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NITRATE FILM TESTING FOR
THE NATIONAL ARCHIVES
DECEMBER 1978 FIRE INVESTIGATION

*M. C. Hudson, Naval Ordnance Station, and
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INDIAN HEAD, MARYLAND

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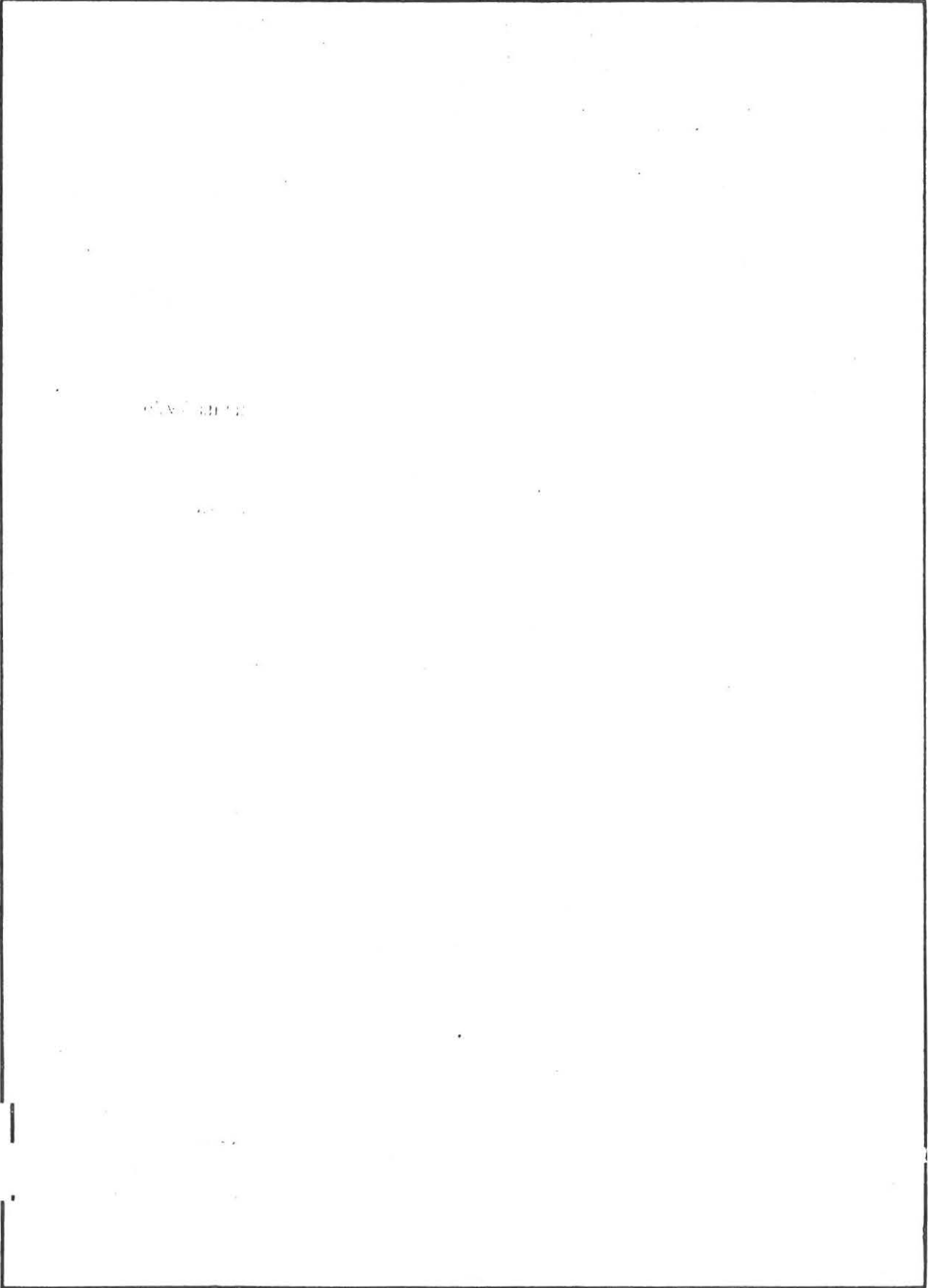
NITROCELLULOSE -- IGNITION (AS)

FILMS (PHOTOGRAPHY)

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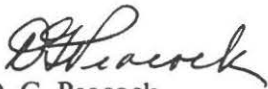


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FOREWORD

In December 1978, the National Archives motion picture film storage facility suffered a major fire. The Naval Ordnance Station, Indian Head, was requested to conduct testing to characterize the ignition and combustion of cellulose nitrate film. Areas of concern were film chemical stability, likelihood of ignition from accidental forces, and intensity of reaction. This report presents the results and conclusions derived from the testing and from literature reviewed during the investigation.

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INTRODUCTION

Cellulose nitrate based film was used for commercial theater motion pictures until the early 1950's. Nitrate films dating prior to that time are a major component of the records stored in the National Archives, Washington, D.C. In December 1978, a major fire occurred in the film storage facility of the National Archives, and the Naval Ordnance Station was requested to conduct testing to characterize the ignition and combustion of cellulose nitrate film.

PROPERTIES OF NITROCELLULOSE

Cellulose nitrate or nitrocellulose (NC) is obtained by treating cellulose (as cotton linters or wood pulp) with mixtures of nitric and sulfuric acids.¹ By varying the acid concentration, temperature, and time of reaction, products containing various percentages of nitrogen (N) are obtained. Of these, three types are distinguished by name. They are pyroxylin or collodion (8% to 12% N), pyrocellulose (12.6% N), and guncotton (13% N). The pyroxylin which was used in film manufacture contained 11% to 12% N.

Nitrocellulose is unstable and undergoes decomposition even when highly purified.^{2, 3} Impurities and external factors such as heat and moisture increase the rate of decomposition. The decomposition reaction is exothermic and, under conditions retaining the heat produced, can bring the nitrocellulose to ignition temperature.^{4, 5} Before igniting, NC under most conditions will give off red-brown fumes. Indeed, some film samples in the tests conducted at Indian Head fumed to decomposition without igniting to visible flame. It has been demonstrated that NC (film grade) is not explosive in itself.⁶ The gases given off, particularly those generated under confinement and pressure, can form explosive mixtures with air when vented.⁷⁻⁹

This discussion of NC properties can be summarized by listing the factors affecting decomposition and some observations applicable to film storage.

Factors Affecting Decomposition:

Purity: The literature covers this quite well with emphasis on the effects of residual acidity causing decomposition. An increasing acidity content is a characteristic of decomposing NC.

¹ Department of the Army, *Military Explosives*, Technical Manual TM 9-1300-214, November 1967.

² Frank D. Miles, *Cellulose Nitrate*, Interscience Publishers, Inc., 1955.

³ Emil Ott, *Cellulose and Cellulose Derivatives*, Interscience Publishers, Inc., 1954.

⁴ James W. Cummings, National Archives and Records Service, and Alvin C. Hilton and Howard Silfin, National Bureau of Standards, "Spontaneous Ignition of Decomposing Cellulose Nitrate Film," *J. Soc. Motion Picture Television Engrs.*, March 1950.

⁵ "Fox Film Storage Fire," *National Fire Protection Association Quarterly*, vol 31, No. 2, 1940.

⁶ Albert F. Sulzer, "The Epoch of Progress in Film Fire Prevention," *J. Soc. Motion Picture Engrs.*, April 1940.

⁷ J. M. Calhoun, "The Physical Properties and Dimensional Behavior of Motion Picture Film" *J. Soc. Motion Picture Engrs.*, vol 42, No. 4, October 1944.

⁸ National Bureau of Standards, *Summary Report of Research at the National Bureau of Standards on the Stability and Preservation of Records on Photographic Films*, by B. W. Scribner, May 6, 1939.

⁹ A. H. Nuckolls and A. F. Matson, "Some Hazardous Properties of Motion Picture Film," *J. Soc. Motion Picture Engrs.*, Spring 1936.

Moisture: The moisture content of film is determined almost solely by the relative humidity of ambient air. Increasing the moisture content causes more rapid decomposition. The effect is not only that of accelerating decomposition but catalyzing the reaction by converting the released gases to acid. Propellants with stabilizers also are affected in that moisture results in reactions bypassing the stabilizer reaction. Note that moisture is not considered a factor in decomposition reactions in the temperature range of 20° to 30° C. It definitely becomes a factor at 50° C (122° F).^{10, 11} Two NC fires have occurred recently at Indian Head where moisture, temperature, and reduced ventilation were factors.

Ventilation: The decomposition gases normally diffuse from NC. A restricted air supply to the stored NC will speed decomposition by retaining these gases in contact with the material and available to combine with moisture.

Temperature: Elevated temperatures increase the rate of decomposition.

Heat: The decomposition reaction is exothermic. Under normal storage, this heat is transferred to the surroundings. With an increase in temperature, the decomposition accelerates and heat transfer to the surroundings is reduced. (Propellants loaded in cartridge cases, 3 inches or less diameter, do not present a hazard of spontaneous ignition because of the proportion of metal-to-propellant and the heat conducting properties of the metal.)¹² An average flat can of film calculates to 0.0174 pound of film per square inch of can surface; the 3-inch, 50-caliber cartridge case has a value of 0.0212 pound per square inch. Configuration and stacking make significant differences in heat transfer, and these values are for reference only.

Aging Effects: NC, either naturally or oven aged, has decreased stability.^{13, 14} Old film, visibly deteriorated by natural aging, has a stability similar to film which has been oven aged 10 to 15 days at 100° C.

