WEEKS OF
CONTACT AT THE GIVEN CONDITIONS

Reaction Conditions	Air Temp (°C)	Sample ¹ Temp (°C)	Ignition ¹ Temp (°C)	Peak Temp (°C)	ΔT	Spark Test ²
Resin from	160	155	Exothermic	195	40	
7N HNO ₃		155	"	230	75	+
at 50°C		155	"	215	60	Explosion
Extract from		175	"	200	25	
7N HNO ₃		200	"	390	190	
at 50°C	185	165	"	195	30	
Resin from	160	167	"	250	83	
7N HNO ₃	205	220	"	297	77	+
at 100°C	163	165	"	225	60	-
Extract from	165		175	245	70	
7N HNO ₃	205		205			
at 100°C	195		155	215	60	
	155		150	195	45	
	215		175	215	40	
	190		160	205	45	
	185		165	210	45	
Resin from	170	135	Exothermic	275	140	+
12N HNO ₃	355	275	"	435	160	
at 50°C	190	135	"	290	155	Explosion
	385	290	"	465	175	
	200	135	"	280	145	
	435	300	"	535	235	
Extract from		125	"	205	80	-
12N HNO ₃	185	165	"	225	60	-
at 50°C						
Resin from	180	145	"	235	90	Explosion
12N HNO ₃		165	"	325	160	-
at 100°C						
Resin from	180	145	"	235	90	Explosion
12N HNO ₃		165	"	325	160	-
at 100°C						
Extract from	160		140	315	175	+
12N HNO ₃	180		145	325	180	
at 100°C						

TABLE IV
(Concluded)

Reaction Conditions	Air Temp (°C)	Sample ¹ Temp (°C)	Ignition ¹ Temp (°C)	Peak Temp (°C)	ΔT	Spark Test ²
Wet Resin	185	135	Exothermic	205	70	
from 7N HNO ₃	265	205	"	515	310	-
at 50°C	85	125	"	210	85	Explosion
		220	"	300	80	+
	450	300	"	500	200	
	95	135	"	195	60	Explosion

¹ If the sample did not spontaneously ignite then the temperature of the start of the exothermic reaction was recorded under sample temperature.

² A positive sign indicates the smoke burned when ignited by a spark gun. A negative sign indicates the smoke did not burn. A blank space indicates the spark test was not attempted. The word "explosion" indicates that an explosion occurred when the smoke was ignited with a spark gun.

TABLE V
IGNITION TESTS ON RESIN AND EXTRACT MIXTURES AFTER 2 WEEKS OF CONTACT AT THE GIVEN CONDITIONS

Reaction Conditions	Air Temp (°C)	Sample ¹ Temp (°C)	Ignition ¹ Temp (°C)	Peak Temp (°C)	ΔT	Spark Test ²
Resin + Mayon Extract		170	Exothermic	260	90	Explosion
from 7N HNO ₃ at 50°C		160	"			Explosion
Resin Extract + Mayon	155	135	"	165	30	-
Extract from 7N HNO ₃		125	"	165	40	-
at 50°C						
Resin + Mayon Extract		115	"	235	120	-
from 7N HNO ₃ at 100°C		115	"	235	120	-
Resin Extract + Mayon	165		140	270	130	Explosion
Extract from 7N HNO ₃	180		150	225	75	Explosion
at 100°C						

TABLE V
(Concluded)

Reaction Conditions	Air Temp (°C)	Sample ¹ Temp (°C)	Ignition ¹ Temp (°C)	Peak Temp (°C)	ΔT	Spark Test ²
Resin + Mayon Extract from 12N HNO ₃ at 50°C	225 185	135 115	Exothermic "	305 300	170 185	Explosion
Resin Extract + Mayon Extract from 12N HNO ₃ at 50°C	135 135	115 115	" ")- No sudden temperature rise			
Resin + Mayon Extract from 12N HNO ₃ at 100°C		115 125	" "			Explosion Explosion
Resin Extract + Mayon Extract from 12N HNO ₃ at 100°C	170 160		135 Exothermic	235 245	100 115	+ Explosion
Resin + Thermoplastic Extract from 7N HNO ₃ at 50°C	175 165	115 130	" "	375 310	260 180	+ +
Resin Extract + Thermo- plastic Extract from 7N HNO ₃ at 50°C		140 130	" "		165 35	- -
Resin + Thermoplastic Extract from 7N HNO ₃ at 100°C	130 130	115 115	" "	215 215	100 100	- Explosion
Resin Extract + Thermo- plastic Extract from 7N HNO ₃ at 100°C	185		150 Exothermic	225 205	75 60	+ Explosion
Resin + Thermoplastic Extract from 12N HNO ₃ at 50°C	155 165	110 110	" "	315 295	205 185	- Explosion
Resin Extract + Thermo- plastic Extract from 12N HNO ₃ at 50°C	155 155	125 125	" "	215 215	90 90	Explosion Explosion
Resin + Thermoplastic Extract from 12N HNO ₃ at 100°C	185 190	160 155	" "	195	35	+ Explosion
Resin Extract + Thermo- plastic Extract from 12N HNO ₃ at 100°C	180 180		145 155	240 225	95 70	+ +

1 If the sample did not spontaneously ignite then the temperature of the start of the exothermic reaction was recorded under sample temperature.

