# DETECTION OF NITROESTERS AND MOISTURE IN COMBUSTIBLE CARTRIDGE CASE WALL BY INDICATOR STRIPS AND INSTRUMENTS

FINAL REPORT

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# EXECUTIVE SUMMARY

Previous studies by AMCCOM, Honeywell, and ORNL have demonstrated the importance of nitroesters and moisture in the deterioration of combustible cartridge case (ccc) munitions, particularly the adhesive joint strength and the case wall hardness. Accelerated environmental exposures and modelling have predicted field lifetimes under various conditions, but considerable round-to-round variability in adhesive joint tensile strength led to large confidence intervals in predicted lifetimes. This observation suggests the need for technologies for monitoring at the individual round level to supplement lifetime predictions in the quality assurance of ccc munitions.

Two approaches to individual round monitoring appear to be needed to assure munitions performance and safety. Indicator strips which could be affixed to ccc rounds and which would change color in response to the buildup of nitroesters or moisture in the case wall would allow gun crews to rapidly determine the condition of munitions. Portable instruments which could rapidly and nondestructively measure these components in the ccc wall also are needed for more quantitative measurements. Such instruments could be used by the Quality Assurance Specialist - Ammunition Surveillance in confirming the rounds identified as being defective by the indicator strips, and by ordnance personnel in the reconditioning and testing of the munitions.

In the previous phase of this project, chemistries which could detect nitroesters and moisture were screened for their suitability in indicator strips. In this phase, those chemistries were further developed and the performance of prototype indicators was demonstrated in the laboratory. A nitroester indicator based upon a solid state version of a modified Griess reagent was found to change in color from white to red when exposed to nitroester concentrations of 0.6 to 13 mg/g in a period of several d. The intensity of color development was proportional to the nitroester concentration of the test squares. Cupric chloride was chosen for the moisture indicator, which turns from brown to blue-green when exposed to moisture. With this indicator, the length of time required for the color change was inversely proportional to the moisture content of the test squares. Periods of 5 to 19 d were required for 6 or 8% moisture, and more than 35 d for a moisture concentration of 2.7%. At their present stage of development, the indicator performance suggests that they would be most suitable for temporary, one-time tests of munitions rather than for permanent installation on the rounds and continuous indication. Further work on these indicators must address questions of indicator stability and lifetime, sensitivity range, potential sources of interferences, and adaptation to and calibration with actual munitions.

Two instrumental techniques were tested for their ability to determine moisture in ccc material. Electrical capacitance measurements were found to rapidly and nondestructively signify the moisture content of ccc material. An inexpensive ($325) commercially available device for determining moisture in building materials could be readily adapted to munitions. It is highly recommended that adaptation and testing of this device be continued. It appears that a working device for field testing could be produced in the near future. Infrared spectroscopy also was briefly tested, but it did not appear at this time to be as useful or promising as the electrical capacitance technique.

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# INTRODUCTION

Nitroester migration into the case wall from the propellant and moisture accumulation within the case have been identified (1-4) as important internal and external (respectively) factors which contribute to the physical deterioration of combustible cartridge case (ccc) munitions. The latter factor also may hinder proper ignition of the ccc and cause incomplete combustion in firing. Visual indicators sensitive to these factors and affixed to ccc rounds would allow quality assurance specialists or gun crews in the field to rapidly determine the potential reliability of individual rounds. Such visual indicator strips or bands would supplement field life predictions from accelerated lifetime testing and modelling in the assurance of munitions safety and performance.

Previous work (5) in this task identified chemistries suitable for the detection of nitroesters and moisture in the ccc wall. A version of the Griess reaction was modified for a dry colorimetric indicator which in the presence of nitroglycerin (NG) or diethyleneglycol dinitrate (DEGDN) generates a brilliant red color. Inorganic salts such as cupric chloride, which changes from brown to blue-green upon hydration, were suggested as promising visual indicators of moisture. Both chemistries are compatible with ccc.

This report describes the development and preliminary testing of prototype nitroester and moisture indicator strips, and the scoping of two instrumental techniques, infrared spectroscopy and electrical capacitance, which could lead to portable instruments for rapid and nondestructive testing of ccc in the field.

## NITROESTER INDICATOR

### Background

As noted in our previous report (5), the ideal nitroester indicator strip should meet several requirements:

a. The indicator strip must be designed for placement on the surface of the ccc wall and indicate the level of total nitroesters (NG plus DEGDN) in the casing. It must not interfere with the storage, chambering, or firing of the round.

b. The color change must be readily visible.

c. The chemistry of the indicator must be compatible with the ccc, and not cause deterioration of the ccc. It should not pose a hazard to gun crews.

d. The indicator strip should have a long lifetime (decades).

To estimate the nitroester concentration in ccc which is associated with significant weakening of the skive joint, correlations and predictions were made from laboratory studies of full-up rounds. In the AMCCOM study (1,2) M829 rounds were exposed to different temperatures and at intervals the tensile strength of the Skive joint was determined using coupons cut from the case wall after the exposures. Nitroesters were measured in samples of the case wall taken from the bottom of the round. A linear regression was made of the tensile strength versus total nitroesters (NG plus DEGDN). The data with the linear regression line and the 95% confidence intervals are shown in Figure 1. The nitroester concentration corresponding to Skive joint failure (0 lbs/in) was calculated to be 122 mg/g. For the more conservative Honeywell suggestion (6) of 100 lbs/in as a minimum acceptable strength, a concentration of 76 mg/g was calculated.

In the ORNL study (4), accelerated environmental exposures of full-up M829 APFSDS rounds were followed by tensile strength tests of the whole skive joints. Nitroester analysis was performed on ccc wall sections taken immediately below the skive joint for 30 rounds selected from 7 accelerated environmental exposure tests. The tensile strengths (calculated as lbs/in from the strength of the whole joint divided by its circumference) were subjected to a linear correlation with the nitroester content. Figure 2 shows the plot with the regression line and the 95% confidence intervals. Nitroester concentrations for two tensile strengths were then predicted from the regression. The nitroester content predicted for a tensile strength of 0 lbs/in was 147 mg/g. The concentration predicted for the lowest tensile strength actually measured in this study, 15.3 lbs/in (227 lbs/joint), was 138 mg/g. This strength of 15.3 lbs/in was for a round which survived the rigors of being exposed in the test chamber, placed in its protective case and transported by truck to the production line test equipment, and

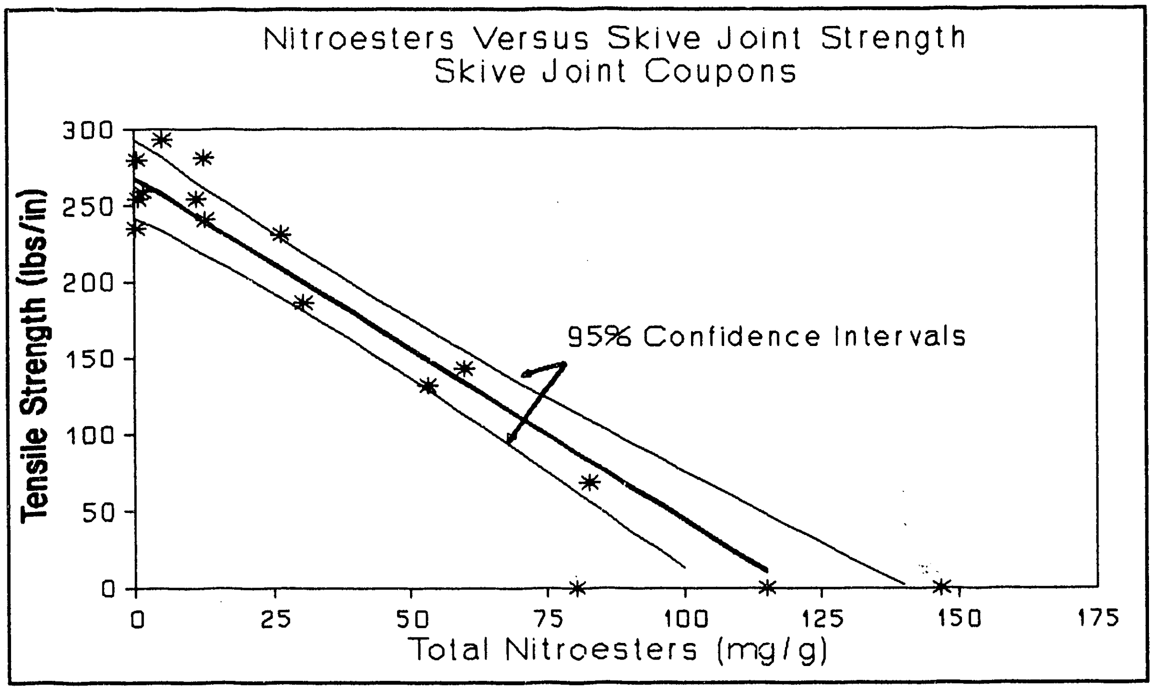


Fig. 1. Skive Joint Coupon Tensile Strength Versus Total Nitroester Concentration (2).

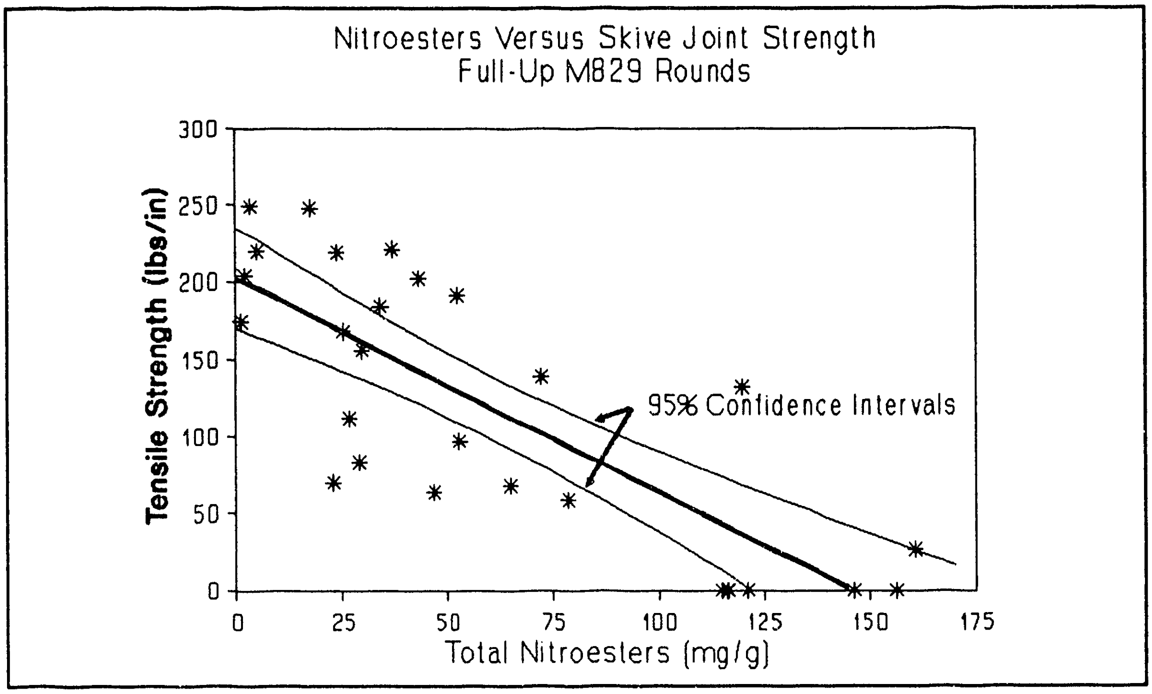


Fig. 2. Tensile Strength Versus Total Nitroester Concentration in Full-up M829 Rounds (4).

tested for chambering with a chamber gauge before being strength-tested using a Slota apparatus. It appears to represent a low strength (but not necessarily the lowest strength) at which the Skive joint is severely weakened, but will still hold together for chambering and firing. The most conservative concentration would be for the 100 lbs/in minimum tensile strength value suggested by Honeywell (6). For this value, a nitroester content of 74 mg/g was calculated. This is in excellent agreement with the estimate from the AMCCOM data. However, the scatter in the ORNL data was considerable, because of round-to-round variability in both tensile strength and nitroester content for a given exposure condition. Therefore, a factor of 5 below the concentration equivalent to the Honeywell lower limit (ca. 15 mg/g) was used as a conservative target for indicator sensitivity to assure that the indicator will change color before the round is severely weakened.

## Experimental

### Test Rectangles or Squares

White blotter paper was used to simulate the surface of a ccc round. Squares of 1.9 cm x 1.9 cm dimensions and weighing ca. 150 mg each were dried in an oven at 100°C. Known volumes of a NG standard in methanol (1 mg/mL) were pipetted onto the blotter paper squares and dried until the surface liquid disappeared. The squares were not allowed to dry completely because the limited masses of NG would not effectively diffuse into the indicator strips without traces of solvent.

### Indicator Strip

The nitroester indicator strip structure is diagrammed in Figure 3. The indicator strip consisted of Nucleopore glass fiber filter with various combinations of the modified Griess reagent and powdered zinc applied to the upper or lower surfaces. The strip was sealed to the test square or rectangle using Bel Art tape.

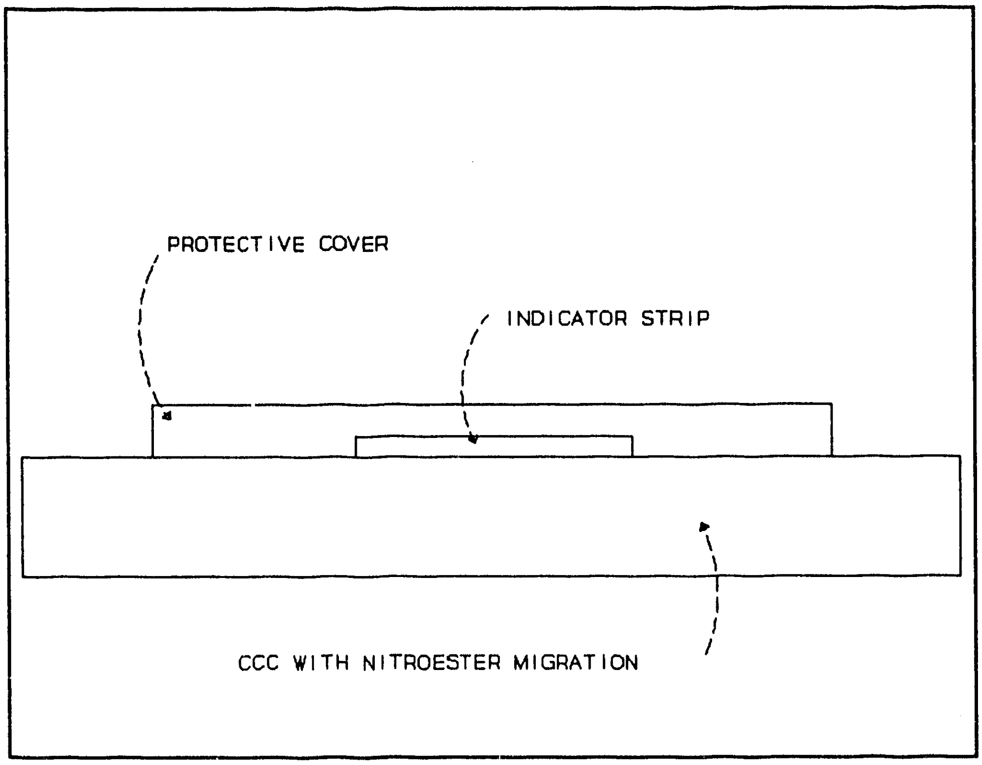
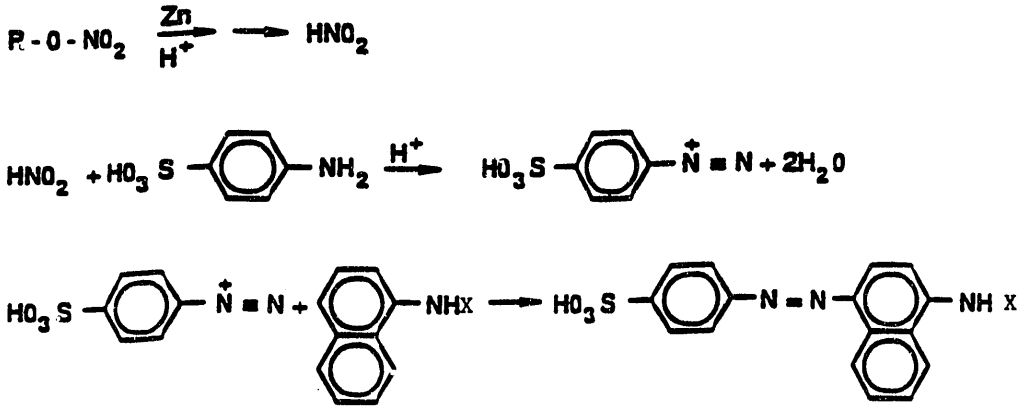


**Figure 3. Diagram of Nitroester Indicator Structure.**

## Results and Discussion

### Indicator Design

The indicator chosen is the modified Griess reagent that is normally used in solution to test for compounds which contain the nitro group (-$NO_3$). This reagent was the only chemistry located in our survey task (5) which satisfied the criteria of being compatible with ccc material and not requiring an auxiliary light source (e.g., UV) for color development or fluorescence detection. In its typical application, a sample is added to a solution of N-(1-naphthyl)ethylenediamine dihydrochloride and sulfanilic acid. (This solution is the modified Griess reagent). Powdered zinc is added to the resulting solution. The zinc reduces nitrate to nitrite which reacts with the sulfanilic acid forming a diazo compound which then combines with the N-(1-naphthyl)ethylenediamine dihydrochloride to form a diazo dye. This reaction is diagrammed in Figure 4.