Storage Conditions Necessary to Cause Spontaneous Ignition:

In considering the effects that these factors have on nitrate film, conditions for naturally occurring spontaneous ignition can be established. These are the following:

- (1) Sustained relatively high temperatures (on the order of 100° F)

¹⁰Frank D. Miles, *Cellulose Nitrate*, Interscience Publishers, Inc., 1955.

¹¹Emil Ott, *Cellulose and Cellulose Derivatives*, Interscience Publishers, Inc., 1954.

¹²Department of the Army, *Military Explosives*, Technical Manual TM 9-1300-214, November 1967.

¹³J. M. Calhoun, "The Physical Properties and Dimensional Behavior of Motion Picture Film" *J. Soc. Motion Picture Engrs.*, vol 42, No. 4, October 1944.

¹⁴J. R. Hill and C. G. Weber, "Stability of Motion Picture Film as Determined by Accelerated Aging," *J. Soc. Motion Picture Engrs.*, Fall 1936.

- (2) Sufficient quantity of film (mass effect) or insulating conditions to reduce heat transfer below generation rate
- (3) Increase in humidity
- (4) Reduced ventilation
- (5) Aged film.

The literature reports that spontaneous ignition in film vaults has occurred in the months of June, July, and August during prolonged hot spells. In all cases, the film was old. The fires normally occurred at night or on weekends when the storage facilities were closed. This would reduce the ventilation causing less diffusion of decomposition gases and heat transfer. That many of the fires occurred at night may be attributable in part to the normal increase in humidity with night fall or reduced "breathing" of structures under calm night winds; although these thoughts must be considered as conjectures. Another conjecture is that the external heat transferring into the building through masonry walls may reach a peak temperature after normal working hours. There was a report on this in a *Scientific American* issue some years ago which could not be located at the time of this research.

NITRATE FILM TESTING

Sample Preparation

The Archives delivered nine boxes of cans of film. These had been selected randomly from somewhat uniform groups. The groups were roughly described as 35-mm film, good (no yellowing); 35-mm film, bad (some yellowing); and 9-1/2-inch film, bad (yellowing and embrittled).

Samples for chemical analysis and stability and sensitivity testing were prepared by taking short sections of film from several of the cans in each box. The samples were identified as shown in Table I. Initially, sample 2 was taken from 4 of the 10 cans in the group. This group was considered bad as all of the films were somewhat yellowed apparently to the loss of the image. Because evidence of instability was encountered early in the testing, this sample was broken down by individual films. Two samples then were labeled according to manufacturer: 2D for Dupont 60 and 2E for Kodak; these samples were used in subsequent testing. The other two films were Dupont 43 and Eastman. To reduce variables, these latter two films were not used in any of the tests except that a percentage of nitrogen value was obtained on Dupont 43 film.

Table I
FILM SAMPLE ORGANIZATION

| Sample No. | No. of cans | No. of cans sampled | Comments |
|------------|-------------|---------------------|---|
| 1 | 9 | 4 | Good |
| 2 | 10 | 4 | MOT8848, slightly yellowed |
| 3 | 9 | 5 | Apparently good |
| 4 | 9 | 3 | Good |
| 5 | 9 | 4 | Yellowed, slightly sticky Univ. news |
| 6 | 9 | 5 | One obviously yellowed, others clear, UN |
| 7 | 2 | 2 | 1930 topo film (9½ inch) |
| 8 | 2 | 2 | 1926 topo film (9½ inch), deteriorated to brittle condition |
| 9 | 9 | 5 | Clear |
| 10 | 7 | 3 ¹ | Missouri River topo (9½ inch), brittle |

¹ Designated as 10X, 10-41, and 10-44.

Sensitivity Testing

Drop Tests of Film Cans:

Drop tests were performed to investigate the possibility of ignition resulting from impact. For this test, cans were dropped in various attitudes from 40 feet onto a heavy steel plate.

Reels of 35-mm film were dropped for flat and edge impact, both with the film normally loose and tightly secured against the can interior at the impact point. The initial exploratory tests were conducted as given below:

9-1/2-Inch Cylinder (Topo Film)—Dropped on end, then on side; film generally snug in can, no additional tightening; no evidence of ignition, film apparently undamaged.

Flat Reel Film Can—Dropped flat, then on edge with film wound tight and secured against can interior at impact point; then dropped with film loose in can causing plastic spool to break by crushing; end of film then pinched between can halves and edge impacted in this area several times; no evidence of ignition or decomposition of film observed in any test of several cans.

Following the exploratory drop test, one can from each sample was subjected to the drop test. Each can was dropped for edge and flat impact (end and side for 9-1/2-inch topo film). In every test of 35-mm film in edge impact, the plastic film spool was broken. No evidence of ignition or decomposition was observed in any drop test. It is concluded that being dropped or falling and impacting on a hard surface is unlikely to cause ignition of the nitrate film.

Impact, Friction, and Electrostatic Discharge Tests:

The nitrate film samples were tested for impact, friction, and electrostatic discharge sensitivity. These tests were the same as conducted to evaluate rocket propellants and explosives for likelihood of initiation from processing and accidental mishandling forces.

The impact test is a modified Bureau of Mines procedure with No. 6 tools. A 20-mg sample is placed in a 0.2-inch-diameter hole in a steel block and covered with a steel plunger which is impacted with a 5-kg weight. After each negative result, the weight drop height is increased in 25-mm increments until three consecutive "fires" occur. The lowest height at which this occurs is reported.

The ABL friction test measures the sensitivity to initiation by friction between two metal surfaces; one a sliding block, the other a stationary wheel. The sample is placed on the

block and pressure is applied by a hydraulic ram. A weighted pendulum is swung from a predetermined position in such a manner that it strikes the end of the block, imparting a velocity to it.

The result is recorded in terms of the maximum force which can be applied to the wheel without causing the sample to decompose. Normally, 20 consecutive negative results must be obtained to define the sensitivity of a material. The test range for this machine is 1 pound (sensitive) to 1000 pounds (insensitive). A shot is defined as any decomposition of the test material as evidenced by smoke, fumes, odor, sparks, flame, or audible noise over and above the normal testing noise and as indicated by examination of the sample and metal surfaces. Impact and friction test principles are illustrated in Figure 1.

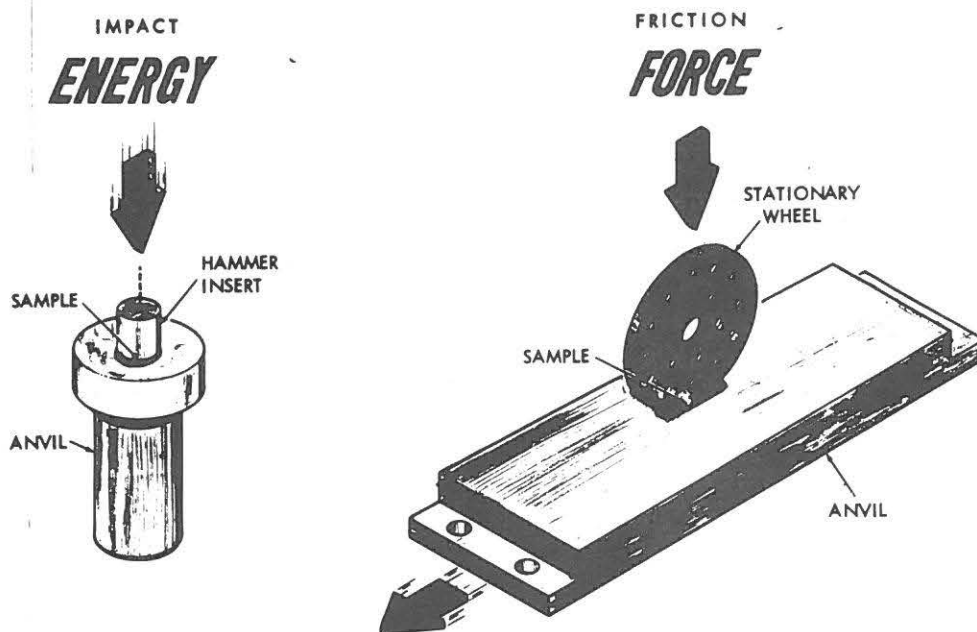


FIGURE 1. OPERATING PRINCIPLE OF IMPACT AND FRICTION TEST APPARATUS

The electrostatic discharge test (ESD) apparatus is a 5000-Vdc source which charges a variable capacitor system. The stored energy, ranging from 0.001 to 12.5 joules, is released from a needle point into the sample which rests on a metal test plate. The discharge circuit is designed to simulate human body electrical discharge characteristics. The maximum energy giving 20 consecutive negative (no smoke or fire) results is reported.

Three individual film sections were tested of each sample, 1 through 9 (a total of 27 sections). Sample 8 had only two films represented, so the results are for a duplicate sample of one of the cans. The sensitivity test results are given in Table II.

Table II
NITRATE FILM SENSITIVITY TEST RESULTS

| Sample | Impact (mm) | Friction (lb) | Electrostatic discharge (j) | Sample | Impact (mm) | Friction (lb) | Electrostatic discharge (j) |
|--------|-------------|---------------|-----------------------------|--------|-------------|---------------|-----------------------------|
| 1 | A | 175 | ≥980 | 6 | A | 150 | ≥980 |
| | B | 150 | ≥980 | | B | 175 | ≥980 |
| | C | 175 | ≥980 | | C | 175 | ≥980 |
| 2 | A | 175 | ≥980 | 7 | A | 150 | ≥980 |
| | B | 175 | ≥980 | | B | 150 | ≥980 |
| | C | 175 | ≥980 | | C | 175 | ≥980 |
| 3 | A | 175 | ≥980 | 8 | A | 150 | ≥980 |
| | B | 150 | ≥980 | | B | 150 | ≥980 |
| | C | 150 | ≥980 | | C | 150 | ≥980 |
| 4 | A | 150 | ≥980 | 9 | A | 150 | ≥980 |
| | B | 150 | ≥980 | | B | 150 | ≥980 |
| | C | 175 | ≥980 | | C | 175 | ≥980 |
| 5 | A | 150 | ≥980 | 10 | | 175 | ≥980 |
| | B | 175 | ≥980 | | | | ≥12.5 |
| | C | 150 | ≥980 | | | | ≥12.5 |
| | | | | 10-41 | 150 | ≥980 | ≥12.5 |

Results shown for the tests indicate that the sensitivity of the film is on the order of that of nitrocellulose propellant (12.2% to 12.6% N). The only observed difference is that less film actually decomposed in a test than would a like sample of propellant.

