

**NONLETHAL ANTIAIRCRAFT APPLICATION OF SUPERACIDS AND OTHER  
VERY AGGRESSIVE CHEMICAL AGENTS**

By John B. Alexander, Ph.D.  
Los Alamos National Laboratory

This is a presentation to the NATO Advisory Group on Aerospace Research and Development (AGARD) study on Nonlethal Means for Diverting or Forcing Non-Cooperative Aircraft to Land. The attached slides comprise the entirety of the briefing to be presented. It addresses the applications of superacids, supercaustics, solvating agents, and catalytic depolymerization agents against materiel targets of interest.



**NONLETHAL ANTIMATERIEL APPLICATION OF SUPERACIDS**  
**AND OTHER VERY AGGRESSIVE CHEMICAL AGENTS**

**PRESENTED TO:**

**AGARD STUDY AAS-40**

**NONLETHAL MEANS FOR NONCOOPERATIVE AIRCRAFT**

**ROMA, ITALY**

**26-30 SEPTEMBER 1994**

**PRESENTED BY DR. JOHN ALEXANDER**

**SPECIAL TECHNOLOGIES GROUP**

**LOS ALAMOS NATIONAL LABORATORY**

# CHEMICAL NON LETHAL DEFENSE

---

## Chemically-based NLD

- Types of Agents
  - Gases, Liquids, Gels, Solids, Polymers
- Mechanisms of Action/Effects:
  - Corrosion/Dissolution  $\Rightarrow$  Penetration
  - Polymerization  $\Rightarrow$  Fouling, Clogging, Adhesion
  - Depolymerization  $\Rightarrow$  Mechanical Failure
  - Fracture/Embrittlement  $\Rightarrow$  Failure under Load

## CHEMICAL NON LETHAL DEFENSE

### Legal and Ethical Ramifications of Chemical NLD

- All Current and Anticipated Intended Uses of Chemicals are Antimaterial
- Substantial Industrial Uses (carpet mfg., etc.)

## CHEMICAL NON LETHAL DEFENSE

### Assessment of Targets, Agents, and Methods:

- Requires Input from Users as to:
  - Targets—Thickness, Exposure, Type, etc.
  - Constraints— Time, Temperature, Distance, Light, Weight, etc.
  - Operational Requirements—Timing, Mission Factors, Capabilities

## CHEMICAL NON LETHAL DEFENSE

---

### Representative Chemical Technology & Potential NLD Applications

- Superacids: Commercial Use—DuPont Stainmaster® Carpet
  - Among the Most Corrosive Materials Known
  - Dissolves Glass, Composites, Metals
  - Evaluated for Classified Application by LANL for NCSC
- Excellent Penetrant for HEPA (High Efficiency Particulate) Filters [Protection Systems for Nuclear, CBW, and Computing Facilities]
- Attacks Electronics via Solder Joints, Traces
- Destroys Image Quality of Optical Component

# **Many Systems are Vulnerable to Attack by Chemicals**

**Electronics**

**Components, filters, leads, solder mask,  
traces, LEDs, tubes**

**CBN Infrastructure**

**HEPA Filters, control systems,  
submunition containers, agents**

**Vehicles**

**Filters, electronics, rubber components,  
fuel systems**

**Missles, Aircraft**

**Solid propellant, jet engines, electronics,  
flight surfaces**

**Los Alamos**

# Materials are Attacked in a Variety of Ways

<u>Material</u>	<u>Mechanism of Attack</u>
Metals (solder, titanium)	Dissolution (corrosion), vaporization, conductor-to-insulator, crystallization
Composites (graphite, GRP)	Delamination, pitting, corrosion
Glass (optics)	Etching, pitting, stress cracking, darkening, occlusion
Polymers (rubber, plastics)	Hardening, depolymerization, dissolution
Fuels (diesel, JP-5)	Viscosification

Los Alamos

# Corrosion of Materials is a Large Industrial Problem

- Databases on material corrosion: RUST (E.I. Du Pont)
  - Used for material selection in chemical process design
  - Subscription service available
  - Primary focus is on metals, polymers for material containment

Los Alamos

# WHAT ARE "SUPERACIDS"?

- ❖ A "Superacid" is any acid stronger than 100% Sulfuric Acid
- ❖ The Acidity of strong acids is measured by the Hammett acidity function, -Ho, on a *logarithmic scale*.