$X = -CH_2 - CH_2 - NH_2 \cdot 2HCl$

Figure 4. Mechanism of the Modified Griess Reaction used for the Nitroester Indicator.

The choice of the medium used to support the indicator reagents affects the stability of the indicator. When sulfanilic acid solution was placed on common cellulose-based filter paper, after a short time the color of the paper changed to a pale yellow. It is likely that impurities in the cellulose reacted with the sulfanilic acid. Three other types of paper supports were tested with the modified Griess reagent solution: Whatman no. 40 ashless cellullose-based filter paper, Nucleopore prefilter paper (no. 211707), and Nucleopore glass fiber filter paper (no. 211825). After 17 days storage in the dark at room temperature the Whatman ashless filter paper turned purple, similar to the reaction with nitroester. The Nucleopore prefilter paper changed to a light gray, and no change was observed for the glass fiber-based paper. Thus, the Nucleopore glass fiber filter paper was used as the indicator support medium.

A protective coat or surface shield also is necesary to protect the reagents from contact with air and also from physical damage. several commercial household glues, polyurethane, epoxy, and plastic tapes were evaluated. Bel Art tape (described in more detail in the next chapter) was found to give the best protection for the nitroester indicator strip.

The stability of the components of the indicator reagent also is important to the lifetime of the indicator strip. Of the reagents used, the sulfanilic acid appeared to be the least stable. It was observed to decompose with time and change from white to pale yellow in color. The sodium salt should be more stable, so a test was made of its suitability to replace the free acid in the modified Griess reagent. Using the 2 layer reagent configuration, it did not permit a nitroester-specific color change to be produced, and was judged unsuitable. Apparently, it cannot convert nitrite to nitrous acid, which is required for reaction with the sulfonic acid to form the diazonium salt. Additional work is needed to identify more stable reagents.

In early attempts to perfect a test strip, many different means of applying the modified Griess reagent and the powdered zinc to the indicator were tested. Experiments were conducted to apply a thin, even layer of zinc powder onto paper by spraying an aqueous zinc suspension. This approach was not successful. It was found that simply brushing the zinc on using a small brush was satisfactory. In one test, a glass fiber filter paper was wetted with the modified Griess reagent which was then dried by vacuum desiccation. Powdered zinc was then dusted on the reverse side of the filter paper. This test square was brought into contact with a surface containing a nitroester. If there was a sufficient quantity of the nitroester to migrate through the filter paper, it would readily yield a color change. However, these test squares were very sensitive to small amounts of nitroester and developed a significant color change over extended periods of time even in the absence of NG. The reagent also is light-sensitive, which adds to the blank problem. Test plates were normally wrapped in aluminum foil while waiting for color development to protect the reagents from photodegradation.

Frequently, test materials prepared as described immediately above would develop a slight color before applying the powdered zinc. Experiments were then conducted with the dry materials. At first, the modified Griess reagents were blended in a 1/1 mole ratio. Fiberglass filter paper was dusted with zinc. A test strip of this zinc-coated filter paper was placed in contact with a test square containing NG. A small portion of the dry Griess reagent mix was placed on the surface of the test strip and the entire unit then sealed against a glass plate for color tests. This is the general preparation method used for the performance tests described below.

## Performance of Nitroester Indicator Strip Designs

The performance of three reagent configurations was tested. A nitroester test was started on 6-8-92 for the configuration with zinc powder on the back side of the indicator strip, and the modified Griess reagent [N-(1-naphthyl)ethylenediamine dihydrochloride plus sulfanilic acid] on the top side. The reason for placing the zinc powder behind the strip was to prevent the dark color of the powder from obscuring the visual detection of the colored dye. In this configuration, the nitroesters are reduced to nitrite on the bottom of the strip, and the nitrite then diffuses into the Griess reagent on the top of the strip to form the colored diazo dye. The configuration of the test plate in Figure 5 is listed in Table 1.

Table 1. Relative Positions and Nitroester Concentrations of Test Rectangles in Figure 5.

| Relative Position and Nitroester Concentration, mg/g | | |
|---|---|---|
| 3 | 0 (Blank) | 3 |
| 6 | 0 (Blank) | 6 |
| 9 | - | 9 |

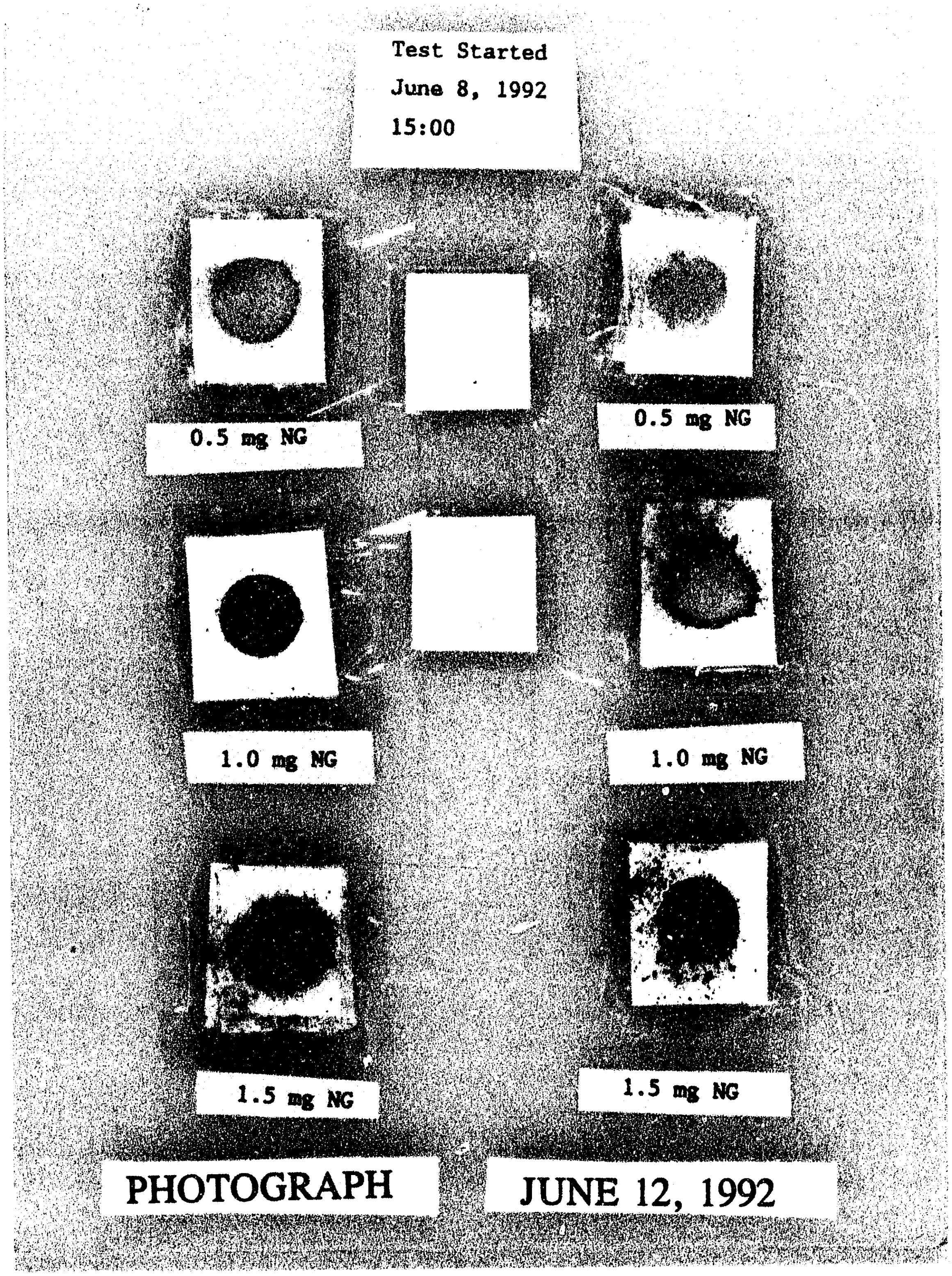


FIGURE 5. PHOTOGRAPH OF NITROESTER INDICATOR STRIP TEST PLATE AFTER 4 D OF EXPOSURE.

The photograph in Figure 5 was taken after 4 d of exposure (6-12-92). This test shows that color development was rapid and the color density was proportional to the NG concentration. The blanks had only a slight discoloration and were not significant in relation to the other test strips.

The performance of the 3 reagent configurations was demonstrated in a simultaneous test. The test plate was similar in makeup to the above. The first configuration had the N-(1-naphthyl)ethylenediamine dihydrochloride on the surface of the indicator strip with a mixture of the sulfanilic acid and zinc powder on the reverse side. The second configuration had the dry modified Griess reagent on the surface of the indicator strip with zinc powder on the reverse side. The final configuration had a mixture of the dry modified Griess reagent on top of the zinc powder, all on the surface of the indicator strip. Table 2 diagrams the relative positions and configurations of the indicator strips on the test plates shown in Figures 6 and 7.

Table 2. Relative Positions, Reagent Configurations and Nitroester Concentrations for Test Plate in Figures 6 and 7.

| Relative Position for Concentration of Nitroester, mg/g Reagent Configuration | | |
|---|---|---|
| 0 (Blank)<br>A/B+C | 0 (Blank)<br>A+B/C | 0 (Blank)<br>A+B+C/ |
| 0.6<br>A/B+C | 0.6<br>A+B/C | 0.6<br>A+B+C/ |
| 3<br>A/B+C | 3<br>A+B/C | 3<br>A+B+C/ |
| 13<br>A/B+C | 13<br>A+B/C | 13<br>A+B+C/ |

A= N-(1-naphthyl)ethylenediamine dihydrochloride

B= Sulfanilic acid

C= Powdered zinc

Photographs of the test plate after 1 d of exposure (Figure 6) showed a marked color change for the 13 mg/g nitroester test squares for all 3 reagent configurations. By 16 d of exposure (8-20-92, Figure 7) there were significant color changes at all concentrations of nitroester. The configuration with all 3 reagents present on the surface of the indicator strip gave the

Nitro Ester Test

8-4-92

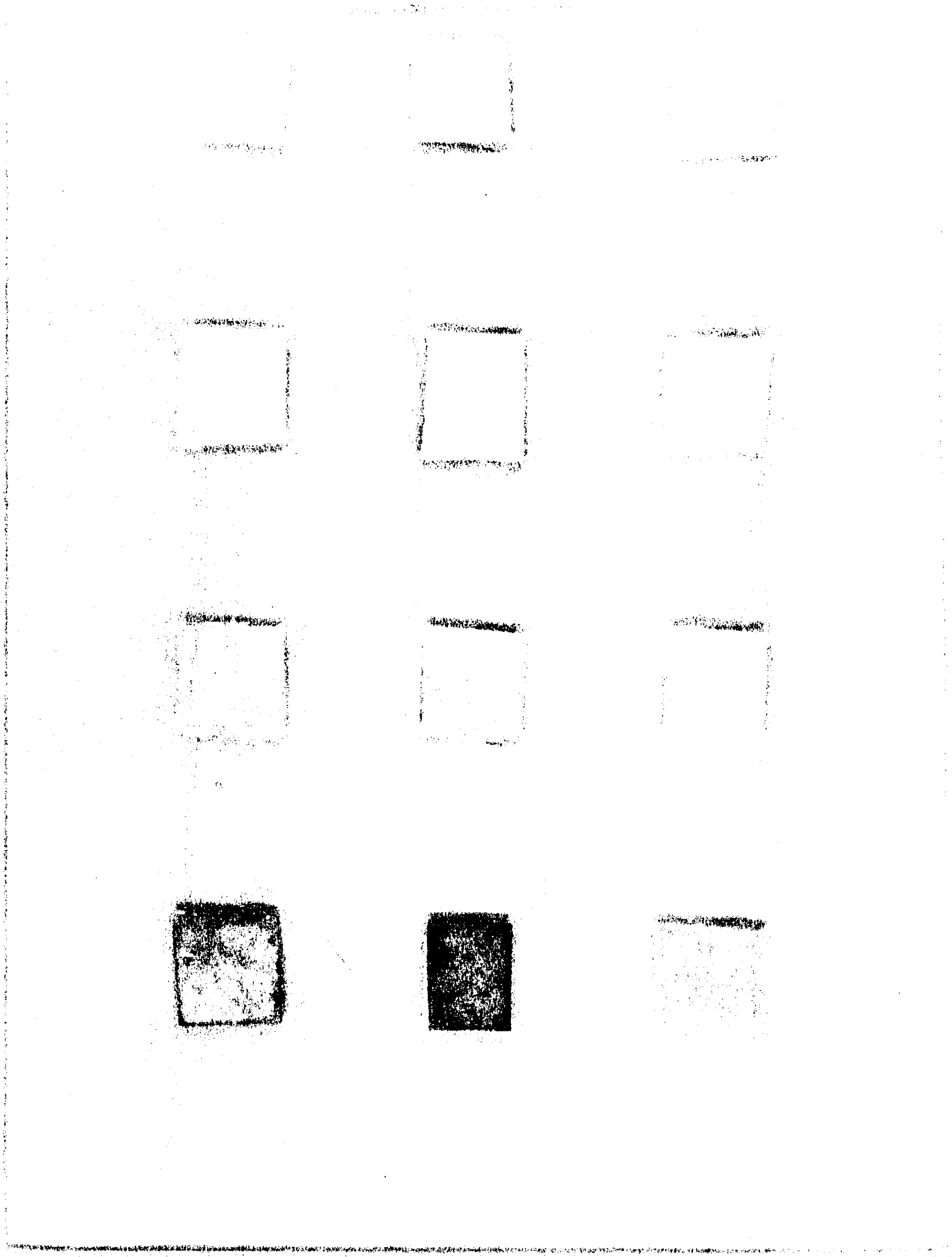
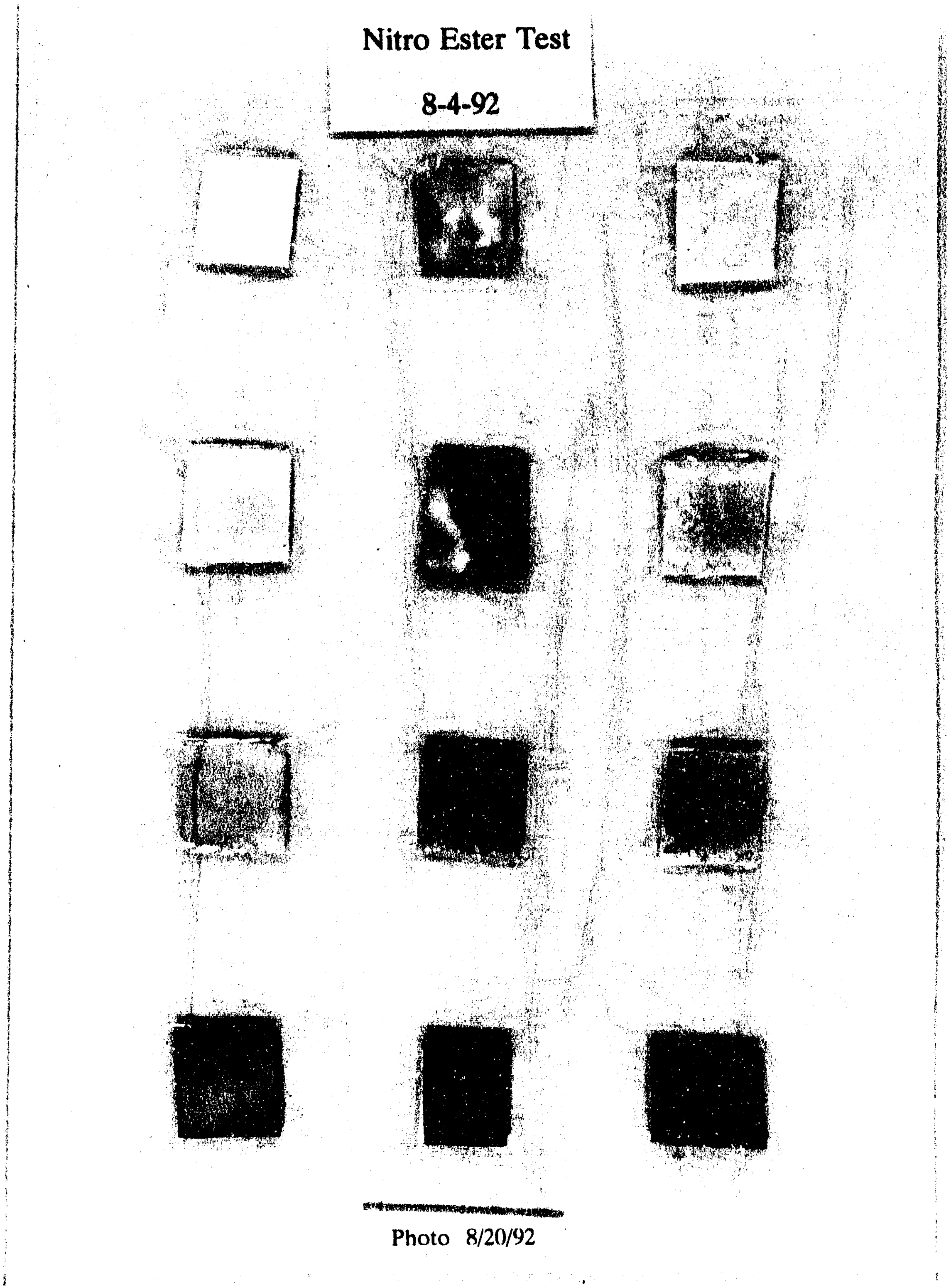


**FIGURE 6.** PHOTOGRAPH OF NITROESTER INDICATOR STRIP TEST PLATE AFTER 1 D OF EXPOSURE.



Nitro Ester Test

8-4-92

Photo 8/20/92

FIGURE 7. PHOTOGRAPH OF NITROESTER INDICATOR STRIP TEST PLATE AFTER 16 D OF EXPOSURE.