Basically, the impact results of 150 to 175 mm are considered medium sensitivity for propellants, and handling presents no unusual hazard. Note that this is a severe test akin to pinching the material between a steel pad and a hammer. Accidental dropping of a can of film could not approach the force loads of this test.

The friction test results are negative in that no reaction was observed at the maximum test condition. This is not unusual for relatively soft, nongrit containing samples (i.e., no solid particles).

The electrostatic discharge test results are in the medium sensitivity range of the test. With the exception of sample 10 specimens (cans 41 and 44), test results were in the range 0.275 to 0.50 joule. Medium sensitivity range for this test is 0.0125 to 0.875 joule.

Sample 10 specimens (9-1/2-inch topo film) did not ignite in this test. Later ignition testing of these films in the cans resulted in the films being consumed in a smoky gas evolution reaction without visible flame. These films also had low nitrogen values on analysis.

From the results of the sensitivity testing, it was concluded that the films are not a hazard from the ignition potential in friction, impact, and ESD forces of normal handling.

Chemical Analysis

Nitrogen Content:

Decomposition of NC results in weight loss and changes in physical properties.¹⁵ These changes are caused by breakage of the NO₂ linkages and loss of NO_x by diffusion. Therefore, samples were tested for percentage of nitrogen using the nitrometer method normally applied to propellant grade NC. Because the film contained emulsion constituents, a method to separate the film base was developed. In this method, approximately 10 grams of film was cut up and extracted for 24 hours with 50/50, by volume, acetone/methanol. The lacquer then was decanted and poured into distilled water to precipitate the NC. The NC was recovered by filtration, dried, and redissolved in acetone. The lacquer was again precipitated with water, filtered, and dried. About 1.1 grams of the dried, recovered NC was taken for analysis. As a check on the method, a sample of NC of known nitrogen content was put through the same series of extractions and precipitations. The nitrogen content was 11.95% originally and 11.93% after two precipitations. The following percentages of nitrogen were obtained:

| <u>Sample No.</u> | <u>Nitrogen (%)</u> |
|-------------------|---------------------|
| 1 | 11.29 |
| 2 | 10.87 (clear film) |
| 5 | 11.66 |
| 6 | 11.36 |
| 7 | 11.74 |
| 8 | 10.63 |
| 10 | 10.93 |

Plasticizer Content:

Because there appeared to be an observable difference in properties of ignition and vigor of combustion between Kodak and Dupont film, an analysis for camphor content was made on selected samples. Four samples of nitrate film were examined for camphor content by a gas chromatographic technique.

¹⁵J. R. Hill and C. G. Weber, "Stability of Motion Picture Film as Determined by Accelerated Aging," *J. Soc. Motion Picture Engrs.*, Fall 1936.

The emulsion was removed prior to sampling by use of pancreatin enzyme. Portions of film (1.0 gram each) were dissolved in 50.0 ml of acetone with 100 μ l of methyl salicylate added as an internal standard. A standard, consisting of 0.1115 gram of camphor plus 100 μ l of methyl salicylate, was diluted to 50 ml and used to calibrate the gas chromatograph. The results are given below:

| <u>Sample No.</u> | <u>Camphor (%)</u> |
|-----------------------------|--------------------|
| 10X, Kodak Topographic 1928 | 5.6 |
| 2D, Dupont 43 Nitrate | 0.8 |
| 3, Dupont 60 Nitrate | < 0.01 |
| 2, Dupont 51 Nitrate | 0.8 |

Samples 10X and 2D were from the film reels subjected to other tests. Both were obviously yellowed as in the first stage of decomposition. Samples 2 and 3 were selected reels of Dupont film from the corresponding sample populations and not specifically subjected to other tests. Note that normal camphor content is usually on the order of 10%.

Stability Testing

Initially, it was planned to conduct Taliani¹⁶ and differential thermal analysis (DTA) testing on the film samples. Changes were made because the Taliani testing was stopped when some samples decomposed before the 100° C starting temperature was attained. Methyl violet tests were substituted.

DTA Test:

In the DTA test, a 1-gram sample is placed in a test tube stoppered with glass wool to provide some retention of decomposition products. The sample is instrumented with a thermocouple and placed in an oven. The oven temperature is increased 1° C per minute, and the differential between the oven and the sample temperature is recorded. Normal, good quality NC propellants will begin self-heating and ignite around 135° to 140° C.

Figures 2 through 5 represent the results obtained in these tests. A normal result is shown in Figure 2. Note that prior to the ignition point there is a negative differential temperature area. This is volatilization and gas evolution generally. Results of the DTA test are given in Table III.

¹⁶Department of the Army, *Military Explosives*, Technical Manual TM 9-1300-214, November 1967.

Table III
DTA TEST RESULTS

| Sample No. | Self-heating temperature (°C) | Ignition temperature (°C) | Comments |
|------------|-------------------------------|---------------------------|------------------------------------|
| 1 | 144 | 152 | Normal |
| 2D | 100 | 108 | Ignition temp 140° C after burning |
| 2E | 144 | 155 | Normal |
| 4 | 140 | 152 | Normal |
| 7 | 142 | 150 | Normal |
| 8 | 95 | 114 | |
| 9 | 140 | 150 | Normal |
| 10X | 102 | 116 | Did not fully ignite |