Thus, an increase of 1 in -Ho equates to a 10-fold increase in acidity.

ACID	-Ho	ACID	-Ho
H <sub>2</sub> SO <sub>4</sub>	11.9	HF/AsF <sub>5</sub>	19~20
HClO <sub>4</sub>	13	HSO <sub>3</sub> F/SbF <sub>5</sub> (4:1)	19
HSO <sub>3</sub> CF <sub>3</sub>	14.6	HSO <sub>3</sub> F/SbF <sub>5</sub> (1:1)	~20
HAICl <sub>4</sub>	15	HF/SbF <sub>5</sub> (4:1)	22
HF (anhydrous)	15.1	HF/SbF <sub>5</sub> (1:1)	~23
HSO <sub>3</sub> F	15.5		

- ❖ For comparison, HF/SbF<sub>5</sub> is a stronger acid than H<sub>2</sub>SO<sub>4</sub> by the same amount that H<sub>2</sub>SO<sub>4</sub> is a stronger acid than dilute (1N) nitric acid.
- ❖ The corrosiveness of superacids is caused by the presence of Lewis Acids such as SbF<sub>5</sub>. The two resulting effects are: 1) Lewis acids increase the concentration of strongly acidic, coordinating species such as H<sub>2</sub>F<sup>+</sup>; and 2) The Lewis acids themselves coordinate strongly to metal atoms, creating soluble species.

# PROPERTIES OF TWO VERY STRONG SUPERACID SYSTEMS

10% SbF<sub>5</sub>/HF:

- Approx. 100 torr vapor pressure at 25° C.
- Viscous

25% SbF<sub>5</sub>/HSO<sub>3</sub>F

- < 5 torr vapor pressure at 25° C
- Highly fluid
- Commercially available

BOTH SYSTEMS

- Hammett acidity > 19 ( $10^7$  times stronger than 100% H<sub>2</sub>SO<sub>4</sub>).
- Aggressively attack many common organics and many metals.
- Easily handled in fluorocarbon (Teflon®) apparatus.
- Compatible with powerful oxidizers.
- Indefinitely stable.
- High electrical conductivity.
- Toxic (skin contact and inhalation/ingestion).
- Incompatible with water.

Los Alamos

# ENHANCING CORROSION OF SUPERCAUSTICS

- ◆ The addition of strong oxidizers to superacids may increase the corrosiveness of these materials by adding oxidation, thermal shock, and corrosive cracking as mechanisms to increase the solubility or failure of the substrata.
- ◆ The aggressiveness of the "Nitrofluor" solvent system ( $\text{FNO}\cdot6\text{HF}$ ) is attributed to the oxidizing power of  $\text{NO}^+$  in solution with hydrogen fluoride. This system rapidly attacks Zircalloy-2 and 304 S.S. even at room temperatures.
- ◆ Many very strong oxidizers are fluorine compounds and are highly soluble in HF:  
 $\text{BrF}_3$ ,  $\text{ClF}_3$ ,  $\text{NO}_2^+ \text{SbF}_6^-$ ,  $\text{XeF}_6$ ,  $\text{KrF}_2$ ,  $\text{O}_2^+ \text{SbF}_6^-$ .

These materials routinely shatter fluoropolymer (Kel-F) tubes when HF is added, indicating a strong synergistic effect.

Los Alamos

**URGENT USE TITLE**  
The Sunshine Project | <http://www.sunshine-project.org>  
**Toxicity of Superacids**

- ♦ While severely corrosive and irritating, these compounds lack the persistence, immediacy, and magnitude of lethality found in "Typical" War agents.
- ♦ Superacids are rapidly hydrolyzed and diluted in water to form very weak acids with minimal toxicity (e.g. H<sub>2</sub>SO<sub>4</sub>).