# MOISTURE INDICATOR

## Background

Moisture accumulation in ccc munitions, from exposure to very wet environments or from the round actually lying in a pool of water, causes the case wall to soften and weaken, and the adhesive joint tensile strength to decrease (4). Visual indicators would allow the identification of individual rounds which have accumulated moisture, and which could be removed from deployment for drying out.

As noted in our previous report (5), the ideal moisture indicator strip should meet several requirements:

a. The indicator strip must be designed for placement on the surface of the ccc wall and indicate the level of moisture in the casing. It should not interfere with the storage, chambering, or firing of the round.

b. The color change must be readily visible.

c. The chemistry of the indicator must be compatible with the ccc, and not cause deterioration of the ccc. It also must not pose a hazard to gun crews.

d. The indicator strip should have a long lifetime (decades).

e. The indicator strip reaction should be reversible. (If the strip indicates high content of moisture the round is transported to a drying area where moisture is to be removed. Indicator color should reverse, indicating the removal of the moisture.)

The target moisture concentration to be detected by indicator strips was estimated from previous ccc coupon experiments (4,5). Uncoated ccc coupons (cut from only the nitrocellulose/wood fiber portion of the M829 case wall, and not including the cellulose adapter) equilibrated with ambient laboratory air (ca. 45- 65% RH) to a moisture content of 4.4 ± 0.51% (n = 3). When exposed to air saturated with water vapor, the moisture content increased to 13.0 ± 0.15% (n = 3). As shown in Figure 8, this process reached a value close to equilibrium within 7 d of exposure. The reason for the drop in moisture at d 11 is not clear. The results for the longer exposures suggest a slow climb to a slightly higher degree of hydration by 28 d. This behavior suggests that more than one mechanism for hydration or water uptake is present. For example, the cellulose sites in the nitrocellulose/cellulose matrix may take up water much more rapidly than do the nitrocellulose, which could lead to a rapid initial uptake of moisture, and then a slower uptake by the lower affinity nitrocellulose. Significant decreases in case wall indentation hardness (10% decrease) and adhesive joint tensile strength (39% decrease) were observed (4) in ccc coupons exposed to air at 21°C/97% RH for 29 d. Moisture effects appeared to be reversible upon drying, if an elevated temperature were not present during the exposure to water vapor. When the coupons were soaked in water, the ccc coupon moisture concentration increased to 20.2 ± 2.8% (n=3). This hydration required 4 to 8 d to reach an apparent equilibrium, as depicted in Figure 9. After 17 d of soaking, case wall indentation hardness decreased by 14%, and the adhesive joint tensile strength dropped by 44%. A separate experiment for the infrared spectroscopy test (see later chapter) yielded a 32% moisture content, but only one replicate was run. These results suggest that a 20 to 30% moisture content can be reached by ccc material, but effects can be observed with moisture concentrations of 13%. Allowing a conservative factor of 2 or 3 for the indicator strip, target moisture concentrations of ca. 10% appear desirable. Accordingly, the range of moisture concentrations used in the indicator strip tests approached 10%.

## Experimental

Two forms of moisture indicators were developed. One was based upon glass fiber paper saturated with cupric chloride ($CuCl_2$), and the other was based upon cupric chloride pellets.

### Impregnated Glass Fiber Indicator

For the glass fiber based indicator, Nucleopore glass fiber paper with a 7 μm porosity (part number 211825) was saturated with cupric chloride by soaking 3.8 cm x 7.6 cm (1.5 in x 3 in) strips in concentrated cupric chloride solution (10 g of $CuCl_2 \cdot 2H_2O$ per 100 mL of water) and drying overnight at 110°C. During the drying step the salt was dehydrated ($CuCl_2$). The dry, dehydrated strips were cut into smaller squares or rectangles for testing, and were sealed to the test squares with tape to prevent atmospheric moisture from interfering with the response.

### Pelletized Indicator

300 to 400 mg of $CuCl_2$ were pressed into a thin pellet using a 1.27 cm (0.5 in) pelletizer at 10,335 $kP_a$ (1,500 psi) for 30 sec. The pellets were placed in an oven held at 100°C for redrying and storage. They were supported by placing in a cardboard strip with a round hole cut to the same diameter as the pellet.

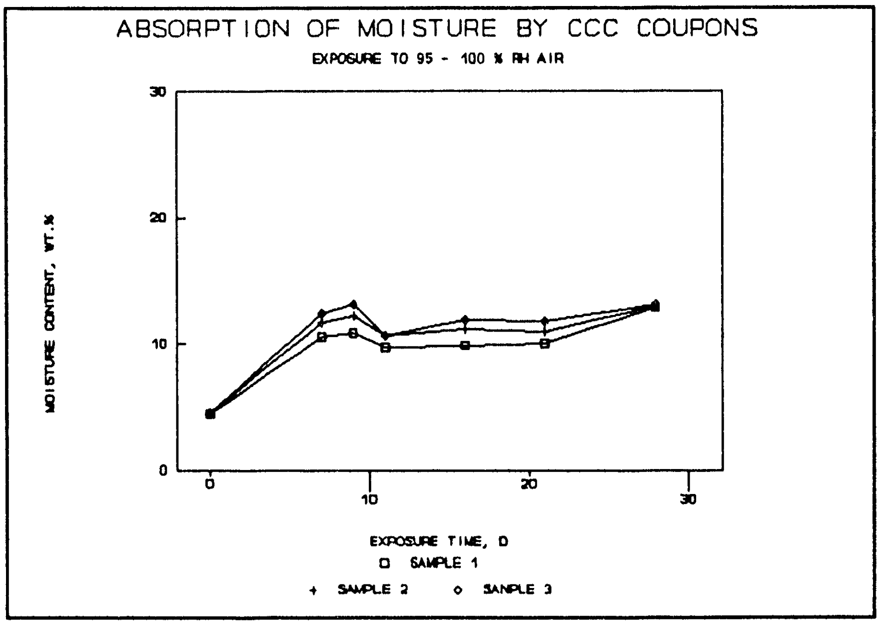


Fig. 8. Uptake of Moisture by CCC Exposed to 95-100 % RH Air.

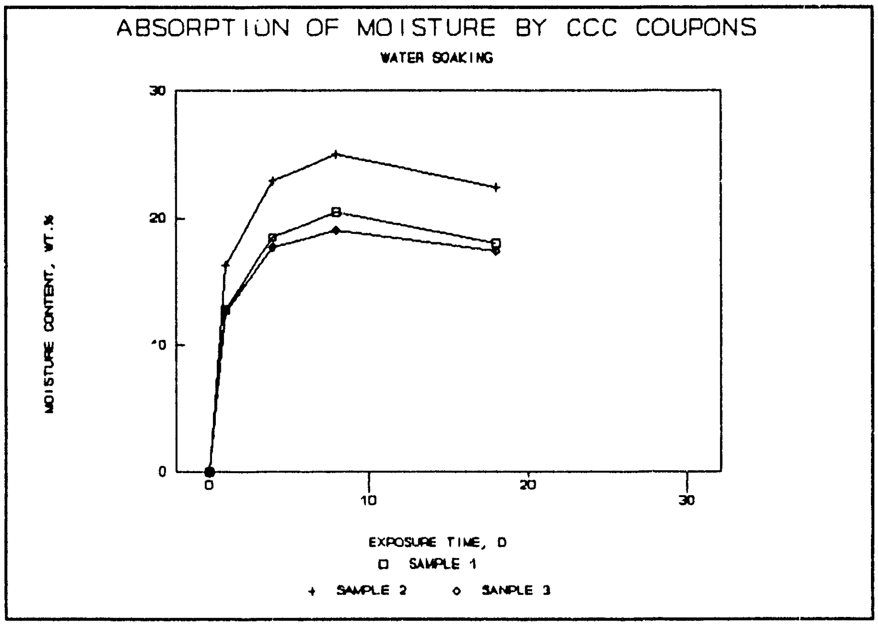


Fig. 9. Moisture Uptake by CCC Placed in Water.

## General Design of Indicator Strips

In contrast to the nitroester indicator, it was necessary to place a semipermeable barrier between the indicator and the test sample to potentiate the indicator response. Accordingly, the test sample was covered with plastic tape. To provide a path for the moisture to diffuse to the indicator, small holes (ca. 20 per indicator strip) were punched in the tape, using the point of a pencil compass. The indicator, consisting of either the impregnated paper or the salt pellet supported in a cardboard square, was then sealed onto the test strip using adhesive tape to prevent uptake of atmospheric moisture by the indicator. The structure of the moisture indicator strip is diagrammed in Figure 10.

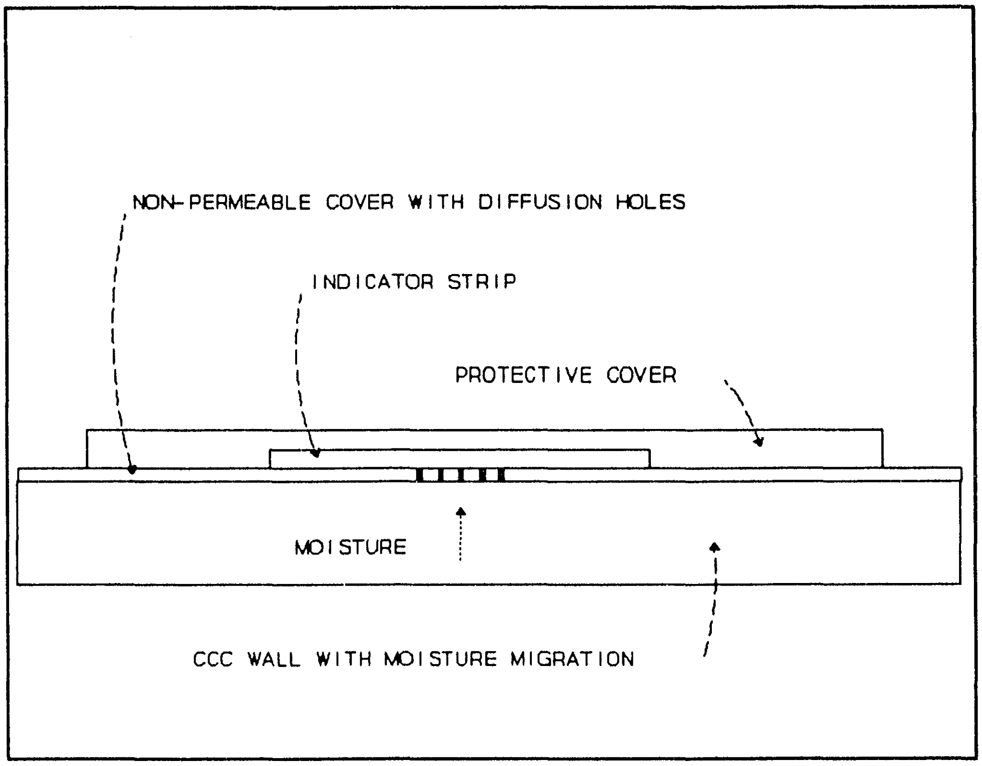


**Fig. 10. Diagram of Moisture Indicator Design. (Relative thicknesses are not shown to scale.)**

## Results and Discussion

### Indicator Design

Indicators are compounds that change color as they become hydrated. The chosen moisture indicator compound, due to its marked color change, is cupric chloride. The molecular weight of $CuCl_2$ is 134, and in the presence of moisture it hydrates to $CuCl_2 \cdot 2H_2O$ (molecular weight 170). This means that 1 g of the dry $CuCl_2$ will absorb 0.27 g of water. In the dry form the cupric chloride is brown but it turns to a blue-green when hydrated. It is a stable, non-corrosive salt which should not damage ccc material.

These salts are able to draw moisture from a contacted source having a very low concentration of moisture. If that moisture is replaced or the source has sufficient moisture to completely hydrate the salt the color change will develop in time. Naturally, the color change is slower if the moisture content is low or if a large quantity of the cupric chloride is employed.

During earlier testing of the copper salt, solutions of the salt in water were prepared and test strips were made by wetting glass fiber filter papers with the solution and drying these test strips in an oven. It was found that strips with very low concentrations of the salt were much too sensitive and would change color when contacted with very low concentrations of moisture in the test material. Filters with very high concentrations of the salt were less sensitive but also became hydrated and changed color, although over a longer time period. We finally began pressing pellets of the dry salt. Between three and four hundred milligrams of the salt are pressed in a 1.27 cm (0.5 in) pelletizer at 10,335 $kP_a$ (ca. 1,500 psi). These pellets, containing much more cupric chloride than can be evaporated on a small filter square, required much more moisture to effect a color change. We are able to attach these pellets to a surface and make simple estimates of the moisture concentration based upon the time required for the color change to take place.

The material used to achieve a seal of the test material is quite important to prevent atmospheric moisture from contaminating the indicator and to potentiate the diffusion of moisture from the test rectangle into the indicator. Some plastic tapes, such as 3M Prescription Label Tape were too permeable to moisture. An early sample of what appears to be Bell Arts Lab Label Tape provided the best protection, and the second best tape was from a recent lot of the Bell Arts Lab Label Tape. However, the latter had a slightly different colored tinge on the roll than did the former, suggesting a different formulation. Clear Scotch mailing tape and 3M Highland Brand 371 clear tape also were good. The tape seals well if smoothly applied. It is somewhat difficult to make a smooth seal if the test square is very thick. In cases where wrinkles in the tape seal might transmit moisture, a cross-seal with the same tape is necessary.

### Performance of The Impregnated Glass Fiber Indicator

The performance of the impregnated glass fiber indicator was tested using cellulose rectangles having known moisture contents. To record the color change dependency upon moisture concentration and time, photographs were taken of the test plates at various intervals.

Test rectangles (3.81 cm x 5.08 cm, or 1.5 in x 2 in) were cut from matting board and dried in an oven at 100°C. The rectangles with 0% moisture were used as removed from the oven. Other rectangles were weighed after removal from the oven, and were exposed to the atmosphere to absorb moisture. They were reweighed to determine the moisture gained. Test rectangles with moisture concentrations of 3.5%, 5.3%, and 9% were prepared. The test rectangles were sealed in clear plastic tape to prevent further moisture uptake. An indicator strip of the cupric chloride impregnated glass fiber was mounted on the surface of each test rectangle. To permit moisture from the test square to migrate into the indicator strip, small holes were punched through the tape seal. The fine tip of a drafting compass was used to form these holes (20 holes per test rectangle). Clear plastic tape was used to seal the indicator strip to the test rectangle, thus preventing ambient moisture from reaching the indicator and causing a false response. Table 3 shows the relative positions of the test strips and their moisture concentrations for the test plates in Figures 11 - 14.

Table 3. Relative Positions of Test Strips in Figures 11 - 14 and Their Moisture Concentrations.

| Relative Position and Moisture Concentration, % (Date of Preparation) | | | |
|---|---|---|---|
| 0<br>(4-27) | 3.53<br>(4-27) | 5.25<br>(4-27) | 9.02<br>(4-27) |
| 0<br>(4-28) | 3.53<br>(4-28) | 5.25<br>(4-28) | 9.02<br>(4-28) |

The test plate photograph taken on 5-1-92 (Figure 11) shows that in only 4 - 5 d the indicators mounted on the test rectangles containing 9% moisture have already begun to change. The difference in intensity of color development between the 4-27 and the 4-28 samples is probably due to different masses of cupric chloride impregnated in the indicator strips. The photo of 5-7-92 (Figure 12) shows that in 10 - 11 d the 5% moisture test squares are starting to change and that by 18 - 19 d, on 5-19-92 (Figure 13), all the strips have started color development. By 84 - 85 D of exposure, on 7-21-92 (Figure 14), all the indicators had completely changed indicating complete hydration of the cupric chloride. The response to the 0% moisture test rectangle suggests that either very small traces of moisture remained in the cellulose matts after drying, or, more likely, that the plastic tape outer cover has a very low permeability to moisture which permitted atmospheric moisture to diffuse into the strip.