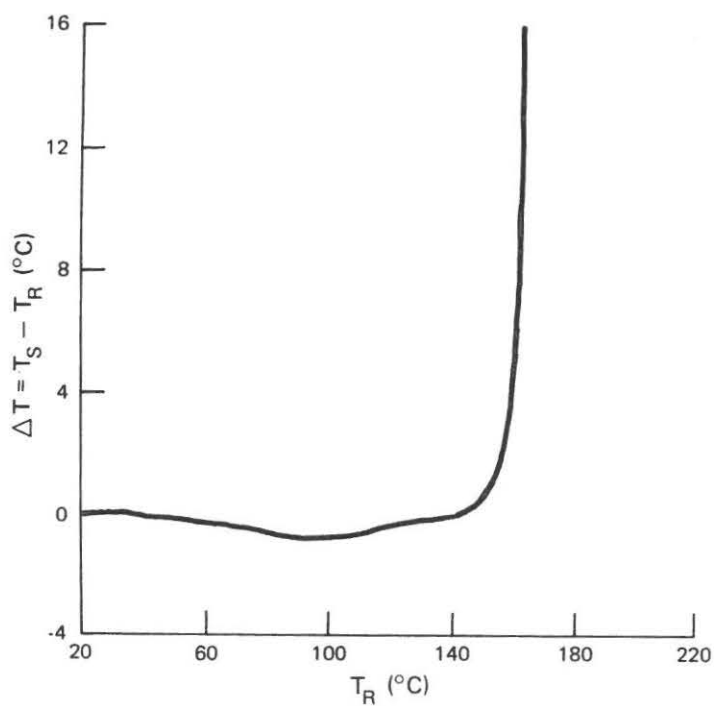


FIGURE 2. NITRATE FILM 1

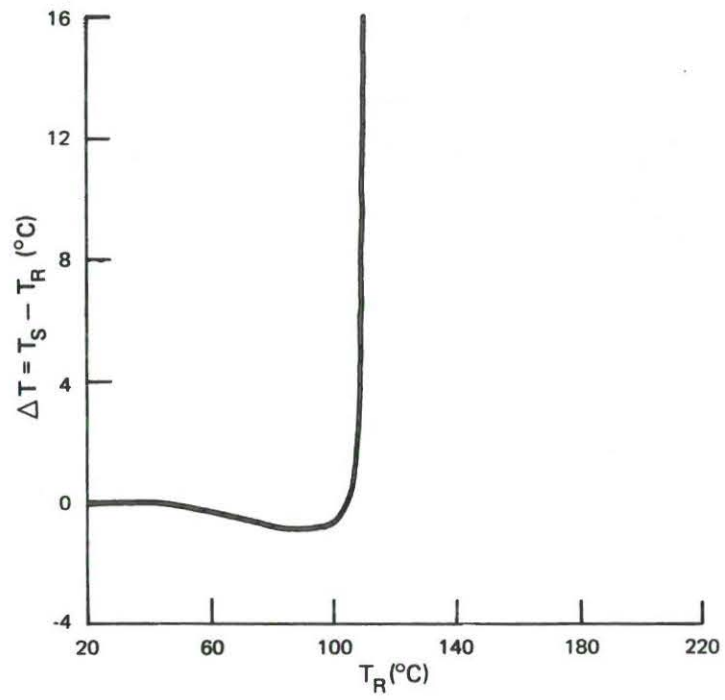


FIGURE 3. NITRATE FILM 2D

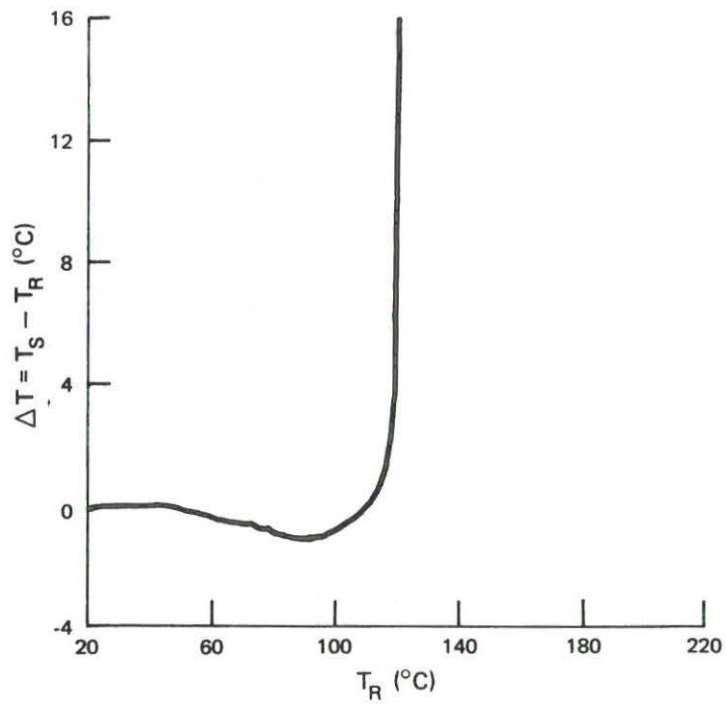


FIGURE 4. NITRATE FILM 8

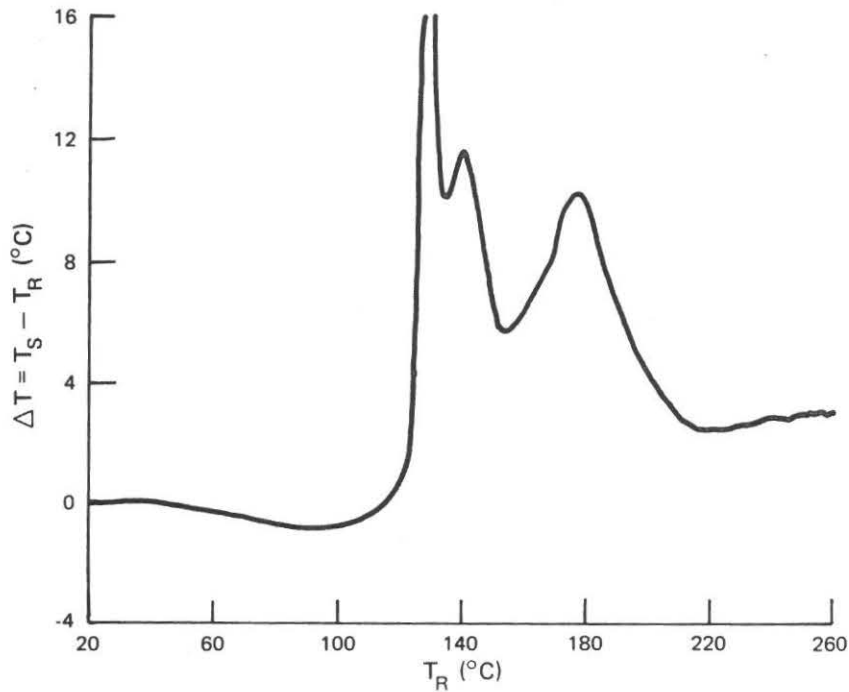


FIGURE 5. NITRATE FILM 10X

The results correspond with the appearance of the film. Yellowed or bad films were 2D, 8, and 10X. The initial trial of sample 2D and that of 10X were anomalies in that heat and gas were given off, but the film did not ignite. Note that the three samples had the lowest percentage of nitrogen content, indicating advanced degradation. The appearance of the sample containers tested is shown in Figure 6. It is apparent that the reactions are different between the bad film (10X and 2D) and the good film (9 and 7). The significant conclusion from this test is that degraded NC film is easier to ignite if thermally stressed with the ignition temperature decreasing approximately 40° C.

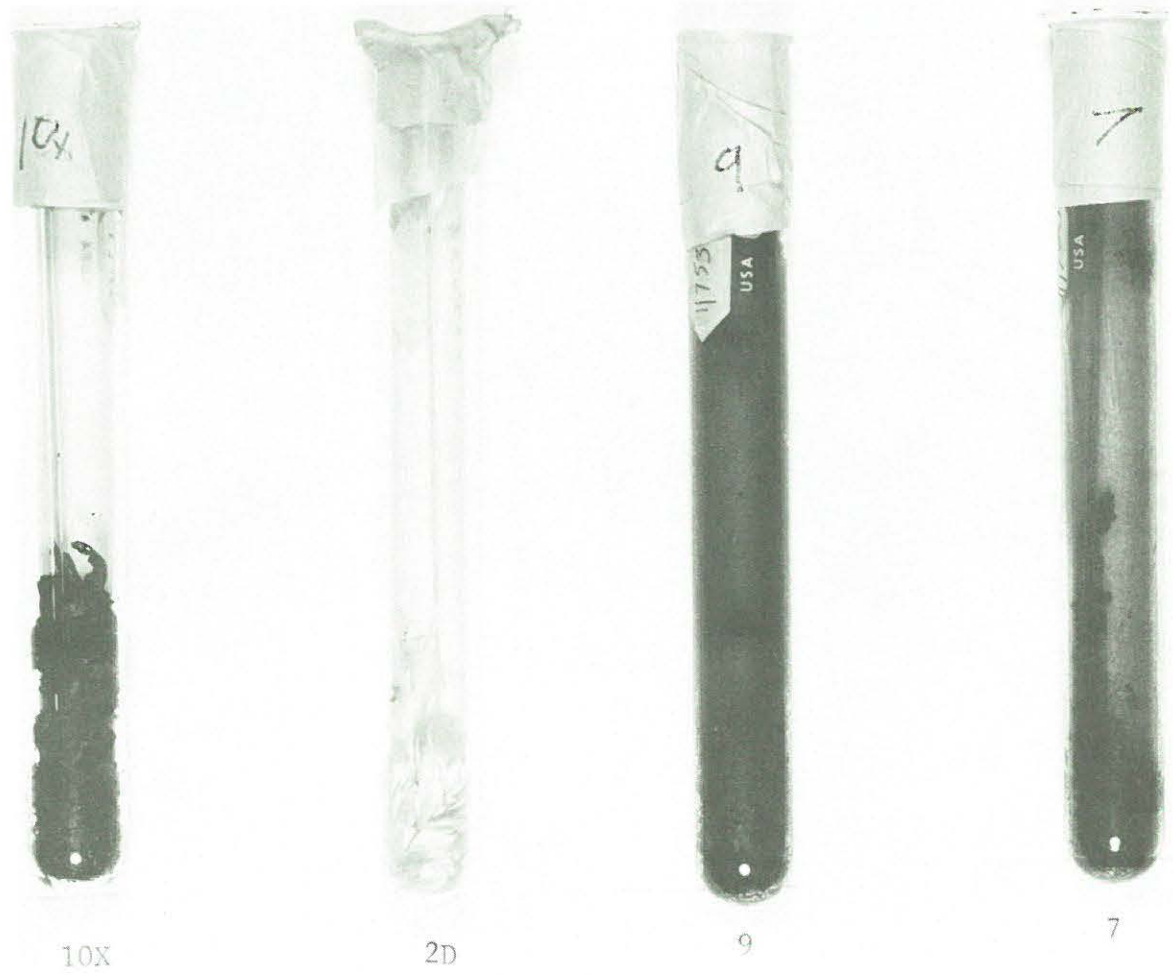


FIGURE 6. FILM SAMPLE CONTAINERS

Taliani and Methyl Violet Stability Tests:

The Taliani test measures the rate of gas evolution from compositional changes or decomposition at 110° C under nitrogen gas.¹⁷ For propellants, it is used as a comparison test as different formulations have different gassing rates. When the results are plotted as volume of gas evolved versus time, propellants with a slope of 1.0 or greater are considered unstable. Two of the nitrate film samples (2D and 10X) evolved gas before reaching 110° C to start the test. This made such a mess in the laboratory that the Taliani tests were terminated.

The methyl violet test at 134.5° C used for testing propellant grade pyrocellulose has been found applicable to NC film.^{17, 18} In this test, a 1-gram specimen is placed in a closed tube with normal methyl violet indicator paper. The time required at 134.5° C for the evolved gases to change the indicator paper to salmon pink is determined. For propellants, any color change within 30 minutes is indicative of unstable material.

In this test, the deteriorated film samples 2D and 10X, fumed off within 8 minutes of the start of the test. Later, samples 1 and 4 passed the test with results of 35+ minutes without change in the indicator paper.

Because of the fume-offs that occurred in the 134.5° C test, it was decided to test samples at 65.5° C where possibly comparable data on propellant were available. Indicator paper of 0.1 normal methyl violet was used in glass containers with 2 grams of film. The deteriorated samples 2D and 10X caused initial indicator changes in 15 to 20 minutes vice 30 minutes expected of stable material. Samples 1 and 4 did not cause any detectable change in 2 hours. At the end of 24 hours, the deteriorated samples had completely changed the indicator paper while the stable samples had not yet caused significant change. The samples were maintained at 65° C for 72 hours without ignition.

Cigarette Testing

Tests to establish cigarette burning and heat transfer to film cans were conducted with enough repetitions to establish valid data. Testing was conducted in an 8- × 15-foot room with the door open for natural ventilation. The ambient temperature was 80° F. In all tests, with reference to the inside and outside of the can, the thermocouple was separated from the cigarette by the can metal thickness.

¹⁷Department of the Army, *Military Explosives*, Technical Manual TM 9-1300-214, November 1967.