**Toxicity Data on Superacids and other relevant materials\***

<u>Compound</u>	<u>Toxicity</u>	<u>Compound</u>	<u>Toxicity</u>
HF (anhydrous)	1760 ppm/1 hr(LC <sub>50</sub> )	CH <sub>3</sub> N(C <sub>2</sub> H <sub>4</sub> Cl) [nitrogen mustard]	370 mg/m <sup>3</sup> /10 min (LCLo)
SbF <sub>5</sub>	>>0.5 mg/m <sup>3</sup> (TWA)	phosphorus (white)	2~200 mg/m <sup>3</sup> (LDLo)
HSO <sub>3</sub> F	>>100 ppm (TWA)	HCN	200 mg/m <sup>3</sup> /10 min (LCLo)
H <sub>2</sub> SO <sub>4</sub>	135 mg/kg (LDLo)	iso-C <sub>4</sub> F <sub>8</sub>	18 ppm/10 min (LC <sub>50</sub> )
<u>Chemical Agents:</u>		SARIN [(CH <sub>3</sub> ) <sub>2</sub> CHO](CH <sub>3</sub> )P(O)F	0.01 mg/kg (LD <sub>50</sub> )
S <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> Cl) <sub>2</sub> [mustard]	9 mg/kg (LD <sub>50</sub> )		

\*Data from Sax: "Dangerous Properties of Industrial Materials," 6th ed., 1987; TWA-Time-Weighted Average (a safe 8 hour occupational exposure level, lethal limits would probably be 100-1000 times higher); LCLo-Lower limit of lethal concentration; LC<sub>50</sub>/LD<sub>50</sub>-Lethal concentration/dose for 50% of the population exposed.

Los Alamos

## DEGRADATION OF METALS

- ◆ High technology metals (e.g. Ti, Al alloys) are less resistant to attack by supercaustics.
- ◆ 0.25" thick Marine-grade Al can be completely penetrated by supercaustics in as little as 30 minutes.
  - Metal surface temperatures increase to >240°C in 10 minutes.
  - The supercaustic system can be adjusted to allow lower temperatures and correspondingly longer penetration times.

Los Alamos

## DEGRADATION OF POLYMERS

- ◆ Mechanisms of Degradation (cont):

- Embrittlement of elastomers: addition of excess crosslinking agent (e.g. sulfur) or catalyst (e.g. thiazoles)
  - addition of radical addition agent (e.g. Br<sub>2</sub>).
  - Requires a solvent for delivery of agent to bulk of elastomer.
  - Increases in Shore 'A' hardness of >30 units achieved in 8-hour exposures.

Los Alamos

OFFICIAL USE ONLY

## Test Conditions

- ◆ Superacid (25% SbF<sub>5</sub> in HSO<sub>3</sub>F): Used as received, 3 ml per test.
- ◆ Substrates: Coupons with approx. 1 cm<sup>2</sup> surface area.

# Metal Corrosion Studies Using 25% SbF<sub>5</sub>/HSO<sub>3</sub>F

Metal	% Wt. Loss (25° C, 1 hr.)	% Wt. Loss (94° C, 1 hr.)	Final Appearance
<b><u>Construction Metals</u></b>			
Cu	100	100	Dark Purple sol'n
Ni	5.8	98.0	Dark green sol'n; dull metal
Al	<0.1	0.2	Lt. brown sol'n; dull grey metal
Ti	<0.1	59	Blue-green sol'n; highly pitted metal
Hastelloy C-22	<0.1	0.2	Lt. brown sol'n; shiny metal
SS304	24.0	100	Blue-black sol'n; minor dark residue
SS316	1.0	31.2	Dark green sol'n; dull metal
Mild steel	1.9	5.3	Purple sol'n; flat grey metal
Brass	14.7	21.9	Viscous grey suspension; dull brown metal
Zircalloy II	<0.1	<0.1	Lt. brown sol'n; shiny metal

# Metal Corrosion Studies Using 25% SbF<sub>5</sub>/HSO<sub>3</sub>F

Metal	% Wt. Loss (25° C, 1 hr.)	% Wt. Loss (94° C, 1 hr.)	Final Appearance
<u>Other Metals</u>			
Pb	11.6	68.5	Chalky blue-grey sol'n; dull pitted metal
Mo	<0.1	<0.1	Lt. tan sol'n; shiny metal
W	<0.1	<0.1	Colorless sol'n; shiny metal
Ga	0.2	~60	Grey Suspension
Ta	<0.1	6.4	Lt. brown sol'n; med brown metal
Nb	0.3	2.1	Turbid med. yellow sol'n; dull grey metal
Cr (shot)	1.7	43.5	Black sol'n; dull grey metal
Ca (ingot)	21.4	100	Deep purple sol'n
Mg	2.7	17.6	Purple-black sol'n; flat grey metal
Be	<0.1	4.7	Lt. brown sol'n; dull grey metal