The response of this design of the impregnated glass fiber indicator strip thus is a temporal function, in that the time required for color development indicates the moisture concentration

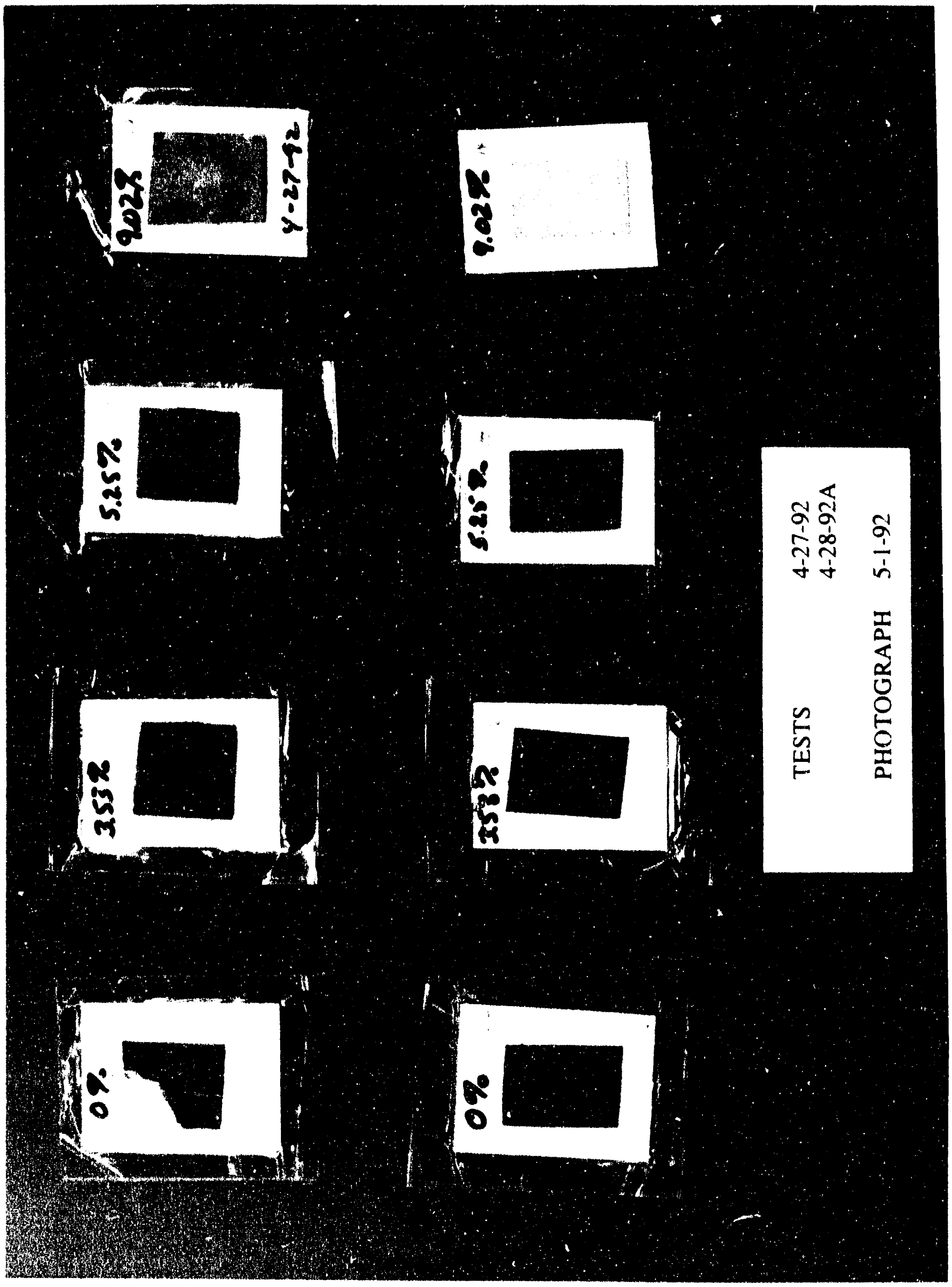


FIGURE 11. PHOTOGRAPH OF MOISTURE INDICATOR TEST PLATE AFTER 4 - 5 D OF EXPOSURE.

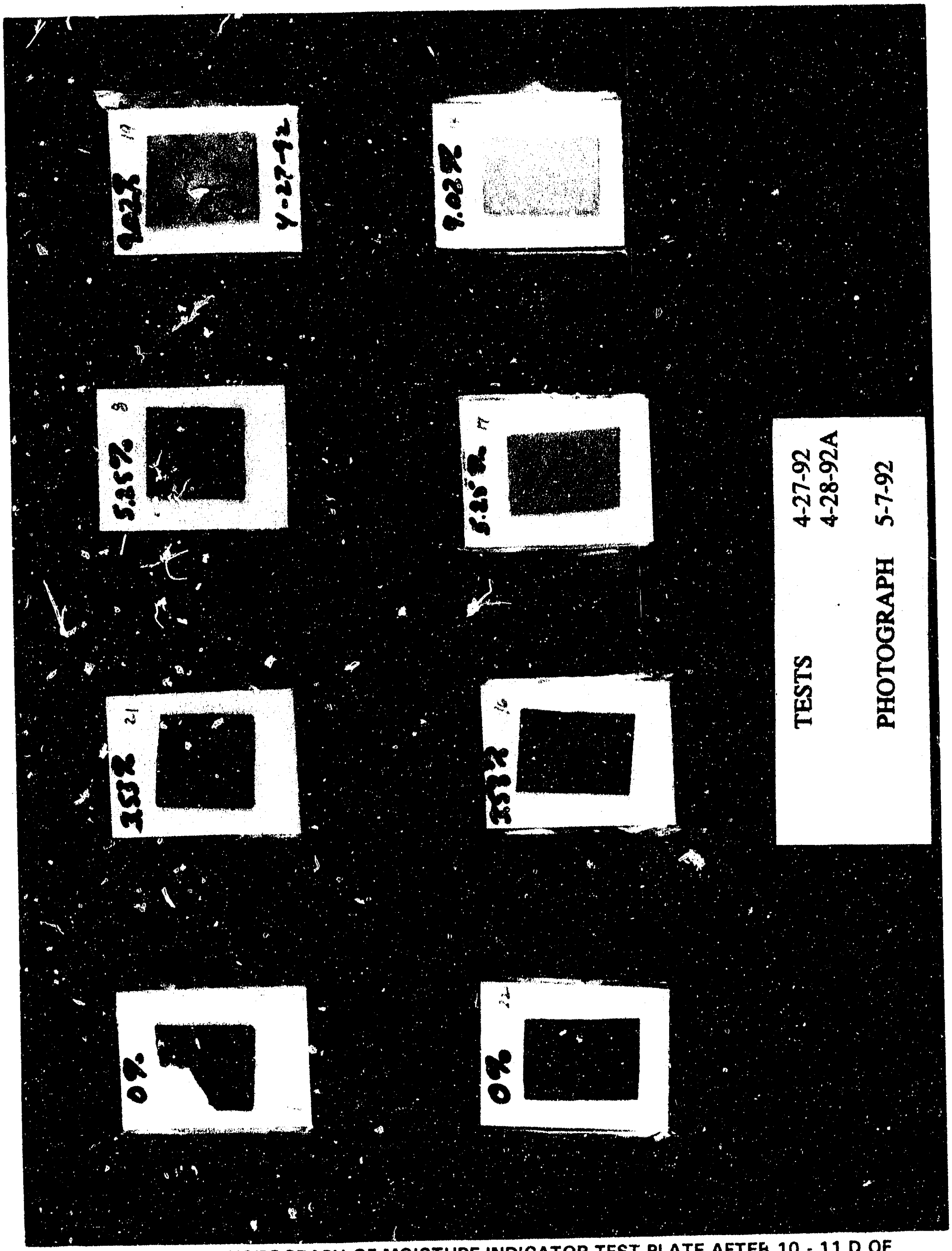


FIGURE 12. PHOTOGRAPH OF MOISTURE INDICATOR TEST PLATE AFTER 10 - 11 D OF EXPOSURE.

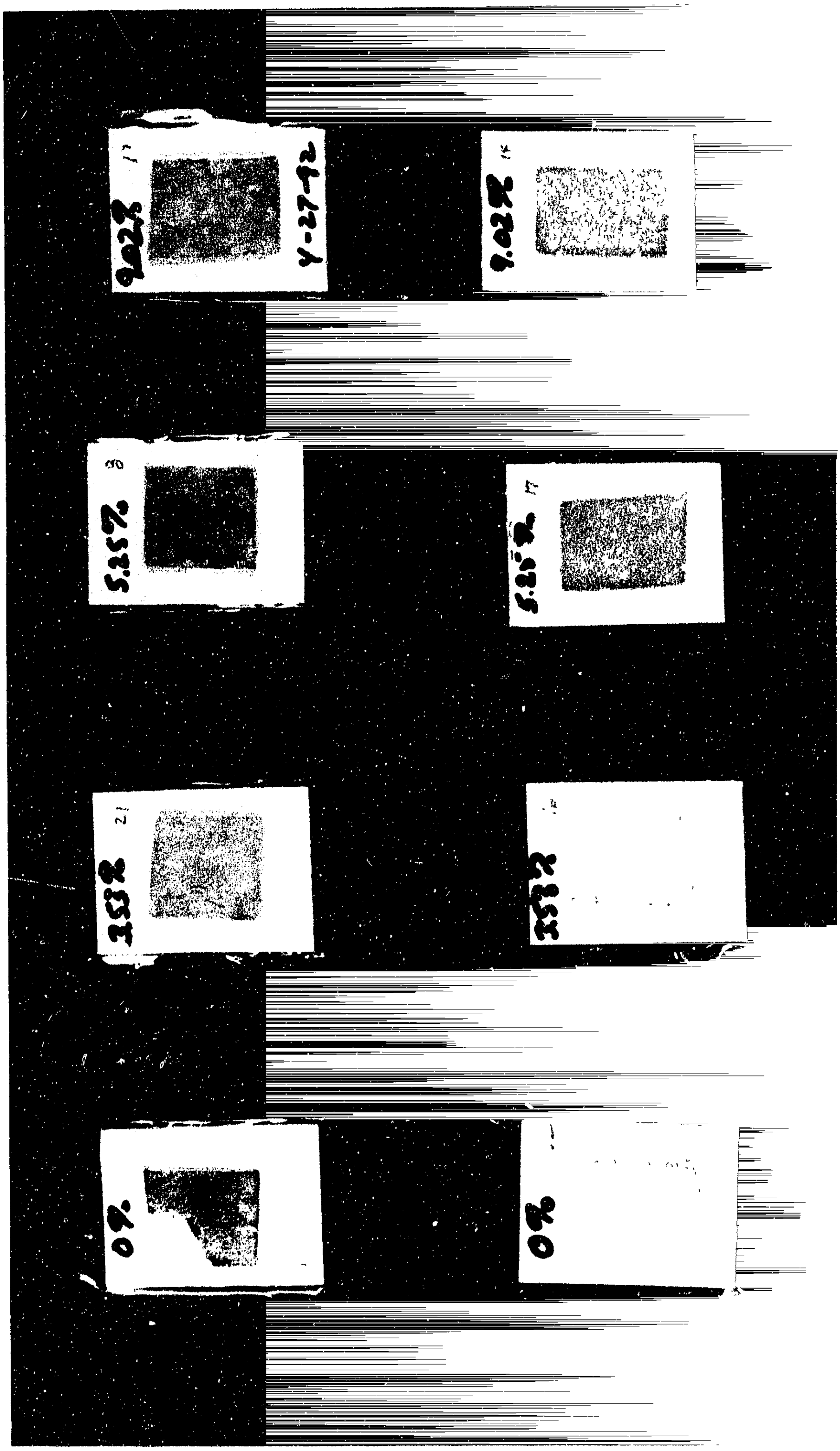


FIGURE 13. PHOTOGRAPH OF MOISTURE INDICATOR TEST PLATE AFTER EXPOSURE.

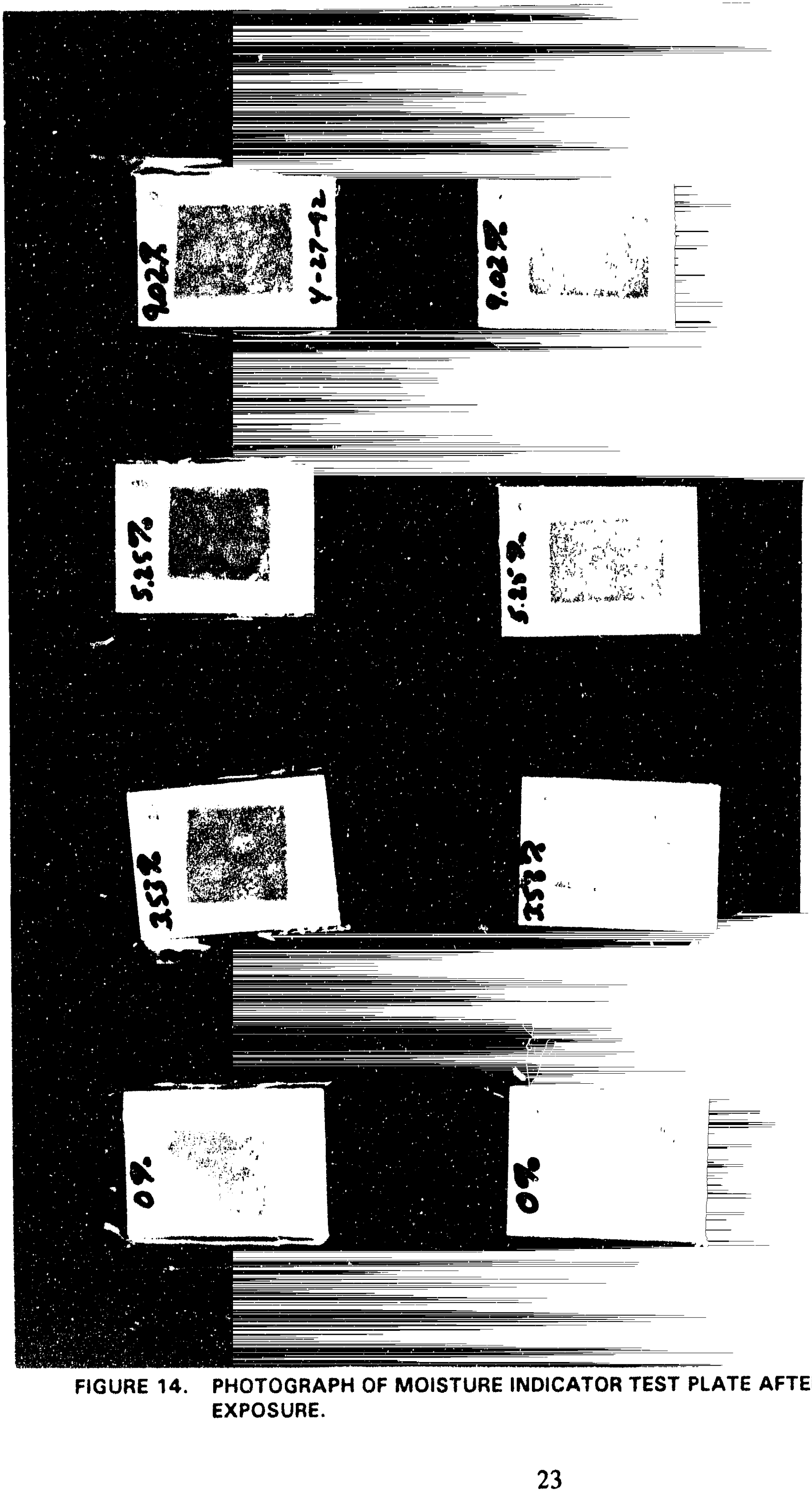


FIGURE 14. PHOTOGRAPH OF MOISTURE INDICATOR TEST PLATE AFTER 8
EXPOSURE.

of the test rectangle. Discrimination power appears to be limited to concentrations of moisture above ca. 5 to 9%.

**Performance of The Pelletized Indicator**

As noted above, the sensitivity of the impregnated glass fiber indicator led to the development of the pelletized indicator design. The indicator performance test was conducted similarly to that for the impregnated glass fiber indicator. Test squares of cellulose matting board were prepared by drying at 100°C and allowing moisture to be absorbed in the matting material. The mass change in the test square determined the moisture content. The test squares were then sealed in the 3M Highland Brand clear mailing tape. Pellets mounted in cardboard squares were sealed on the surface of the test squares immediately after holes were pierced in the test covering to permit moisture migration from the test square into the pellet. Table 4 shows the relative positions and moisture concentrations of the test strips.

Table 4. Relative Positions and Moisture Concentrations of Test Strips in Figures 15 - 17.

| Relative Position and Moisture Content, % | |
|---|---|
| 0 | 0 |
| 2.7 | 2.8 |
| 6.3 | 6.4 |
| 8.0 | 8.1 |

Photos taken of the test plates on 7-21-92, 8-4-92, and 8-20-92 are shown in Figures 15 - 17. By 5 d of exposure (Figure 15, 7-21-92), the indicators for the 8% and 6% moisture test squares have considerably changed, and the 0% and 2.7 % moisture tests showed no change. By 19 d of exposure (Figure 16, 8-4-92), the 6% and greater moisture tests showed nearly complete color change but the 2.6% or less moisture tests showed no change. By 35 d (Figure 17, 8-20-92) the 2.7% test showed only slight changes around the edges, which may not be readily visible in the photo. With longer exposure time, the color would be expected to develop. It is important to note that over the test period, the 0% moisture test square did not change color. The pelletized indicator thus appears to provide better performance than does the impregnated glass fiber indicator.