¹⁸J. M. Calhoun, "The Physical Properties and Dimensional Behavior of Motion Picture Film" *J. Soc. Motion Picture Engrs.*, vol 42, No. 4, October 1944.

Base Tests:

A base test to determine how long a cigarette could burn in a closed can without film indicated that combustion ceased in 2 to 3 minutes. Note that this would not be the case if NC film were present to supply oxidizer. In these tests, a thermocouple on the outside of the can just under the cigarette measured a local temperature of 100° F just after the cigarette was placed inside.

For approximately 1 minute, the temperature increased slightly or was maintained. At 2 minutes, the temperature had dropped from 100° to 95° F. At 3 minutes, the cigarette was out and the can returned to an ambient temperature of 80° F.

A modification of this test with the thermocouple over the cigarette combustion zone, both in an empty and closed can, gave the following temperature-time pattern:

| <u>Time(s)</u> | <u>Temperature (°F)</u> |
|----------------|-------------------------|
| 0 | 600 |
| 15 | 610 |
| 30 | 630 |
| 45 | 620 |
| 60 | 580 |
| 75 | 540 |
| 90 | 475 |
| 105 | 390 |
| 120 | 340 |
| 135 | 280 |
| 180 | 125 |
| 210 | 105 |

The temperature profile of a burning cigarette in free air was determined using an iron-constantan thermocouple of 30-gage wire size. The profile areas are shown in Figure 7. Measured temperatures are given in Table IV. Note that, had the thermocouple wire size been smaller, measured temperatures would have been higher as less heat would be conducted away by the wires. Drafting was varied to achieve maximum temperatures in the combustion zone with excessive drafting causing a decrease in temperature. The values are consistent with those found in the literature.¹⁹

¹⁹ J. R. Vockers and L. Segal, "Cigarette Fire Mechanisms," *National Fire Prevention Association Quarterly*, vol 49, No. 3, January 1956, pp 213-222.

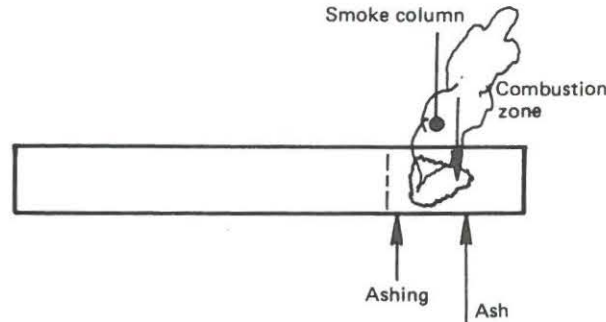


FIGURE 7. CIGARETTE TEMPERATURE PROFILE

Table IV
CIGARETTE TEST TEMPERATURES

| Parameter | Temperature (°F) | |
|-------------------------------------|------------------|----------------|
| | Rest | Drafted |
| Ashing where paper just turned gray | 580 | 780° F |
| Fire zone where tobacco is glowing | 800 to 1000 | 1100 to 1300+ |
| Smoke column 1 mm above surface | 400 to 500 | - ¹ |

¹Down because of air pulled into the fire zone.

Inadvertent Ignition Possibilities:

A common filter king-sized cigarette (6-mm long) was used in all testing for temperature or inadvertent ignition. Tests results and data are presented.

Test A:

The burning rate was determined by placing a cigarette half-on and the lighted half over the edge of a film can simulating a cigarette put down between puffs. The conditions were relatively still air in a room with an open door and no draft.

The burning rate, without drafting, of the suspended portion of the cigarette was 0.5 cm/min. The burning rate at the time the combustion zone was over the can supported portion was about 0.3 cm/min with an apparent decreasing rate.

At the end of 9 minutes, with the cigarette combustion zone ~1.5 cm in from the edge of the can and obvious incomplete burning at the can/cigarette interface, the temperature at the ash zone was 180° to 190° F. At 11 minutes the cigarette was out, and >1 cm of unburned cigarette remained.

Test B:

Cigarettes were placed on top, under, and 1 to 2 mm under film cans with and without fiberglass insulation to confine the heat. Temperatures were measured on the inside of the can. The worst case condition tested is shown in Figure 8.

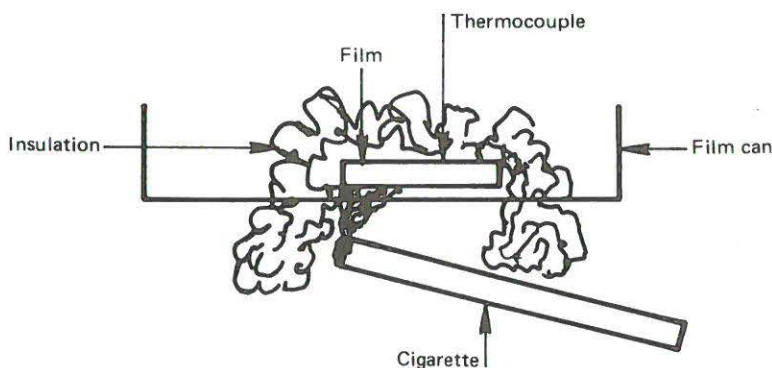


FIGURE 8. WORST CASE CONDITION

Small sections of deteriorated film were placed between the thermocouple and the can for some of the tests. These did not appear to change conditions as the maximum measured temperatures in all conditions was 140° F, with most temperatures in the 110° to 120° C range. The film samples did not ignite in these tests, although film sample 2D was used.

Test C:

One layer of deteriorated film was held flat approximately 1 mm above a cigarette glowing without drafting. The film blistered and ignited in ~12 seconds.

Test D:

Attempts to ignite carbonless duplicating paper with cigarettes were unsuccessful. However, wadded sheet, insulated with drafting of cigarette and paper, would glow to a moderate degree and add to the heat of the cigarette. The best effort achieved 140° F at the can interior surface after 14 minutes.

Test E:

To simulate the temperature of a cigarette and the possible contributing paper combustion, a nichrome heating strip was utilized. The test setup was as shown in Figure 8 with the cigarette replaced by the nichrome heater. The electrical current (4.2 amps) was designed to give the nichrome heater a dull red glow. Temperature of the heater was 850° to 900° F. This condition generated localized temperatures inside the can at 185° to 190° F steady state in 2 minutes without film.

Tests with the nichrome heater with small sections of deteriorated film inside the can resulted in ignition in approximately 2 minutes at measured temperatures on the order of 250° F. Note that difficulties with thermal expansion caused problems in maintaining a constant gap between the nichrome heater and the can and caused scatter in these data. Temperatures approaching 700° F could be obtained inside the can. Because the nichrome heater is a relatively large source compared to a cigarette and could be better insulated as it did not need ventilation to maintain heater generation, higher temperatures resulted. The heater on occasion shorted out to the can. This generally resulted in a decrease in temperature as less heat was given off by the shorter effective length of heater strip.

Cigarette on Exterior of Can:

Cigarettes were placed on the outside of cans containing film. The films were located against the inside of the can in the area where the cigarette was to be in contact with the exterior. Tests were generally conducted with drafting of the cigarette using a hand vacuum pump and reservoir flask. In trial observations, a moderate pumping rate produced cigarette burning representative of mild puffing; really vigorous pumping could approach a "heavy drag" condition. Initially, tests were conducted with the film can on a sheet metal surface to represent shelving in use at the storage facility. Later tests, attempting to attain conditions that would result in ignition, were made with insulation to reduce heat losses. Cigarettes against the edge, top and beneath cans failed to ignite the film in all trials, even when insulation was used. This correlates with the temperature measured in can heat transfer tests. The typical appearance of a cigarette on the outside of a can with extensive ash, partial burning at the can surface, and tar and residues deposits on the can is shown in Figure 9.

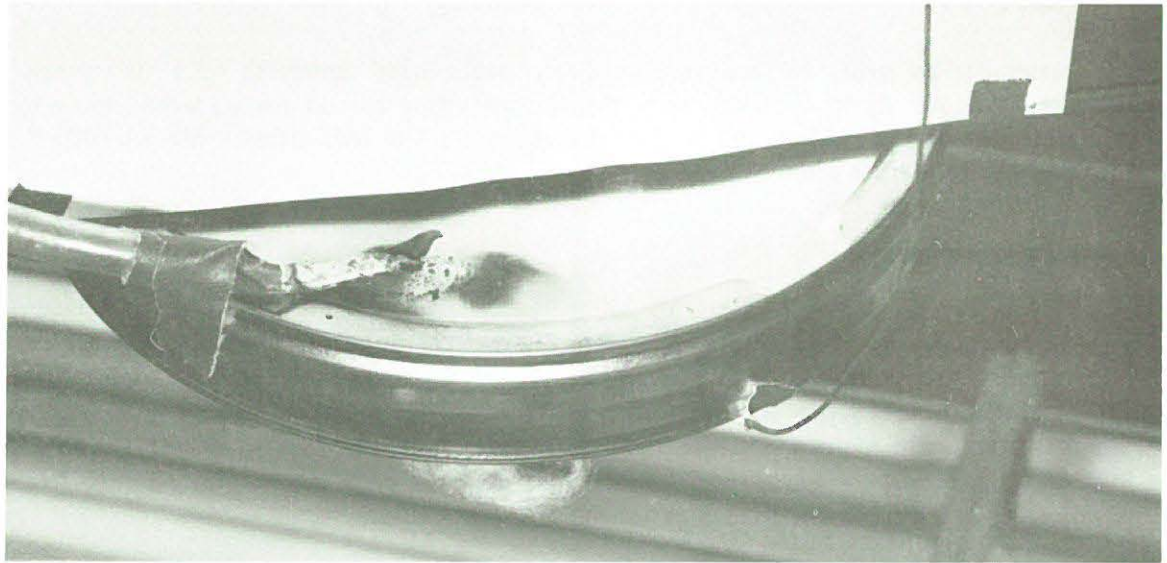


FIGURE 9. TEST WITH CIGARETTE ON CAN EXTERIOR

Attempts were made to achieve film ignition by using a cigarette to ignite loosely wadded sheets of the carbonless paper form attached to each film can. These were unsuccessful. Typical results are shown in Figure 10.