# Metal Corrosion Studies Using 25% SBF<sub>5</sub>/HSO<sub>3</sub>F

The Sunshine Project | <http://www.sunshine-project.org>

Metal	% Wt. Loss (25° C, 1 hr.)	% Wt. Loss (94° C, 1 hr.)	Final Appearance
<u>Platinum Group Metals</u>			
Pt	<0.1	<0.1	Lt. Tan sol'n; shiny metal
Au	<0.1	<0.1	St. tarnishing of metal; lt. brown sol'n.
Rh	<0.1	<0.1	Med brown sol'n; shiny metal
Pd	<0.1	<0.1	Peach colored sol'n, shiny metal with black sheen
Ir	<0.1	1.4	Tarnished metal; lt. brown sol'n
Ag	19.9	44.2	Purple sol'n; dull grey metal
<u>Lanthanide Metals</u>			
Pr (ingot)	17.0	20.8	Dark grey suspension; grey-black metal
Gd (ingot)	26.1	30.9	Blue-grey suspension; grey metal
Lu (ingot)	9.0	41.8	Dark blue-green sol'n; flat black metal

Source: LA-UR-89-3628

OFFICIAL USE ONLY

**LOS ALAMOS**  
Los Alamos National Laboratory  
Los Alamos, New Mexico 87545

# Metal Corrosion Studies Using 25% SbF<sub>5</sub>/HSO<sub>3</sub>F

Metal	% Wt. Loss (25° C, 1 hr.)	% Wt. Loss (94° C, 1 hr.)	Final Appearance
<u>Actinide Metals</u>			
Th (ingot)	0.4	27.9	Dark purple sol'n; dull grey metal
U (turning)	17.5	100	Blue-grey suspension
Np (turning)	16.8	>95	Lavender-green sol'n.
Pu/Ga alloy	14.3	>95	Blue-green sol'n

# Corrosion Results in Refluxing 25% Magic Acid.

Metal	% Wt. Loss (155° C, 1hr)	Final Appearance
Pt	0.3	Lt. brown sol'n; shiny metal
Ir	1.5	Lt. brown sol'n; shiny metal
Au	<0.1	Lt. brown sol'n; shiny metal
Pd	10.4	Purple sol'n; dull charcoal grey metal
Rh	<0.1	Lt brown sol'n; shiny metal
W	5.5	Turbid lt. gold sol'n; dull grey pitted metal
Mo	7.8	Turbid deep gold sol'n; dull grey metal/blue coating
Hastelloy C-22	0.7	Very turbid white sol'n; shiny metal w/ clear coating
Zircalloy II	0.7	Lt. brown sol'n; shiny metal
Be	45.5	purple sol'n; flat black metal
Al	<0.1	Turbid white sol'n; shiny metal

## Some Target Materials and Supercaustics Which Degrade Them

Target	Supercaustic	Effect
GRP (fiberglass)	HF/SbF <sub>5</sub>	Wholesale decomposition; Pitting; delamination
Aluminum (& Alloys)	Br <sub>2</sub> /Solvent	Rapid, Massive dissolution; Pitting
Glasses, Optical Coatings	HF/SbF <sub>5</sub>	Immediate surface etching; loss of optical quality
Copper, Silver	HF/SbF <sub>5</sub> , others	rapid, complete decomposition
Rubber	Br <sub>2</sub> /Solvent	Immediate softening; embrittlement, delamination
Ferrous Metals	HF/NO <sub>2</sub> , others	Surface corrosion, cracking

## Time Scale of Effect

Supercaustics can cause significant, measurable degradation in minutes (etching of glasses by superacid), hours (burnthrough of 1/4" Al 5086 in 2-9 hours), or days (embrittlement of tire rubber in 12-36 hours).