By controlling the pellet size carefully and empirically determining a time vs. moisture concentration factor this indicator technique could be used to determine the moisture concentration of a ccc wall casing. The polyurethane coating of the round would

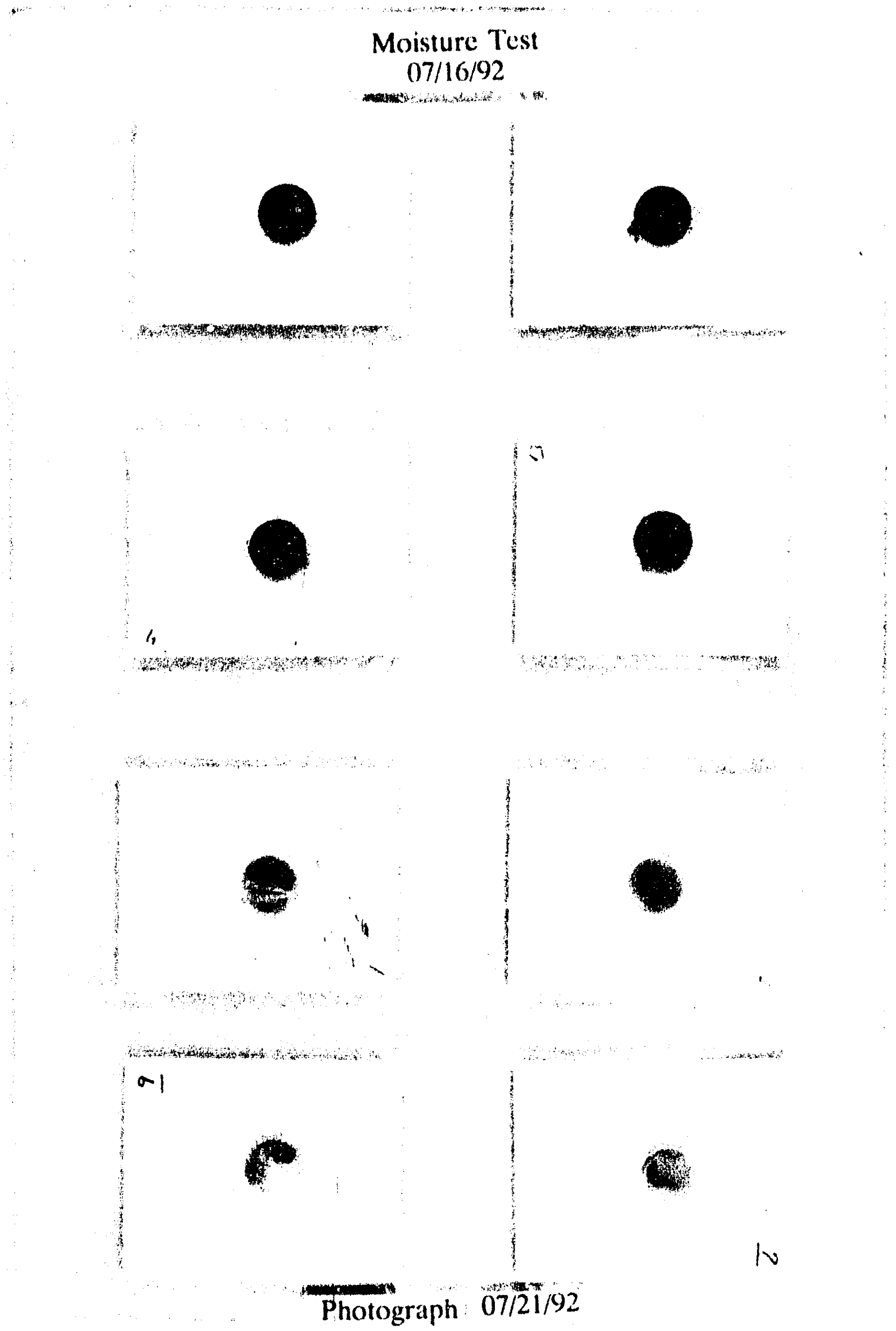


FIGURE 15. PHOTOGRAPH OF MOISTURE INDICATOR TEST PLATE AFTER 5 D OF EXPOSURE.

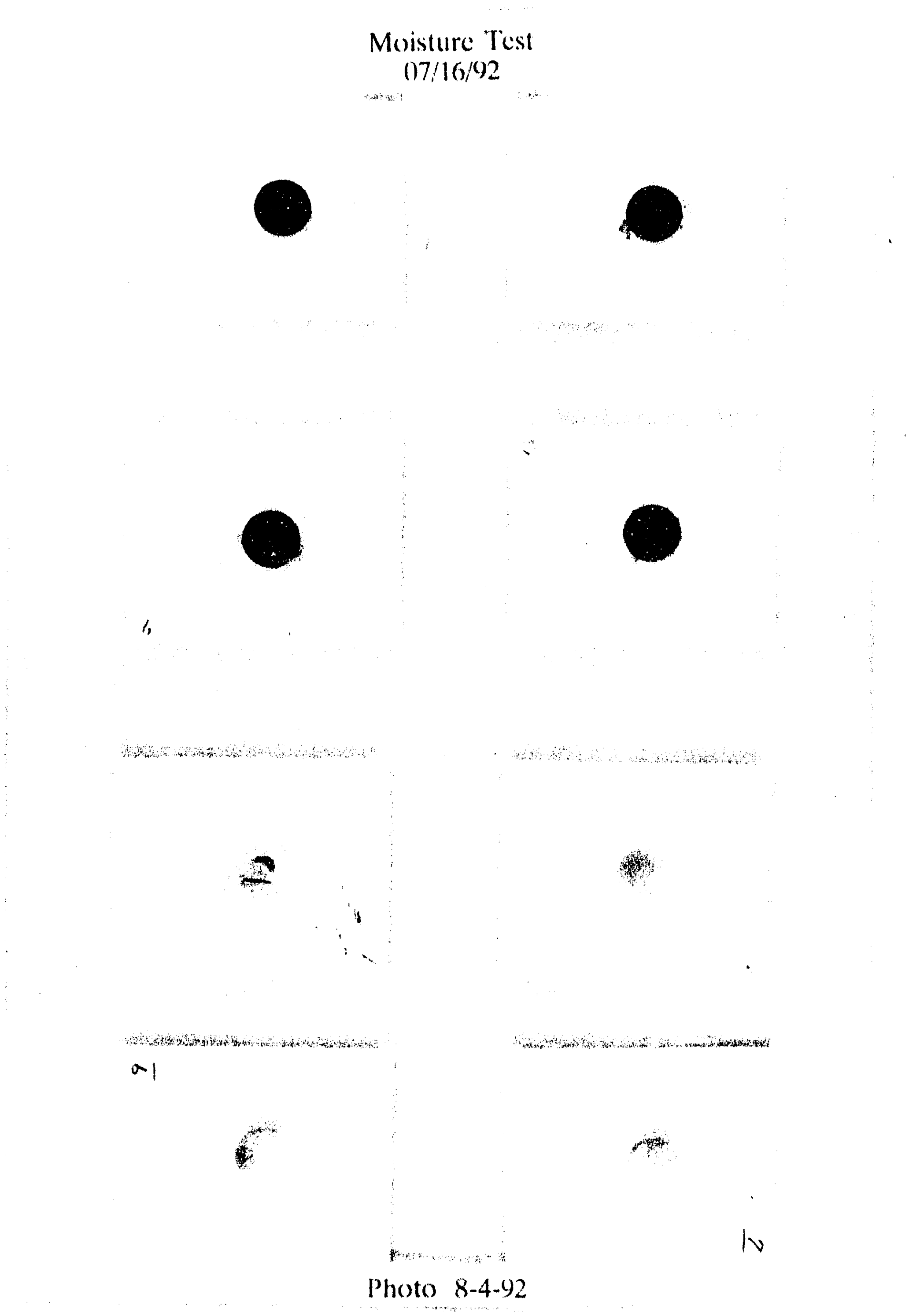


FIGURE 16. PHOTOGRAPH OF MOISTURE INDICATOR TEST PLATE AFTER 19 D OF EXPOSURE.

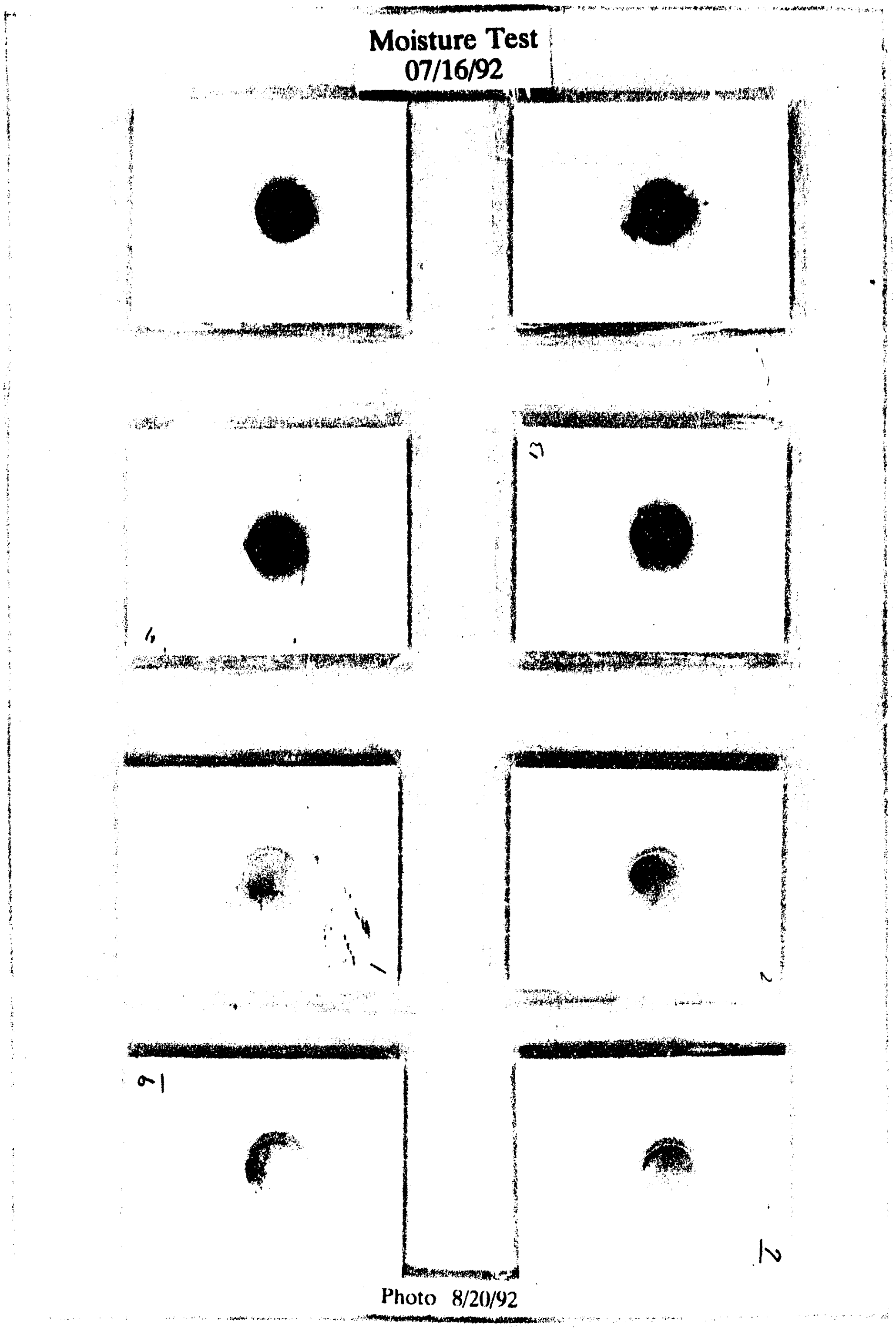


FIGURE 17. PHOTOGRAPH OF MOISTURE INDICATOR TEST PLATE AFTER 35 D OF EXPOSURE.

need to be pierced to permit moisture migration into the pellet. This indicator color change would not be reversible in this application as it would not be safe to heat the round to 100°C as is required to drive off the water of hydration in the hydrated cupric chloride.

## Conclusions and Recommendations

The pelletized indicator is a better design than is the impregnated glass fiber indicator. Both are limited at the present to short-term indication (ca. 1 month) if the moisture content of the test material is above ca. 6%. In its present state of development, the indicator also is not reversible on a practical basis. Clearly much additional development work would be necessary to improve its performance and to demonstrate its performance with actual ccc munitions. Some of the factors requiring work include development of a better potentiating barrier between the indicator and the ccc to increase the useful lifetime of indication, a more durable and less permeable outer covering, development of methodology to apply the indicator to a ccc, and calibration of the indicator response to the actual case wall moisture.

# MOISTURE DETERMINATION BY DIELECTRIC MEASUREMENTS

## Introduction

This chapter describes a preliminary evaluation of moisture determination in ccc munitions materials by measurements of the dielectric properties (capacitance) and conductivity (dissipation factor) or associated electrical impedance of the ccc as a function of frequency. The ultimate goal of this investigation was: (a) evaluation of commercially available portable instruments for non-destructive testing of ccc munitions for moisture accumulation, and (b) recommendation of instrument modifications needed for laboratory testing and field verification with munitions.

There is substantial technology available for moisture detection specifically by dielectric measurements. Advances in electronic instrumentation make this technology feasible and attractive for the application at hand. There are instruments available in the market which could be modified to make moisture detection in ccc munitions simple, easy, rapid, and inexpensive.

## Background and Approach

Moisture and its effects in the deterioration of the quality of materials and products have been extensively investigated. Moisture is classified as bound and free and can be specified by energetic, structural, or operational schemes, per Pyper et al. (7,8). Methods for distinguishing between bound and free moisture are: (a) dynamic dielectric thermal analysis, (b) microwave attenuation analysis, (c) near infrared reflectance analysis, and (d) nuclear magnetic resonance spectroscopy (9). The classification of moisture as free or bound is not precise.

Application of an electric field to a material results in electric charge separation known as electric polarization. Polarization is classified as: (a) electronic polarization, caused by the displacement of electrons with respect to the nucleus, (b) ionic polarization caused by the displacement of negative ions with respect to positive ions, (c) dipolar or orientational polarization, which takes place in materials, known as polar, that have permanent dipole moments, (d) interface polarization, which takes place in electrically heterogeneous materials and is caused by the charging of the interfaces within the material; thus it depends on the dielectric properties of the constituent materials, and (e) counterion diffusion polarization, caused by ionic diffusion in electrical double layers adjacent to charged surfaces; counterion polarization effects are surface phenomena.

The dielectric permitivity $\epsilon$, and conductivity $\sigma$ of a material are macroscopic quantities by which the electrical properties of materials are specified. These quantities depend on the frequency $\omega=2\pi f$ of the applied field and are typically presented as

$$\epsilon=\epsilon'-j\sigma/\omega\epsilon_0\equiv\epsilon'-j\epsilon'' \tag{1}$$

$\epsilon_o = 8.854 \times 10^{-12}$ F/m is the permitivity of free space. $\epsilon'$ represents the dielectric constant of the material and $\epsilon''$ represents the losses of the material. The losses of the material are typically expressed in terms of the loss tangent defined as

$$\tan\delta = \epsilon''/\epsilon' \tag{2}$$

Water (moisture) is a polar material which can exist in a material in the forms of bound, free, or water that has chemically reacted with the host material to produce a new substance. The detection of moisture in a material, via dielectric measurements, relies upon the difference of the dielectric properties of dry and wet material, induced by the presence of highly polarizable water molecules. Water detection in a material dictates that a measurement M can be expressed as a sum of

$$M(f) = M_m(f) + M_f(f) + M_b(f)\ . \tag{3}$$

$M_m(f)$, $M_f(f)$, and $M_b(f)$ are the dry material, free water, and bound water contributions, respectively; The chemically reacted water is neglected, if present it may change the properties of the material.

Analytical expressions of the dielectric permitivities of free and bound water have been developed and they are:

$$\begin{aligned} \epsilon_f'(\omega) &= 5 + \frac{75}{1+(6.3x10^{-11}\omega)^2}, & \epsilon_f''(\omega) &= \frac{4.7x10^{-9}}{1+(6.3x10^{-11}\omega)^2} \\ \epsilon_b'(\omega) &= 88 + \frac{.9}{1+(10^{-8}\omega)^2}, & \epsilon_b''(\omega) &= \frac{9.0x10^{-9}\omega}{1+(10^{-8}\omega)^2} \end{aligned} \tag{4}$$

The relative contributions of free and bound water to $\epsilon$ vary with frequency as follows (7),

$$\begin{array}{cc} \epsilon''/\epsilon' \approx constant/\omega & \omega \le 10MHz \\ \epsilon''/\epsilon' \approx \epsilon_m''/\epsilon_m' + \epsilon_f''/\epsilon_f' + \epsilon_b''/\epsilon_b' & 10MHz \le \omega \le 1GHz \\ \epsilon''/\epsilon' \approx \epsilon_f''/\epsilon_f' & \omega \ge 1GHz\,. \end{array} \tag{5}$$

These results are suitable for the evaluation of the dielectric losses (see Equation 8, later).

The experimental investigation in this project consisted of measurements of the variations of the capacitance and dissipation factor of ccc coupons and simulated rounds as a function of moisture content.

## Experimental

### Equipment and Materials

#### Instruments

The following instruments were used in the measurement of the electrical parameters of the cartridge simulators.

I#1. Hewlett Packard 4192A LF Impedance Analyzer. This is a main frame laboratory instrument suitable for different types of electrical network parameter measurements. This instrument was used to measure capacitances, dissipation factors and impedance as a function of frequency of the simulations to determine the optimum frequency for moisture detection.

I#2. B+K Dynascan corp. 830 Automatic Capacitance Meter. This is a hand-held battery operating instrument suitable for field type measurements. There are several low cost (about $100.00) instruments of this type in the market.

I#3. B+K Precision 875A LCR Meter. This is a hand-held battery operated meter suitable for field measurements. Its cost is $195.00, and measures electrical inductance, capacitance, resistance, and dissipation factor.

I#4. TRAMEX Moisture Encounter Model MF-1. This hand-held battery operating instrument provides non-destructive and non-invasive moisture detection in high electrical resistance materials such as wood, felt-roofing, plaster and brick. Appendix A is the operating manual of the instrument. Its cost is $325.00. The instrument detects moisture via measurement of the impedance of the material under test. The frequency of operation was measured to be about 12.5 kHz. Two flat rubber electrodes provide electrical connection between the instrument and the subject under test. Electrical connection is made by holding the instrument so that the rubber electrodes are in firm contact with the subject under test. Note that this instrument will provide a reading without physical contact because of capacitive coupling. Three different scales provide quantitative measurement of moisture content in timber and wood products, felt roofing, and plaster or brick. The instruction sheet for this instrument is shown in the Appendix.