2 A positive sign indicates the smoke burned when ignited by a spark gun. A negative sign indicates the smoke did not burn. A blank space indicates the spark test was not attempted. The word "explosion" indicates that an explosion occurred when the smoke was ignited with a spark gun.

Conditions for initiating either a fire or an exothermic reaction have not yet been duplicated. Work by the Manufacturing Technical group indicates that no heat buildup is normally encountered in a loaded resin column which is not vented. It appears that an external heat source may be necessary to initiate an exothermic reaction.

E. REACTIONS WITH GASEOUS N_2O AND NO_2 :

Samples of various materials such as Plexiglas, plastic tubing, etc., were exposed to an atmosphere of either N_2O or NO_2 under slight pressure for 9 days. The purpose of this was to determine degradation, if any, and observe any violent reactions which might occur. Both N_2O and NO_2 are the more common nitrogen compounds formed from the decomposition of HNO_3 . The samples were then held in the flame of a Bunsen burner. The treated samples did not have burning characteristics which were different from untreated samples.

The samples were weighed both before and after treating. In most cases, the weight loss or gain was less than 10 percent, and is considered insignificant. There was no evidence of a violent reaction although several of the samples changed color and/or became either more brittle or more flexible. Plexiglas 5009 was found to gain up to 70 percent by weight. Data for these tests are found in Table VI.

We concluded that oxides of nitrogen probably did not contribute to the fire which occurred in Building 71.

RESULTS OF WORK BY THE MANUFACTURING TECHNICAL GROUP

1. Nitric acid will leach both chloride and plasticizer from plastic tubing. Besides chloride, o-phthalic acid, phthalic anhydride, dioctylphthalate, and butylphthalyl-butylglycolate were found in the nitric acid leach.

The tubing tested were:

- (a) Mayon - Distributed by Plasticrafts, Inc., Denver, Colorado.
- (b) Tygon - Manufactured by U. S. Stoneware, (Formula R-3603).

TABLE VI
REACTIONS WITH GASEOUS NO₂ AND N₂O

<u>Material Treated</u>	<u>Gas Used</u>	<u>% Weight Gain or Loss</u>	<u>Description of Treated Material</u>
Window Plexiglas NO. 5009	NO ₂	+68.7	Pliable, turned dark green
Window Plexiglas SE-3	"	+50.0	Softened slightly, turned dark green
Neoprene glove (50 mil. leaded)	"	+ 1.2	Stiffened
Neoprene glove (30 mil.)	"	+ 7.5	Stiffened slightly
Thermoplastic tubing	"	+ 9.1	Stiffened, became yellow-brown
Tygon tubing R-3603	"	- 0.9	Stiffened slightly, became yellow
Mayon tubing	"	-14.7	Stiffened, became yellow-green
Plastic cord	"	+ 0.1	Stiffened and hardened
Window Plexiglas NO. 5009	N ₂ O	+ 0.8	Slight yellowing
Window Plexiglas SE-3	"	+ 0.3	No change
Neoprene glove (50 mil. leaded)	"	+ 0.3	White, gummy deposit on surface, easily wiped off
Neoprene glove (30 mil.)	"	+ 1.1	Thin white deposit on surface, difficult to wipe off
Thermoplastic tubing	"	+ 0.2	White gummy deposit
Tygon tubing R-3603	"	+ 0.3	Slight yellowing
Neoprene sponge	"	+ 1.9	Shriveled and wrinkled
Plastic cord	"	- 0.7	Stiffened, dark yellow spots, white gummy deposit

Tygon tubing was found to be more resistant to nitric acid attack. Nitric acid extracted the least quantity of chloride from this tubing. Mayon tubing produced the greatest quantity of chloride.

2. An ion column was loaded with plutonium and not vented. This was done to simulate the conditions which were thought to have prevailed at the time of the fire. Although a pressure buildup was noted, no significant temperature rise was recorded.

RECOMMENDATIONS

The following recommendations were made by the Manufacturing Technical Group:

- *1. Vent all ion columns when not in operation.
 - *2. Use Tygon tubing in preference to either Mayon or thermoplastic tubing.
 3. Continue a search for a superior type of flexible tubing.
- *Items 1 and 2 are now standard production procedures.

In addition to the above, the following recommendations are made where nitrate form anion exchange resins are used:

1. The resin in ion columns should never be allowed to become dry.
2. Since a low ignition point has been observed, used and degraded resin should be considered a flammable material. Precautions should be taken to prevent spontaneous ignition from external heat sources.
3. Incineration of all used resin would be desirable, rather than disposal by burial.

The following are areas in which we plan to continue our studies:

1. Identify the reaction products when nitrate form anion resin is treated with nitric acid.
2. Perform ignition tests with plutonium loaded resins. It is possible that the ignition temperature is decreased when the resin is loaded.

3. Study the conditions for, and mechanisms of, pyrolytic decomposition of anion exchange resin, especially the nitrate form.