Because of the wide variety of properties, ferrous metals are highly unpredictable in this regard; corrosion could take days or months

Timing of degradation may be amenable to some tailoring through normal methods: accelerators, dilution, etc.

Rate and onset of degradation will be affected by operational factors: Temperature, humidity, application method, etc.

Los Alamos

CONFIDENTIAL - LOS ALAMOS

April 15, 1991

## Some Other Possible Avenues of Exploration

- ◆ *Chemically-Induced Stress Cracking and Failure:* Can surface treatment of structural members (e.g. aircraft wing spars, railroad rails) or hardened materials with supercaustics result in corrosion induced cracking, phase- and microstructural changes which will ultimately result in catastrophic failure under load?
- ◆ *Removal or Degradation of Coatings:* Can anechoic tiles or other stealth-related materials be modified such that “silent running” is impeded or impossible?

## Limitations on Supercaustics

- ◆ Some are water-sensitive.
- ◆ All are toxic and corrosive, though less than CBW agents
- ◆ Countermeasures
- ◆ Limited data base due to proprietary industrial base
- ◆ Fairly high specificity; no "Magic Bullet" for all substrates

## Application Methods

Supercaustics we have examined so far are mobile liquids: besides direct application they may be amenable to dispersal as aerosols, liquid sprays, gelling into a semisolid state, or incorporation into solids.

1 2 3 5 7 8 9  
OFFICIAL USE ONLY

## POSSIBLE DELIVERY MECHANISMS

- PROJECTILES
- SPRAYS AND AEROSOLS
- STATIC, PRESSURE ACTIVATED
- STATIC, TIMED RELEASE

Los Alamos

1 2 2 5 . 0 5 7 5

OFFICIAL USE ONLY

# Fuel Viscosification

- Best associative polymer (tributyl tin fluoride) increases viscosity of fuel 100X at 0.2%
- New polymer provides same level of viscosification at 0.08%
- Assessment of claims for foreign material

## CHEMICAL NON LETHAL DEFENSE

---

### Polymer Applications (LANL)

- Fuel V: Organo Tin Polymers
- Small Amount Rapidly Achieves > 100X Thickening in Fuels
- Reversible with Alcohols

## CHEMICAL NON LETHAL DEFENSE

---

### Filter Clogging Polymers (LANL)

- Nontoxic Commercial Food Industry Polymer
- Polymer Can be Sprayed or Aerosolized
- Shuts off Airflow through exclusion filters (Not cyclone-type filters)
- Small Amount Obstructs High Surface Area Filters (Gas Mask Cartridges)
- Other Potential Applications:
  - Ship Propeller Fouling
  - Submarine Cooling Water Intake Fouling

## CHEMICAL NON LETHAL DEFENSE

---

### Photochromic Agents

- Mechanism: Black Out Windows Reversibly On Demand
- Applications:
  - Embedded in Glass Windshield—Adaptation of Commercial Technology
  - Plastic Film Laminate (Transparent and Undetectable)—Some Engineering Development Required
  - Sprayable Resin (Air Applied, Forced Landing)—Requires Substantial Technical Development

## CHEMICAL NON LETHAL DEFENSE

---

### Foam Applications (SNL)

- Sticky Foam: Tamper-Proofing Secure Items
  - Rapidly deployed, Difficult to Defeat
- Hard Foam: Encapsulation of Detected Mines to Prevent Detonation
  - High Volume Expansion

# CHEMICAL NON LETHAL DEFENSE

---

## Rubber/Elastomers

- Targets: Hoses, Drive Belts, Tires
- Mechanism: Embrittlement, Depolymerization
  - Embrittlement: Reduces Flex, Increase Rigidity, Delamination, Fracture
- Mechanism/Agents
  - Increase Crosslinking–Accelerators, Organic Peroxides
  - Increase Polymer Rigidity (Flexible  $\Rightarrow$  Rigid)–Radical Addition Agents, Trifunctional Agents

## CHEMICAL NON LETHAL DEFENSE

---

### Rubber/Elastomers

- Depolymerization:
  - Converts High Molecular Weight Rubber to Liquid
- Mechanisms/Agents
  - Desulfurization—thermolysis, catalyst
  - Catalytic Depolymerization—polymer backbone rupture

## DEGRADATION OF POLYMERS

### ◆ Mechanisms of Degradation:

- Delamination of layered composites: caustic attack of cloth/adhesive interface.
- Corrosive attack of composites: superacid/supercaustic materials dissolve 1/4" thick G10 fiberglass in hours.