#### Materials

Five ccc coupons (about 9.5 x 2.5 x 0.4 cm) left from the previous hardness and tensile strength test study were first chosen for moisture detection experiments, and instrument I#1 was used for those moisture content measurements.

Three simulated cartridge cases (inert cases) were provided by the Future Ammunition Rearm System group for moisture detection experiments. The shape and configuration of each case was different. Their material composition was different from real cases in that nitrocellulose was not present. The three cases are identified as C#1, C#2, and C#3. Case C#1 was devised as a capacitor by attaching heavy aluminum foil plates to its external walls. Electrical leads from these plates were provided for measurement of capacitance and dissipation factor or equivalent impedances with instruments I#1, I#2, or I#3. Cases C#2 and C#3 were used without modification for measurement of moisture with instrument I#4.

## Measurements

Measurements were conducted on both coupons and simulated cartridge cases (inert cartridge cases).

a. Coupon measurements. Coupons were sandwiched between copper plates to simulate parallel plate capacitors. The assemblies or devices were held together by insulated metallic binding clips. The objective of the procedure was to provide non-destructive and non-invasive tests. A total of five devices ("devices #1 - #5") were constructed and measured using the Hewlett Packard 4192A LF Impedance Analyzer (I#1). The frequency range of measurement was 1KHz-to-13MHz. The capacitance C and dissipation factor $D=\omega CR \approx \omega\epsilon_0\epsilon'/\sigma$ were measured as a function of frequency.

b. Soft Wood Measurements. A crude capacitor simulation of the cartridge was devised as follows. Soft wood was used as the core material, a 2000 mm Pyrex beaker was used as a shell, and heavy aluminum foil was attached on the external walls of the beaker to simulate the metal plates of the capacitor. The premise was that the soft wood will absorb and desorb moisture in a manner similar to the real cartridge. Capacitance measurements were made on the Hewlett Packard 4192A LF Impedance Analyzer. The wooden cylinders, 124 mm diameter x 180 mm high, were fabricated from kiln-dried yellow pine, and were designed so they could be easily inserted and removed from the beaker. This wood has a typical specific gravity of 0.53 and a moisture content of 13.8% (10). The moisture content of wood changes with atmospheric conditions. For this experiment, the wooden cylinders were subsequently exposed to dry air and then room air (RH ≈ 50%). The objective was to demonstrate the feasibility of detection of the change of the moisture content of wood via measurements of the change of the capacitance of the configuration.

c. Simulated Cartridge Case Measurements. Several experiments were made on the three simulated cartridge cases C#1, C#2, and C#3. For greater ease in explanation, the experimental parts of these cartridge measurements are included in the results and discussion section.

## Results and Discussion

### Coupon Study

#### Dry Measurements

The capacitance of all devices monotonically decreased with frequency. The dissipation factor measurements exhibited nonuniform variations, including the phenomenon of hysteresis with frequency. Because of time limitations and the crudeness of the experiment, no attempt was made at this stage to explain these variations on a physical basis.

#### Wet Measurements

The variations of the capacitance (C) and dissipation factor (D) with moisture are demonstrated with results from device #5. C and D were measured with the device dry, and the results are shown in Figures 18 and 19. Then the device was immersed in water for about 20 h. Starting an h after removal from the water, measurements of C and D were made every h for 8 h at the frequency $f = 1$ MHz, with results shown in Figure 20. Seven hours after removal from the water, measurement of C and D were made as function of frequency, and the results are shown in Figures 18 and 19, along with the dry measurements. Peculiarities were noticed in the frequency range between 1 kHz and 10 kHz; these results are shown in an expanded scale in Figure 21.

It is seen that both C and D increase with moisture, and that the changes are largest at low frequencies. The maximum change in C was 775% at $f = 1$ kHz, and the minimum was 9.3% at $f = 13$ MHz. The changes in D were much larger: a maximum of 3250% at $f = 5$ kHz, and a minimum of 95% at $f = 13$ MHz. In addition, there is a "peak" in the graph of D, Figure 21. Such "peaks" are attributed to the presence of bound moisture in the material (11). More measurements of C and D were taken later, which demonstrated that the device recovered to its dry state (see Figure 20).

No attempt was made at this time to provide any physical explanation of these results. However, the results appear to have similar variations with frequency with those reported for moisture in triaminotrinitrobenzene (TATB) (7), Figure 22, obtained from measurements of the dielectric constant as a function of frequency.

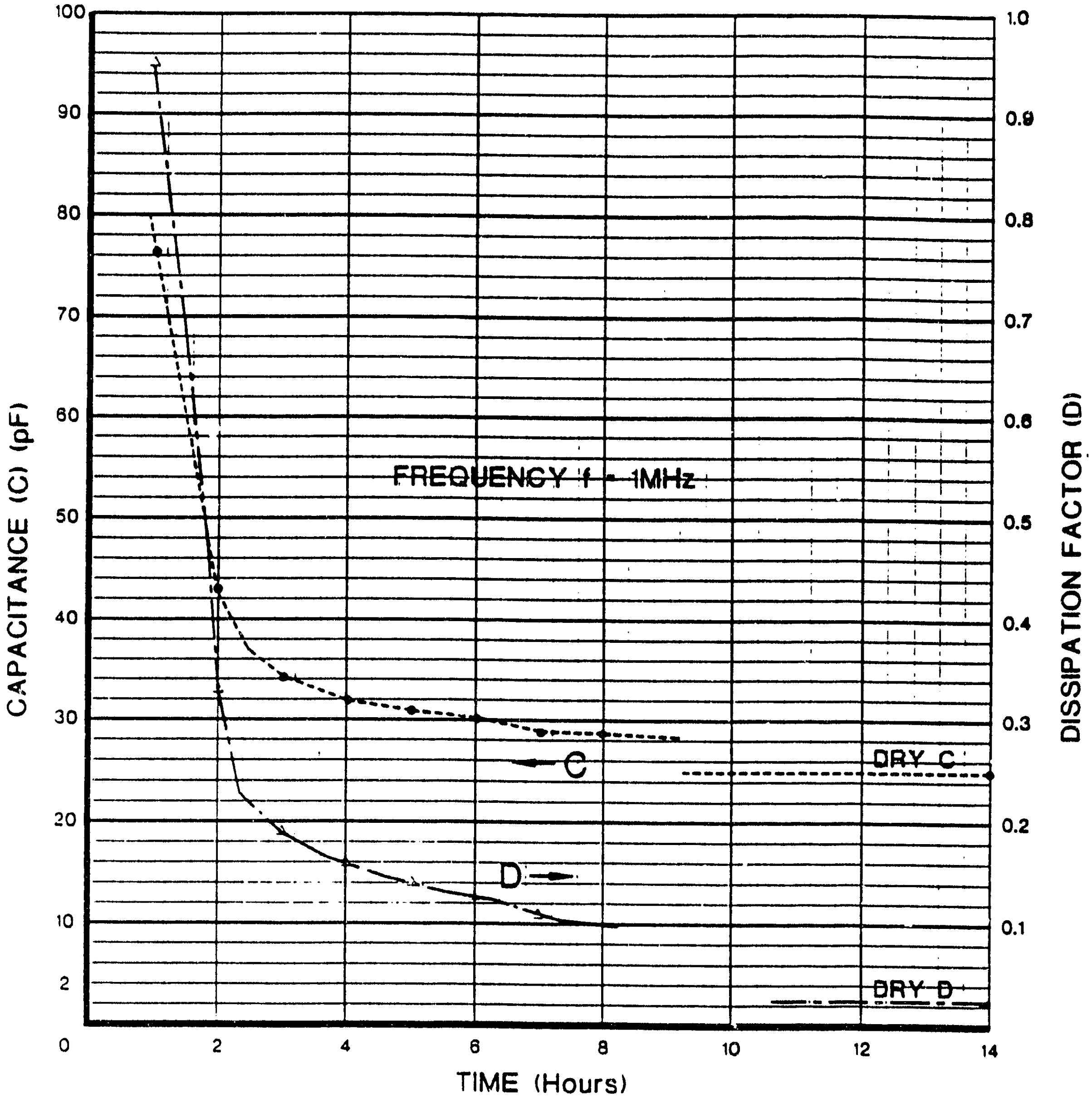


FIG. 18 CHANGE OF CAPACITANCE (C) AND DISSIPATION FACTOR (D) OF DEVICE #5 AS A FUNCTION OF TIME, AFTER REMOVAL FROM THE WATER BATH, AT t=0