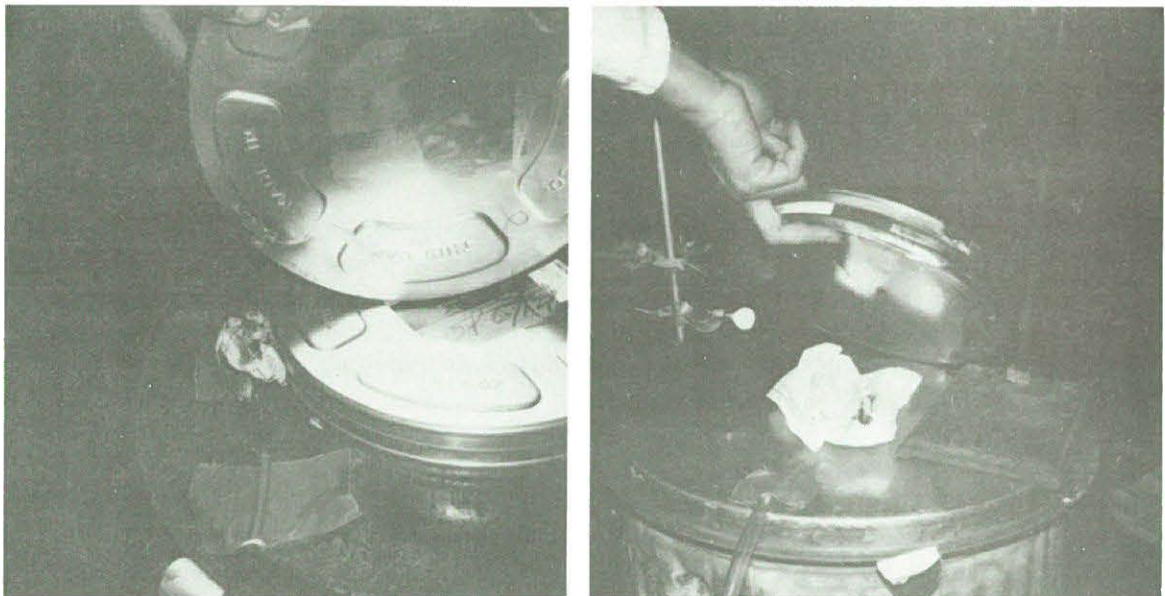


FIGURE 10. RESULTS WITH LOOSELY WADDLED SHEETS OF CARBONLESS PAPER

It should be noted that although ignition of film was not achieved with a cigarette on the outside of a can, conditions where ignition might result are conceivable, if hard to establish in testing. This is considered possible based on the 140° F temperature measured being within ~70° F of the ignition temperatures of some film samples in the DTA tests.

Cigarette Inside Can With Lid Off:

Cigarettes were placed on the film or in contact with the film spool side with the can open (lid off). In most tests, ignition occurred within 10 to 30 seconds after the combustion zone reached the film. Two tests did not result in ignition as the cigarette was in contact with the can metal and cooled till cessation of combustion before the combustion zone reached the film. The typical sequence of ignition was the liquifying of the film near the cigarette, initial slight smoke generation, heavy brown-red fumes generally going to flame combustion after 5 to 15 seconds.

Cigarette Inside Can With Lid On:

Lighted cigarettes were placed in cans such that the combustion zone would be in contact with film after a period of 10 to 20 seconds. The lids were then placed on the cans. This condition normally resulted in ignition of the film. In some tests, cans were stacked with the cigarette in the bottom can. This generally resulted in ignition of the can immediately above, but not of the second can if that can fell off the stack when the lower cans vented. Typical venting was characterized by one side of the can lifting open as shown in Figure 11. Typical burned cans are shown in Figures 12 and 13.

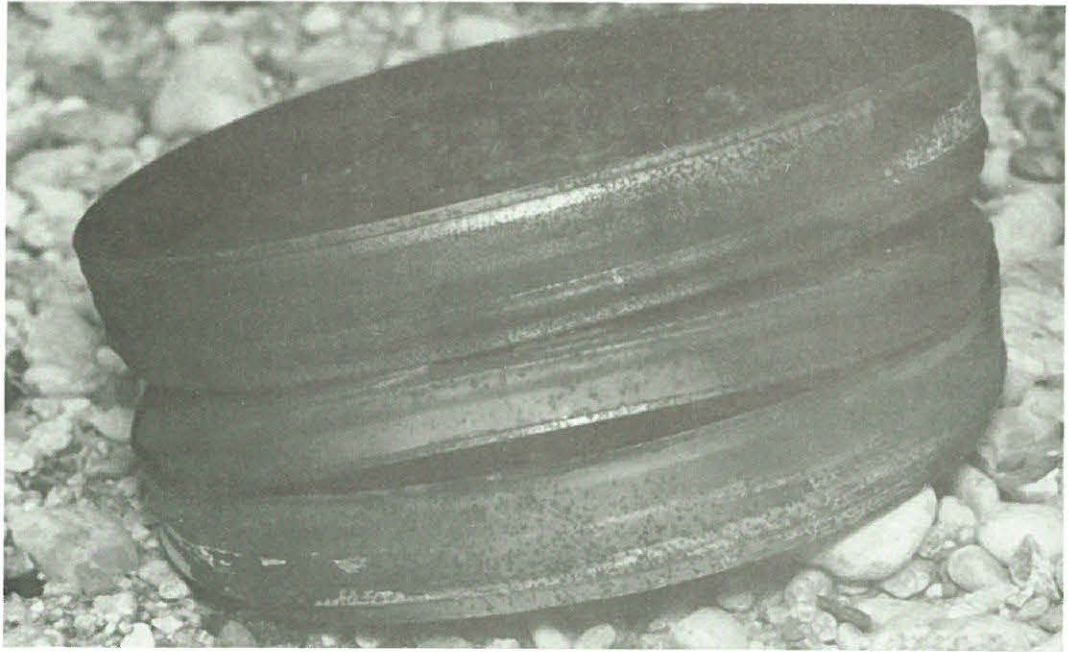


FIGURE 11. TYPICAL VENTING



FIGURE 12. TYPICAL BURNED FILM RESULTS



FIGURE 13. TYPICAL RESULTS WITH 9-1/2-INCH CYLINDER

Carbonless Duplicating Paper:

As each can in storage has a sheet of carbonless duplicating paper taped to the outside of the lid, tests were conducted to determine hazard to film of burning this paper. Initial trials were with one sheet placed flat between two cans so that about one-fifth of the sheet area extended beyond the edges of the cans. The free paper edge was ignited and the sheet burned up to the cans and extinguished without igniting the film in either can.

Trials were made with carbonless paper loosely wadded beneath a can supported 1 to 2 cm above the test surface. Suitable space and some drafting were found necessary to maintain burning or continuous glowing of the paper. The general results were as given below:

(1) One sheet of paper burning with sufficient drafting to maintain flame was not quite adequate to cause ignition of film. Slight modifications in conditions might change this opinion.

(2) Two sheets with flame burning ignited film in the can reliably.

(3) One sheet freely burning with the flame at the bottom of the can gave 160° F inside at the can surface after 35 seconds when the paper was nearly consumed.

(4) One sheet of paper flamed, charred, and flamed again generated temperatures in excess of 240° F and caused ignition of deteriorated film. This was achieved in only one test where the paper was ignited; the flame failed to a slight glow when the combustion zone went into the confined area under the can; then reignited to flame when some drafting ignited trapped gases generated by the initial flame. This scenario could not be duplicated.

One question that the last described test generated was what the effect of volatilization of the carbonless chemicals is on ignition and flammability of the paper. Inquiry to a manufacturer of this type paper elicited the response, "We tell everyone to treat it like regular paper."

Electrical Ignition of Film

Electrical Fault:

Attempts were made to cause film ignition by electrical short, as in a broken power tool line. A controlled voltage 17-amp source was grounded on one line to the film can and the second line was brought into contact with the case or secured to various locations on the outside of the case. The second line consistently welded to the case. The shorted condition was maintained for several minutes without any evidence of heating of the can or ignition of the film. Variations of this test, including random arcing from a current carrying conductor to the film can, were made without causing film ignition.

These tests were also performed with a sheet of the carbonless paper at the short location. There would be charring of the paper in the immediate area of the arc but no ignition. Some of the configurations of electrical faults tested are shown in Figure 14.

The conclusion that the can should be adequate to prevent film ignition from a short condition in any 110-Vac fused circuit was reached.