Los Alamos

# DEGRADATION OF POLYMERS

## ♦ Mechanisms of Degradation (cont):

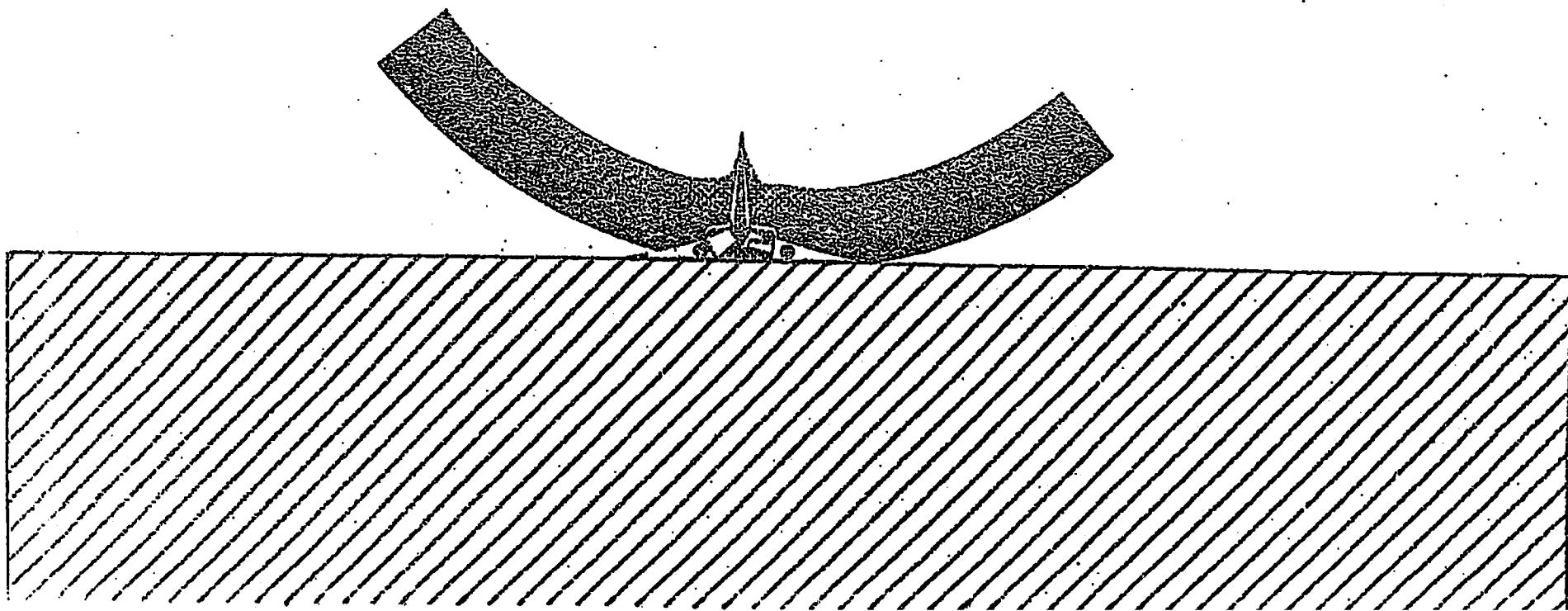
- Catalytic Depolymerization of Elastomers: use of transition metal compounds to degrade high molecular weight polymers ( $MW > 10,000$ ) to liquid organics ( $MW \sim 100-300$ ) has been demonstrated for a variety of polymers.
  - Filled polymers (e.g. tire rubber) will degrade as well as unfilled rubber.
  - Some, not all, catalyst systems are air, moisture sensitive.
  - Because of catalytic nature, smaller quantities are necessary.
  - Control of reaction rate is unknown.
  - May require solvent for delivery to bulk.