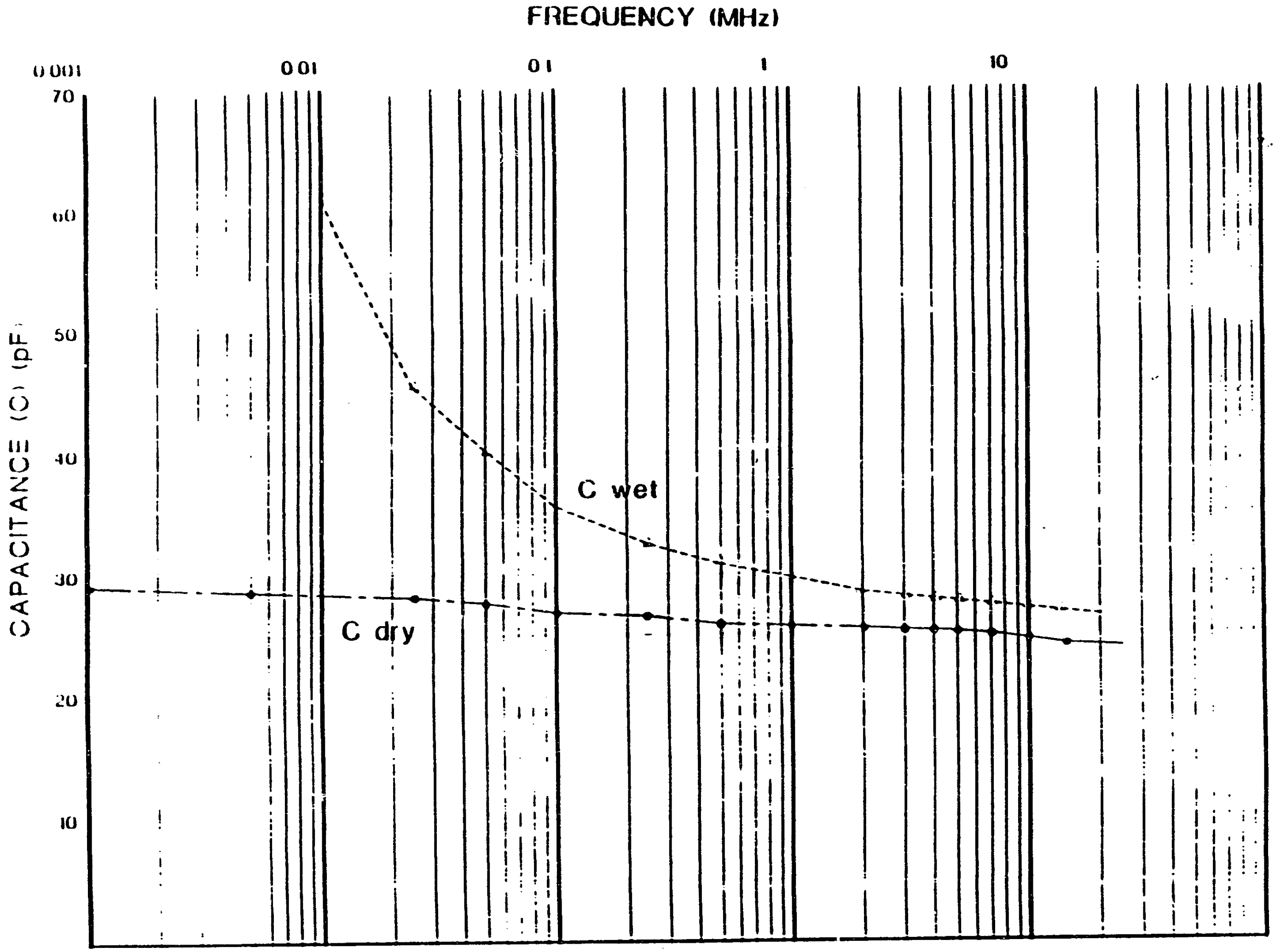


FIG. 19 CAPACITANCE vs FREQUENCY OF DEVICE #5, DRY AND SEVEN HOURS AFTER REMOVAL FROM THE WATER BATH

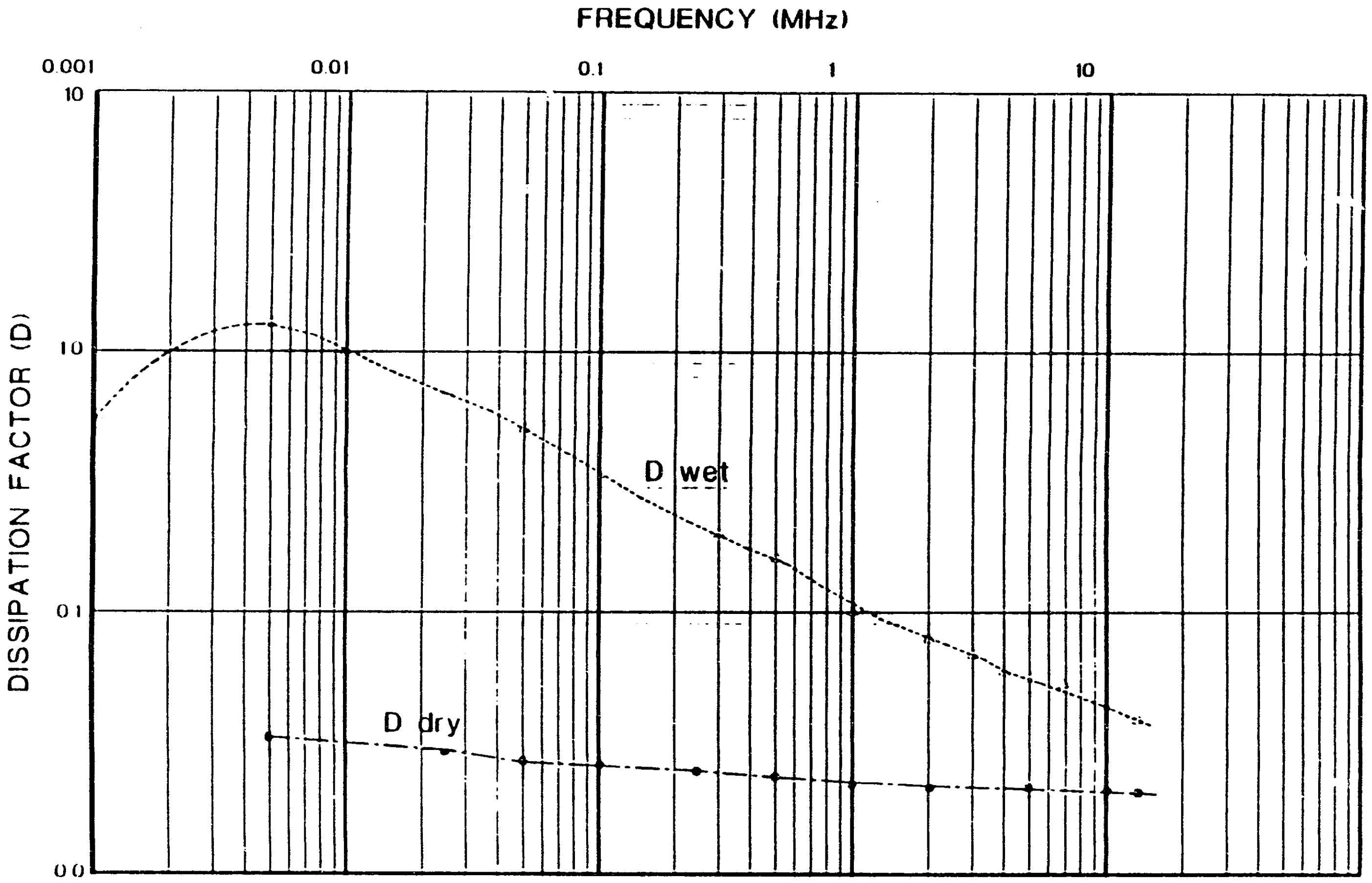


FIG 20. DISSIPATION FACTOR vs FREQUENCY OF DEVICE #5, DRY AND SEVEN HOURS AFTER REMOVAL FROM THE WATER BATH

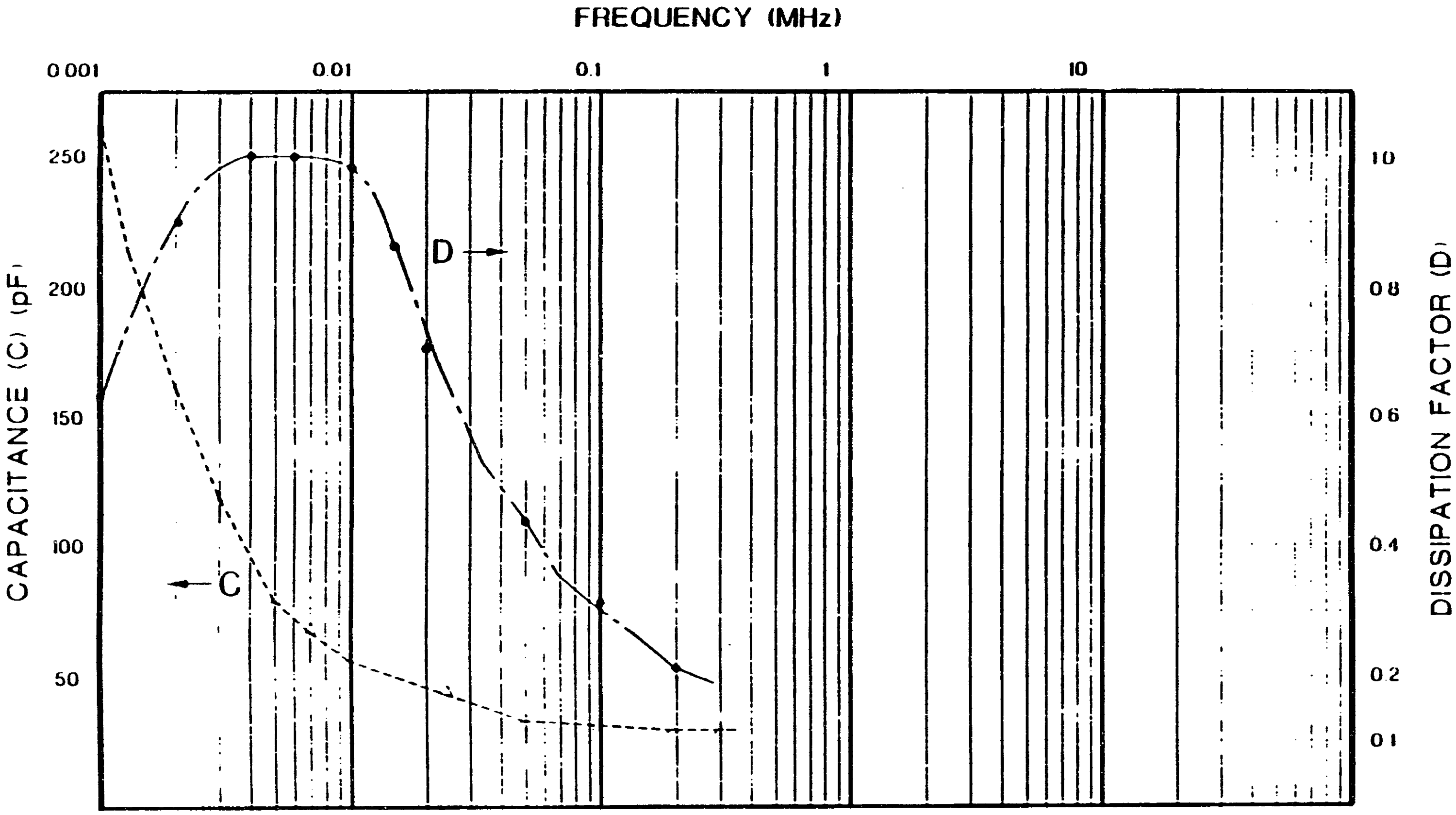


FIG. 21 CAPACITANCE (C) AND DISSIPATION FACTOR (D) vs FREQUENCY OF DEVICE #5 SEVEN HOURS AFTER REMOVAL FROM THE WATER BATH

## Soft Wood Study

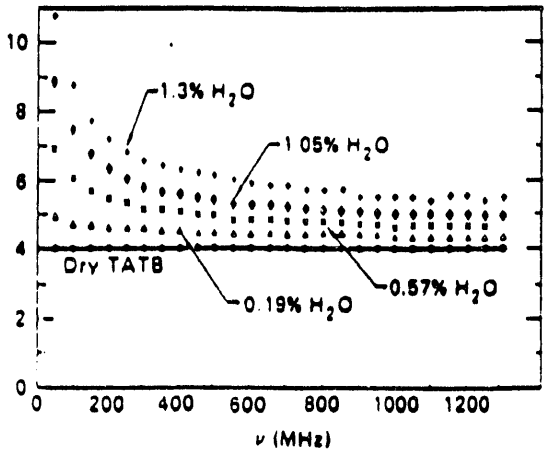
The weight of the cylinder at room air was 1149 g, and the water content (13.8%) was 158.56 g. After several days in dry air the weight of the cylinder was 1128 g, and the water content was about 137.6 gm, a reduction of about 13%. The capacitance measurements were made at the frequency f = 4 MHz. The capacitance of the empty beaker was 15 pF (picofarads). The capacitance with the dry cylinder inserted was 20.45 pF. After the cylinder was exposed to room air for about 24 h, the capacitance was 21.6 pF. Thus, the capacitance change of the whole configuration due to room air moisture was 1.15 pF or 5.6%. This is smaller than the 13% change in moisture obtained from weight measurements. This difference can be explained as follows. The total capacitance C of the simulator consists of the series connection of the capacitance of the glass walls $C_g$, the capacitance of the air layer between the glass and the wood $C_a$, and the capacitance of the wood $C_w$. Thus, the capacitance of the simulator C is

$$\frac{1}{C}=\frac{1}{C_g}+\frac{1}{C_a}+\frac{1}{C_w} \tag{6}$$

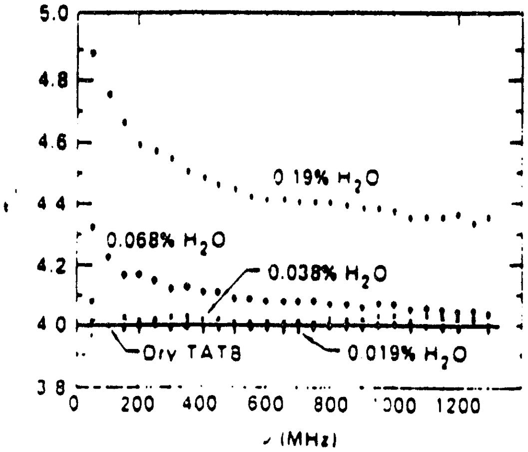
Taking the differential of this equation, the expression of the relative change of $C_w$, in terms of the relative change of the measured capacitance C, is

$$\frac{\Delta C_w}{C_w}=(1+\frac{C_w}{C_a}+\frac{C_w}{C_g})\,\frac{\Delta C}{C} \tag{7}$$

It is seen that the relative change of $C_w$ is larger than the relative change of the measured capacitance C, and depends on the values of the capacitances of the simulator. The dissipation factor of the simulator was not measured in this experiment.



Plots of $\epsilon'_{TATB}$ vs. frequency at higher % $H_2O$ showing low frequency effect



Plot showing detection limit of 0.04% $H_2O$ in TATB

**Figure 22. Dielectric constant vs frequency. Source: Pyper (7).**

## Simulated Cartridge Study

### A. C#2 Measurements

Case C#2 data: height 48.5 cm, diameter 15 cm, mass (dry) 679.5 g. Moisture content (dry) reading ≈ 10% (bottom of scale). All moisture measurements on C#2 were made using the Tramex moisture encounter (I#4) on Scale #1. Visual inspection revealed that C#2 is made up of two visually different sections glued together. No information is available at this time on the material composition of C#2, but we believe that they are wood fiber analogs of the wood fiber/nitrocellulose used in actual ccc munitions.

C#2 was filled with water for about 24 h. Then the water was removed and the moisture content was evaluated by weight measurements. The maximum amount of water absorbed was 75.3 g. or ≈ 11.1% of the mass of C#2. Subsequently, C#2 was exposed to the ambient room environment to dry for several days. During this time the moisture content of C#2 was recorded from measurements by weight and by I#4. The results are depicted in Figure 23. The plot indicates that the moisture content of the two section of C#2, as recorded by I#4, are not the same. In addition, readings of I#4 varied along the height and the periphery of both sections. The latter indicates that water is not uniformly absorbed in the walls of C#2, therefore, the composition of C#2 probably is not uniform. This could be due to an uneven distribution of additive in the case wall.

Because the rubber electrodes of I#4 are configured in a flat plane and the surface of C#2 is cylindrical, complete contact of the electrodes with the surface of C#2 during the measurements was impossible. In fact, even partial contact was possible only with I#4 oriented along the height of C#2. Thus, no quantitative absolute meaning can be attached to the moisture readings on the scale of the I#4.

### B. C#1 Measurements

Four sets of experiments were conducted using C#1.

1. C#1 Tests of Different Meters. C#1 data: height 46.5 cm, diameter 15 cm, mass (dry, including the attached electrodes) 599.6 g. The C#1 configuration was assembled for measurements with instruments I#1, I#2, and I#3. All these instruments are designed to measure the capacitance of electronic components, which are typically low loss and reasonably linear, and frequency independent devices. The capacitance of the configurations of C#1 described below varied with frequency and, thus, was not linear. It was noticed that the capacitance readings of the three instruments were substantially different. Eventually, instruments I#2 and I#3 stopped functioning all together. It was concluded, therefore, that instruments I#2 and I#3 are not suitable for measurement of capacitance, as a means of moisture detection, without major modifications.

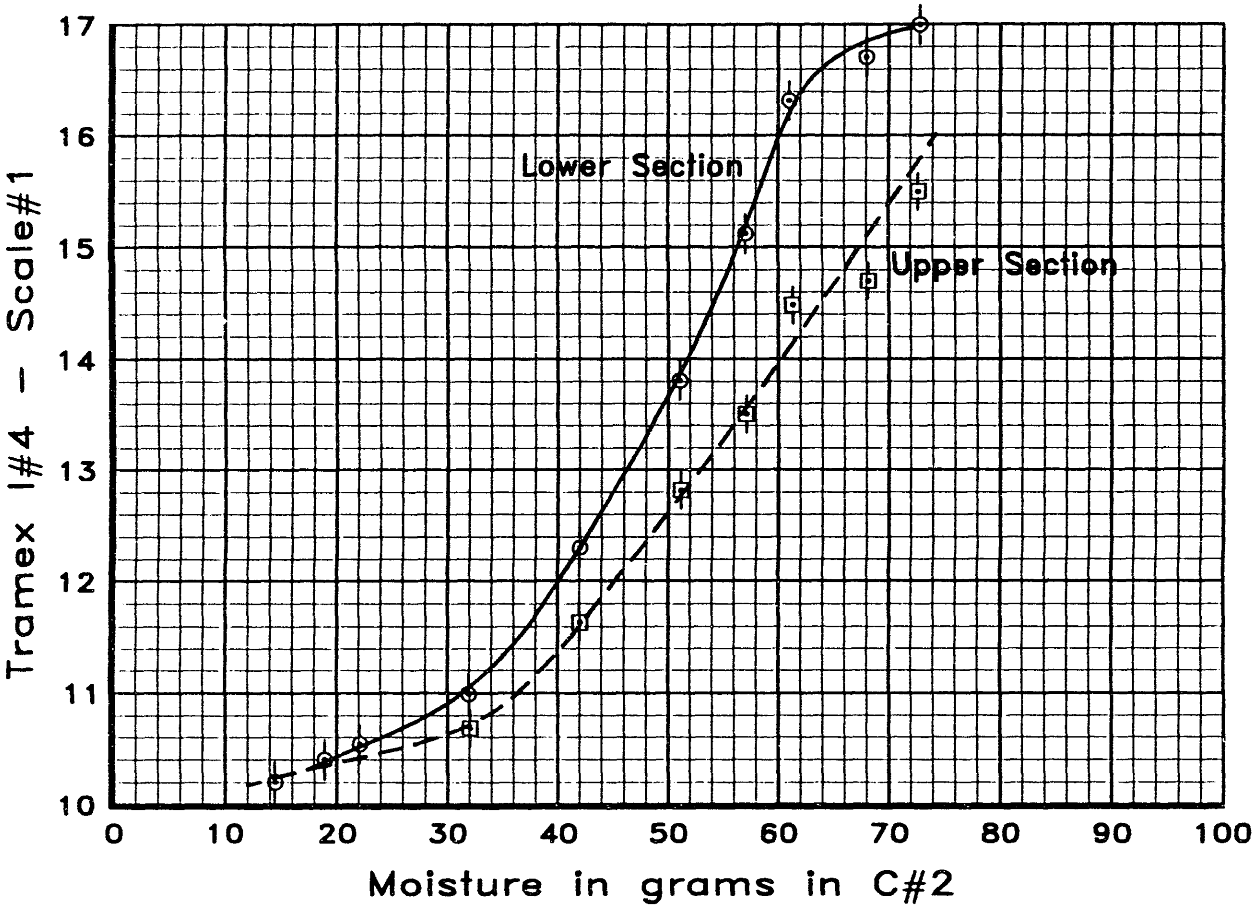


Fig.23 Moisture Detection Using Tramex I#4 – Scale #1 vs Moisture in Grams in C#2

2. C#1 and Soft Wood. The variations of the capacitance C and dissipation factor D with frequency of C#1 empty, were measured using I#1. The results are plotted in Figure 24. Then the soft wood (dry) cylinder was inserted in the center of C#1, and the C and D of this assembly was measured. The results are plotted in Figure 25. As seen from Figures 24 and 25, there are only slight changes in C and D due to the insertion of the wooden cylinder. Subsequently, the wooden cylinder was immersed in water for several days. The weight of the wooden cylinder was 1392 g dry , and 1751 g wet, thus, the water absorbed was 359 g. The wet cylinder was reinserted in C#1 and allowed to dry in the room environment for several d. During this time C and D of the assembly were measured with I#1 at the frequencies of 1 kHz, 10 kHz, 100 kHz, 1 MHz, and 10 MHz; the results for f = 1 kHz, 10 kHz, and 100 kHz are depicted in Figures 26 and 27. The relative changes of C and D at f = 1 MHz and f = 10 MHz were too small to be significant.

   It is seen from Figures 26 and 27 that the changes in C and D were larger at lower frequencies relative to the changes at higher frequencies. The initial values of C and D were small then increased with time to peak values at 5 d and eventually decayed to the dry condition values. The moisture was initially concentrated in the wooden cylinder. As the cylinder dried the moisture migrated to the walls of C#1 where it was absorbed. Thus, during the early days of the experiment the moisture concentration in the cylinder was decreasing , while the moisture concentration in the case wall of C#1 was increasing. Eventually the moisture concentration of the whole assembly decreased to the dry levels. It appears therefore that the variations of C and D follow the moisture concentration in the walls of C#1 rather than the moisture levels in the cylinder. This is in agreement with the results of Figures 24 and 25, which indicate that the most significant contribution to C and D comes from C#1 itself and not the material it contains. The measurements thus appear specific to the case wall.

3. C#1 Filled with Sawdust. C#1 was filled with sawdust and the weight changed from 599.6 g to 1897 g. The moisture content of the sawdust was measured with I#4 (Scale#1) to be about 10%. C and D of the configuration was measured with I#1 in the frequency range of 1 kHz to 10 MHz. The results for the capacitance change are shown in Figure 28. Similar relative changes were found for the dissipation factor D. Comparison of the C and D values with the corresponding C and D values of the empty C#1 revealed that the changes were small. The latter supports the previous observations that the most significant contributions of C and D come from C#1 itself. Subsequently the configuration was enclosed in a high moisture environment for several days in order to absorb moisture. The mass increased from 1897 g to 1912.3 g for a change dW = 24.3 g. Measurements of C, D, and dW were made for several days at the frequencies of 1 kHz, 10 kHz, 100 kHz, 1 MHz, and 10 MHz. The changes were small. For example, at f = 1 kHz, C changed from 59.6 pF dry (dW = 0) to 73.4 pF for dW = 24.3 g, to 67 pF for dW = 16 g. The drying process was very slow and the experiment was terminated at this point.