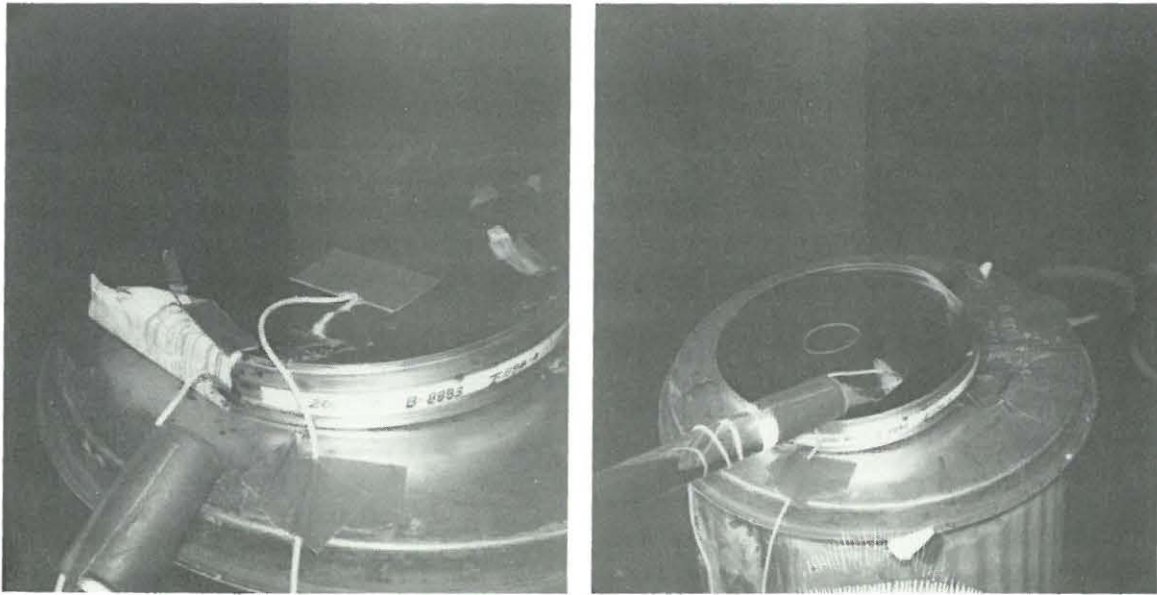


FIGURE 14. ELECTRICAL FAULT TESTING

Electrical Arc:

Film in a grounded can was tested with a copper 16-gauge line at 110 Vac. Contact was both inside and against the film in an open can. There was some sparking and melted copper before the line welded to the case; but even though some film melted where contacted by the arc, film ignition did not occur. An electrical short of this type near exposed film must be considered as a remote possible ignition source. The hot metal particles melted from the wire do not have the heat capacity necessary for ignition.

These tests were repeated with a 10-kV oil burner igniter as the arc source. Ignition could be achieved by inserting the lead in the film perforations next to the bottom of the can (spark gap, 2 mm) and turning on the transformer.

Electrically Heated Wire:

A nichrome electrical resistance wire representing an overheated electric lead at dull red glow ($\sim 800^{\circ}$ F) would ignite the film within a few seconds of contact. Note that, for an equivalent temperature with copper electrical wire as in a short condition, large current would be necessary and fused circuits would fail. A nichrome heater wire, cold resistance of 3.2 ohms, was placed under and ~ 1 mm from a can to simulate heating by a worst possible short, cigarette, etc. The current to produce a dull red glow was 4.2 amps. Insulation was used to confine the heat. Ignition occurred after 23 minutes of heating. In other tests with similar heating by a hot wire and 35-mm square deteriorated film samples inside the can, ignition occurred in considerably less time. The factors causing variation in ignition time are film quantity and heater conditions.

Slow Cook-Off Testing

Cans of film were placed in an oven and the temperature was increased slowly until ignition occurred. Oven and sample temperatures were recorded.

In initial tests, two cans of good Kodak film were stacked flat. One test was conducted with a supply of water in the oven to investigate the effects of humidity. The oven temperature was increased at intervals to maintain approximately 1° F/min rise in the film temperature with the maximum oven setting to be 300° F.

The dry film ignited at 295° F after 6 hours of heating. The wet atmosphere test film ignited at 275° F after 6-1/2 hours indicating that humidity accelerates decomposition as reported in the literature.

In these tests, the film gassed or burned without displacing cans except the lids were raised on one side. The appearance of the oven exterior and interior with cans after a test is shown in Figures 15 and 16.