Los Alamos

CONFIDENTIAL  
DO NOT DISTRIBUTE

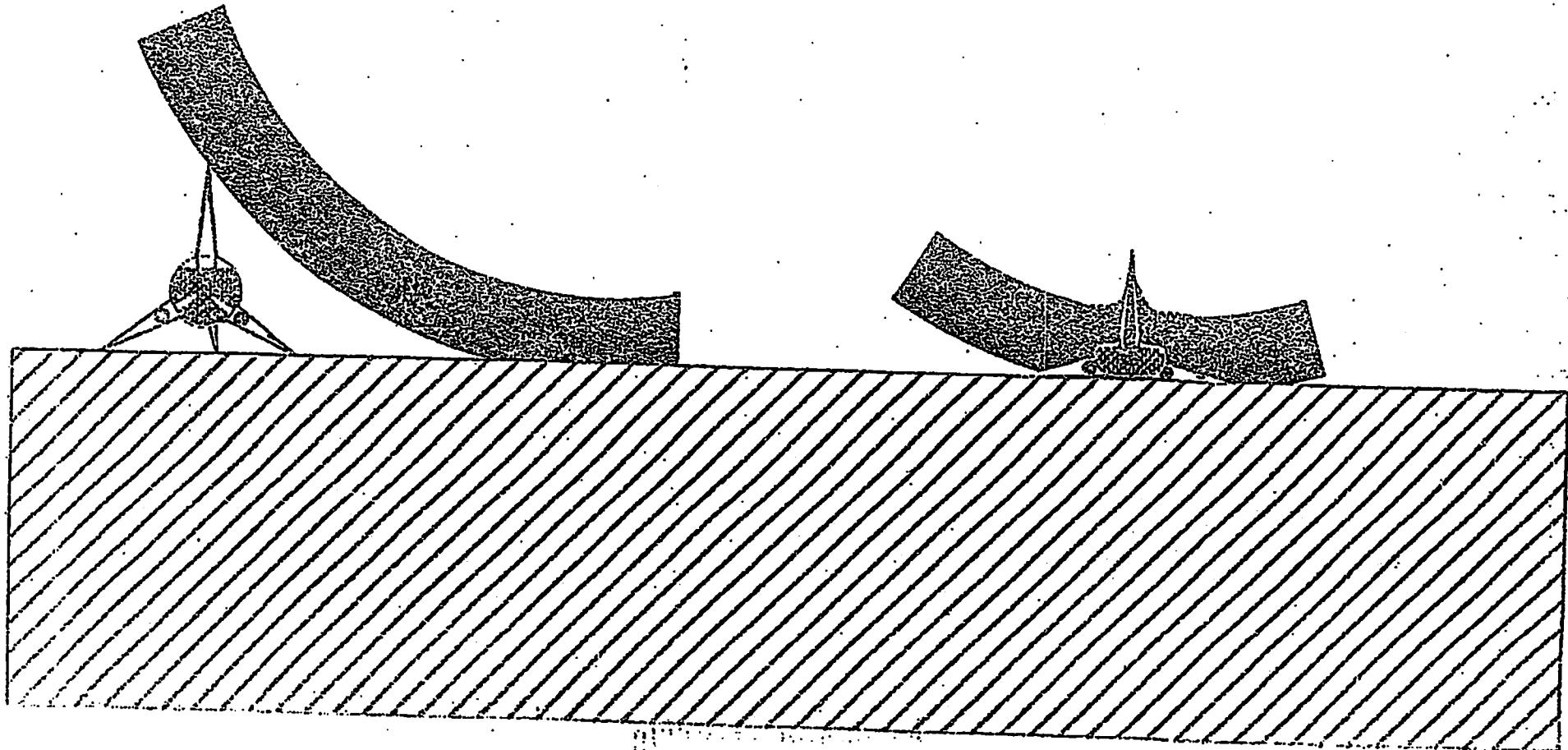
- OFFICIAL USE ONLY -

## DEPOLYMERIZATION SYSTEM TURNS RUBBER INTO LOW MOLECULAR WEIGHT LIQUIDS



OFFICIAL USE ONLY

PENETRATION OF TIRE ALSO INJECTS  
CATALYST AND COCATALYST



# CHEMICAL "CALTROP" USES CATALYSTS TO DESTROY TIRES IRREVERSIBLY