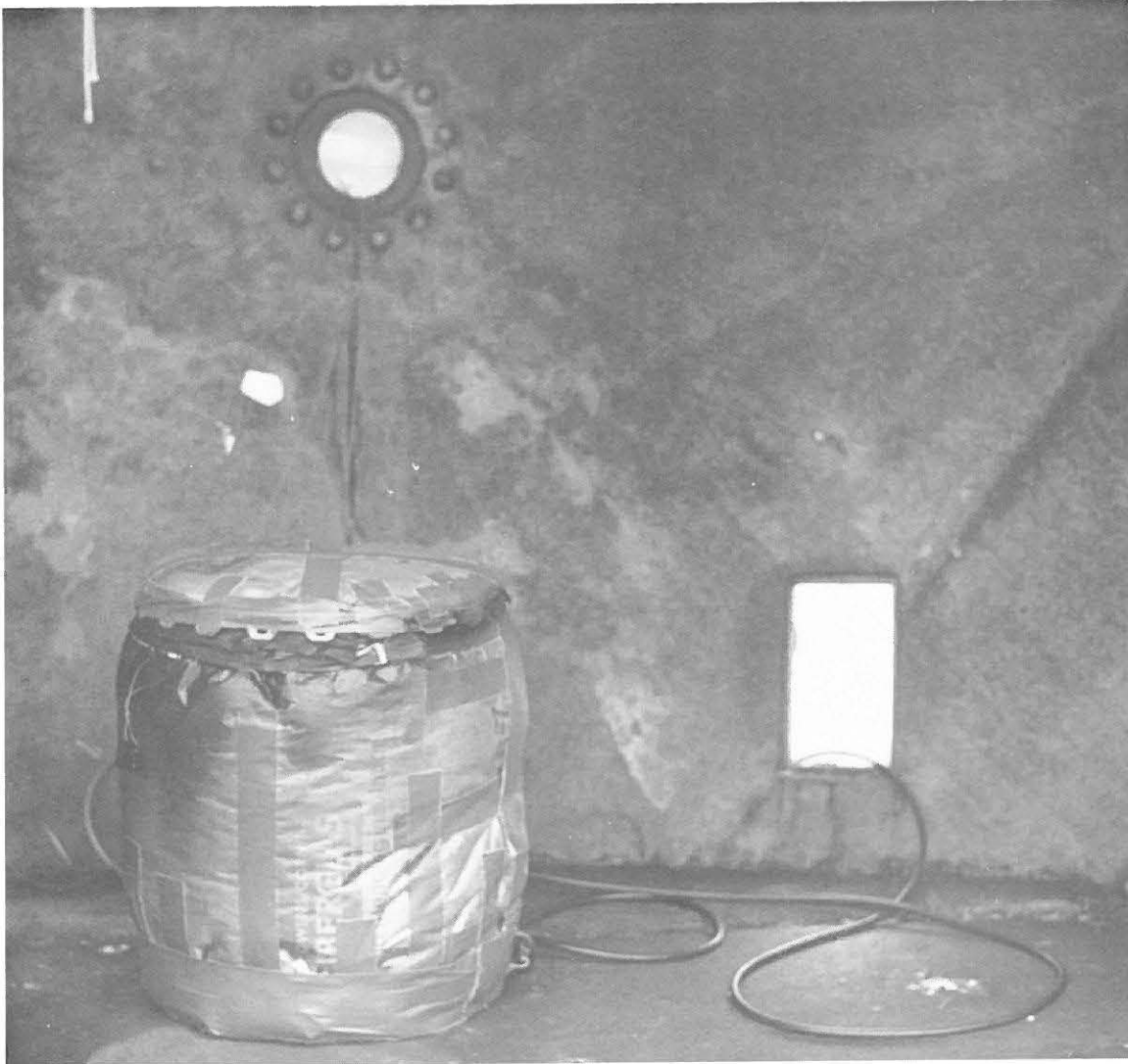


FIGURE 15. EXTERIOR OF OVEN AFTER TESTING

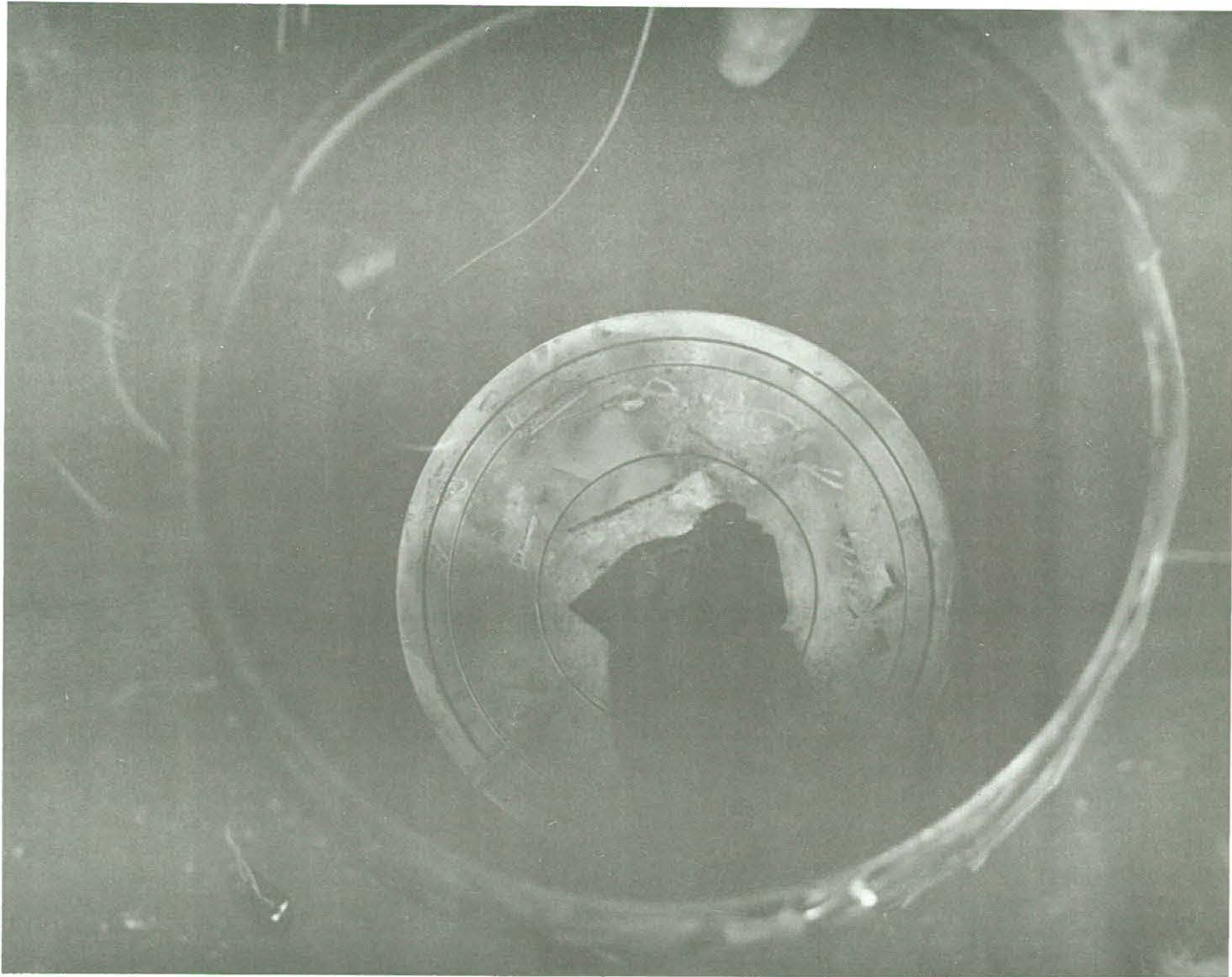


FIGURE 16. INTERIOR OF OVEN AFTER TESTING

Cook-off tests at longer heating times and lower temperatures were conducted using approximately 10-gram samples of bad film in contact with reels of good film to give mass effects. In one test, ignition did not occur in 45 hours at 155° F, but did occur 2 hours after the oven temperature was raised to 180° F. A test with a reel of sample 8, Missouri River 1926 topo, at 170° F ignited in 17 hours; a test at 120° F/24 hours then 135° F/70 hours did not cause ignition.

Comments on Burning Characteristics of Nitrate Film

In ignition of nitrate film by cigarette or other heat source, visual observation was that the film just melts or becomes sticky, then pyrolyzes with red-brown gas evolved, sometimes to complete decomposition without flaming. Flame occurs after some time and it is considered that a higher temperature is required than that at which gassing occurs. Confinement and elevated temperatures would accelerate burning. A typical ignition sequence is shown in Figure 17.

Tests were made with stacked cans of film with internal ignition of the bottom can by cigarette or hot wire. These usually resulted in ignition of cans above without violent displacement. Stacked cans that burned were usually found to have the lid raised on one side.

Note that in these tests, the quantity of film was 2 or 3 reels maximum. In a confining vault, with film at elevated temperature, burning could be more vigorous because of pressure changing the reaction of nitrate decomposition and the temperature increasing the rate of combustion. Greater confinement from higher stacks of film cases also would increase the rate of reaction and consequent displacement of the cans.



FIGURE 17. TYPICAL IGNITION SEQUENCE

CONCLUSIONS

The fire which occurred December 1978, in the National Archives facility at Suitland, Md., was probably not the result of spontaneous combustion, defined as ignition without assignable cause or application of external heat other than that of natural conditions. Weather conditions for that day (50° to 60° F, sky overcast, moderate breeze, medium relative humidity) were not those generally found necessary in previous spontaneous ignition fires. The aged film tested at the Naval Ordnance Station had stability properties similar to those measured in preceding investigations of fires that were attributed to spontaneous ignitions.^{20,21}

In all of the fires attributed to spontaneous combustion, ambient temperature had been around 100° F for several days prior to ignition, the film was in closed vaults and was suspected to have some reels in an advanced (third, soft and gassy) stage of decomposition.²² A more advanced decomposition stage of film results in ignition at lower temperatures. The aged film tested in this program had stability properties comparable to those measured in preceding investigations of fires.^{20,21} The author understands that films in advanced stages of deterioration are regularly removed from the subject storage.

From the tests to simulate inadvertent ignition sources, such as cigarettes, shorted electrical leads, electrical spark, and resistance heater, some general conclusions can be drawn. The first is that film in closed cans is rather well protected from environmental sources of ignition. The can is of good heat transfer and electrical conductance properties. The conductance properties are such that ignition of film inside a can is unlikely by an electrical short of a normal, 15-amp, 120-volt circuit or from a cigarette placed on or under a can without additional factors.

Each can has a sheet of carbonless duplicating paper taped on the lid. A cigarette or electrical short so located that it could ignite some of this paper (not that easy to do) could provide sufficient heat to cause film ignition. However, the carbonless paper is normally between cans, with little access to air, and burns with difficulty or goes out under these heat transfer conditions.

²⁰James W. Cummings, National Archives and Records Service, and Alvin C. Hilton and Howard Silfin, National Bureau of Standards, "Spontaneous Ignition of Decomposing Cellulose Nitrate Film," *J. Soc. Motion Picture Television Engrs.*, March 1950.

²¹J. R. Hill and C. G. Weber, "Stability of Motion Picture Film as Determined by Accelerated Aging," *J. Soc. Motion Picture Engrs.*, Fall 1936.

²²"Fox Film Storage Fire," *National Fire Protection Association Quarterly*, vol 31, No. 2, 1940.

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In any case (i.e., cigarette, short, contribution from carbonless paper) the heat from a small source not in direct contact with the film would have to be confined to bring the film to ignition. It is not impossible that a cigarette, ventilated to keep burning but with the smoke/heat rising to a confining cavity, could result in ignition of a susceptible low stability film. This is believed possible at temperatures as low as 240° F and possibly 180° F if the time of heat application is fairly long. A cigarette dropped onto exposed film almost surely will result in ignition if it is in contact with either the outside of a spool or the flat side (edges of film) of a spool.

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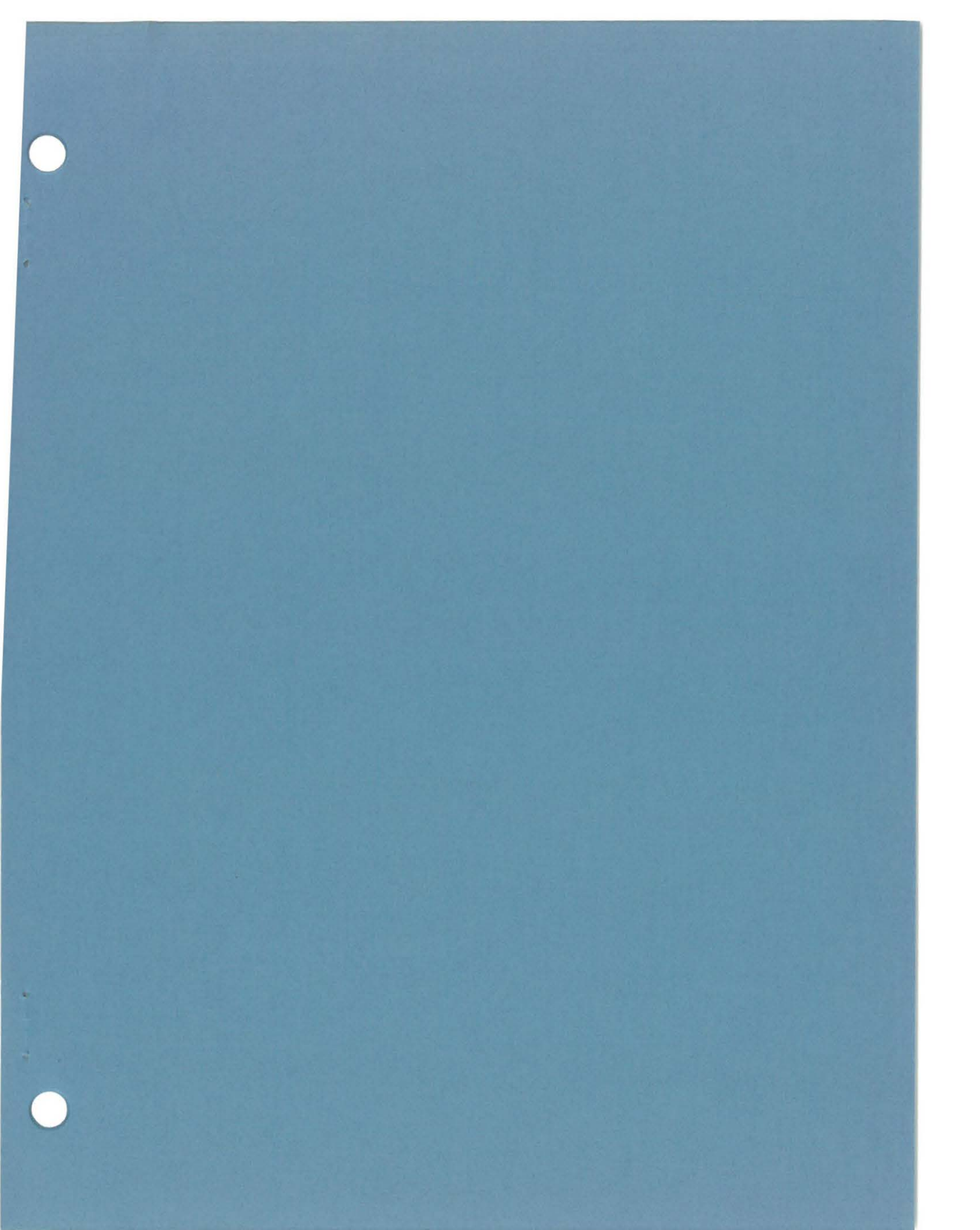
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