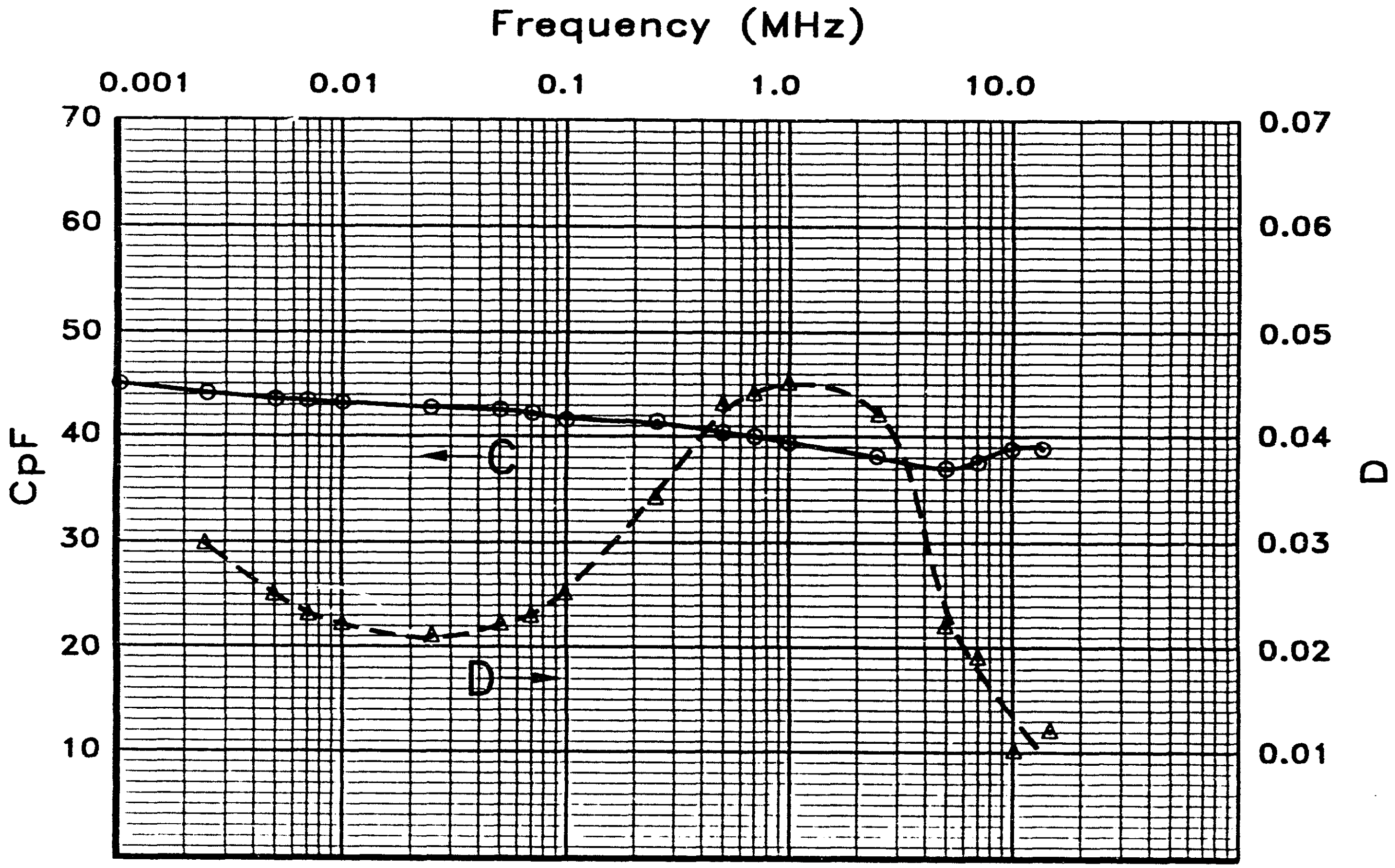


Fig. 24 Capacitance (C) and Dissipation Factor (D) of C#1 Empty as a Function of Frequency

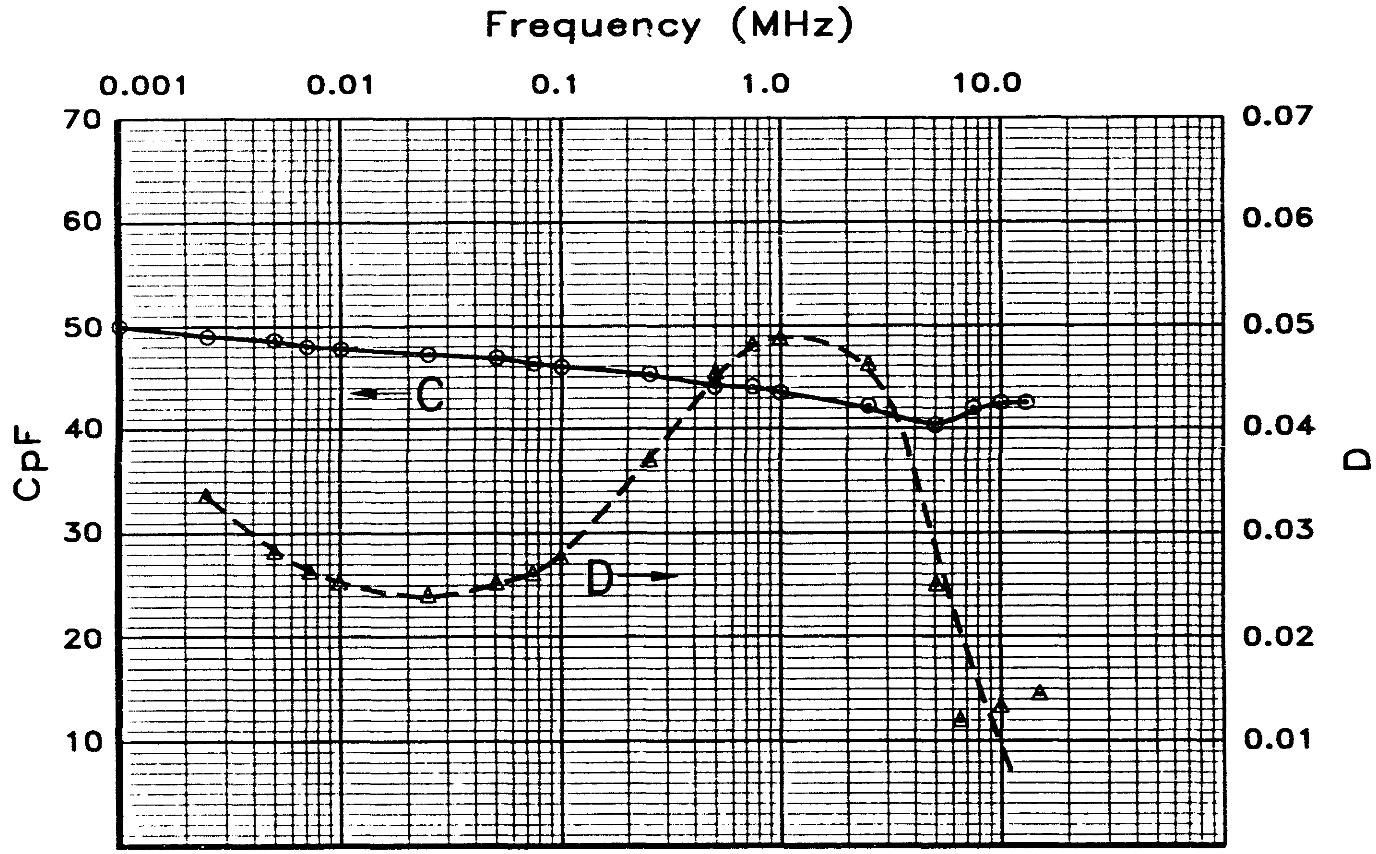


Fig. 25 **Capacitance (C) and Dissipation Factor (D) of C#1, with Wooden Cylinder Inserted, as a Function of Frequency**

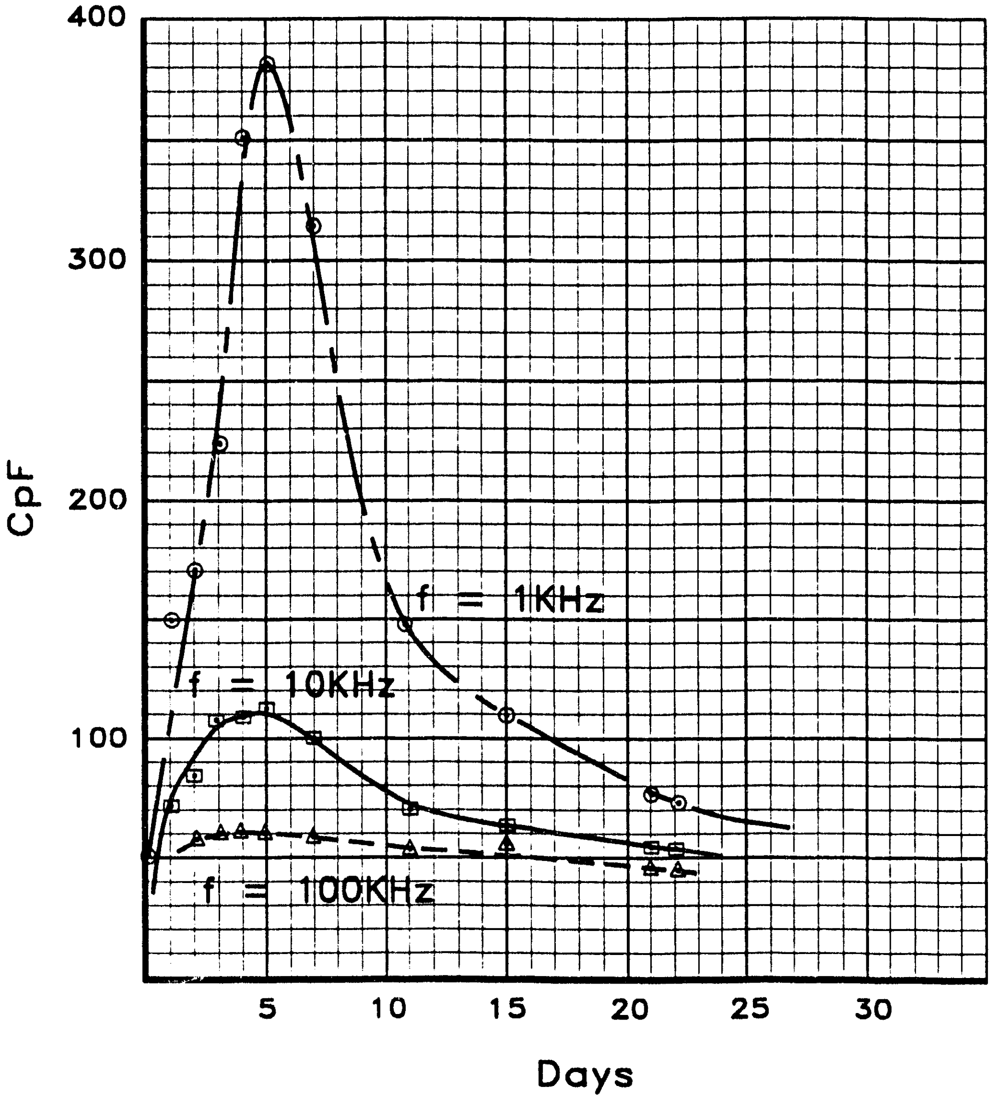


Fig. 26 Variation of Capacitance (C) vs Time of C#1 with Wet Cylinder at its Center

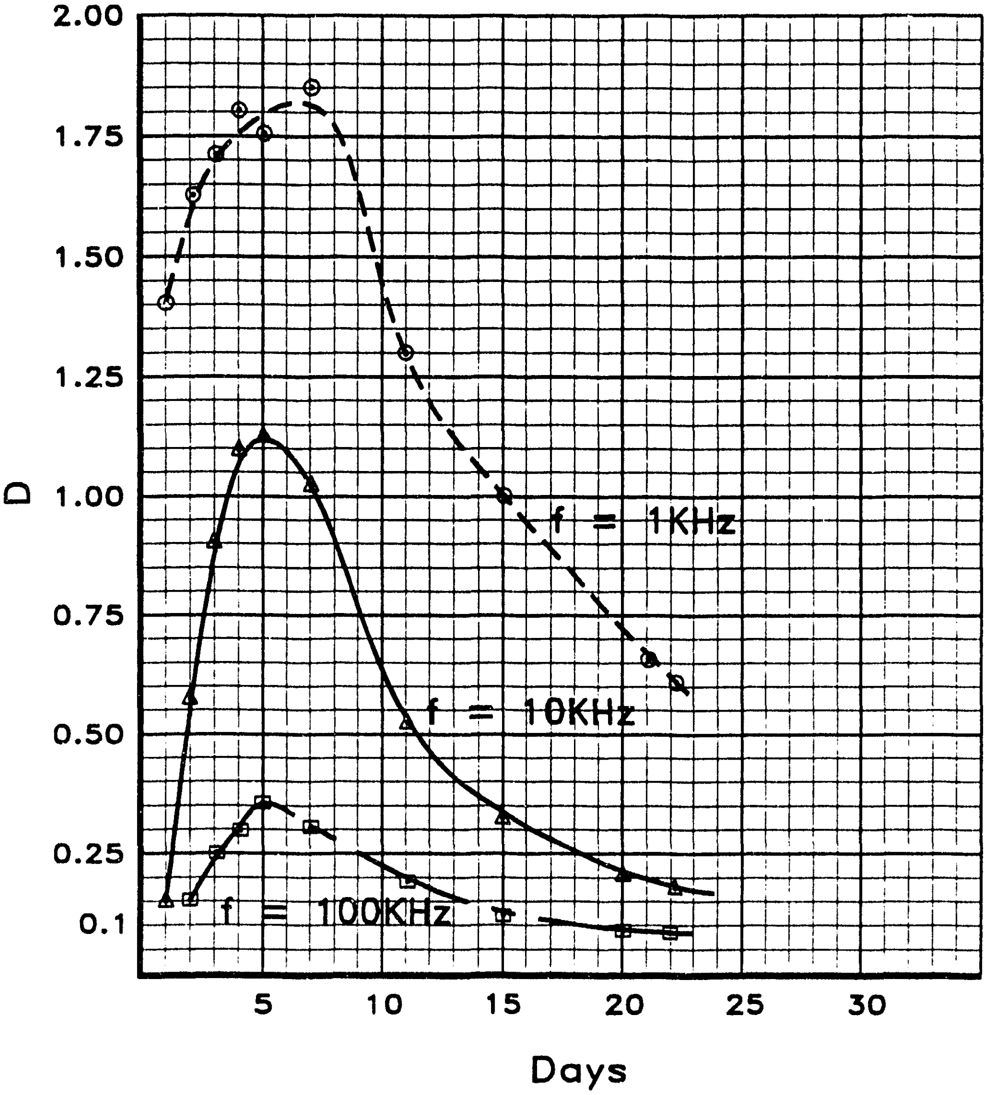


Fig. 27 Variation of (D) vs Time of C#1 with Wet Wooden Cylinder at the Center

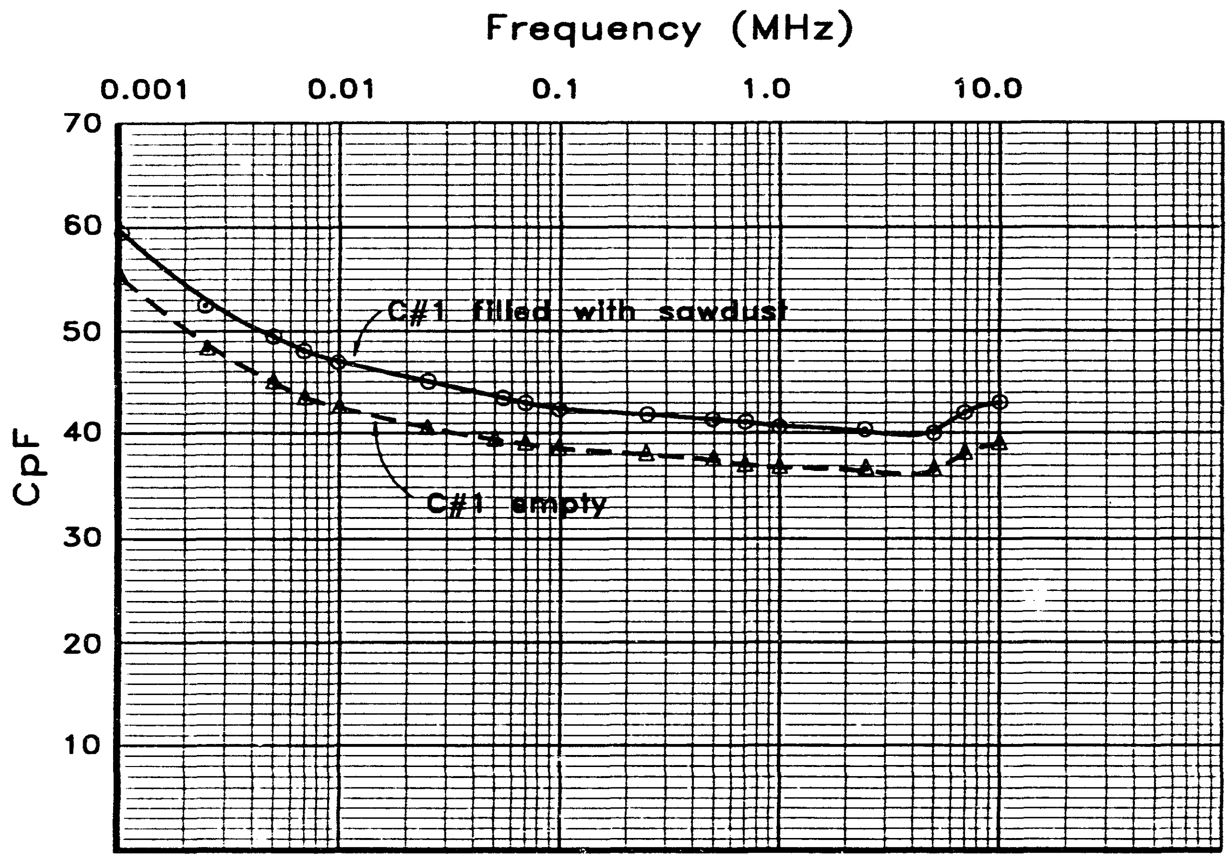


Fig. 28 Variations of the Capacitance with Frequency for C#1 Empty and C#1 Full of Dry Saw Dust

4. C#1 Filled with Wet Sawdust. Subsequently, C#1 filled with sawdust was flooded with water and was allowed to dry. During the drying period the capacitance and impedance of the configuration alorg with the water content was measured. At the start of the measurements the mass of the configuration was 4807 g. Thus, the excess water from the flooding was dW = 2.91 kg. The results of these measurements for the duration of about five weeks are shown in Figures 29 and 30.

Figure 29 depicts the change of capacitance as a function of excess water content at the frequencies of 1 kHz, 10 kHz, 100 kHz, and 1 MHz. These results show that the capacitance increases as the water content increases. The relative changes of the capacitance are larger at lower frequencies. For example, at dW = 2.91 kg, the ratios of the wet to dry capacitances ($C_{wet}$ / $C_{dry}$) were: 70000 at 1 kHz, 7900 at 10 kHz, 810 at 100 kHz,and 73 at 1 MHz. Similar measurements were made of the dissipation factor D. The D measurements showed some erratic variations with water content.

Figure 30 shows the variation of the magnitude of the impedance of the configuration as a function of frequency, with water content as a parameter. These measurements indicate that the impedance variations with water content are more uniform with frequency than the capacitance variations (Figure 29). The latter results suggest that the frequency of operation of a moisture instrument based upon impedance may not be as restricted for capacitance measurements.

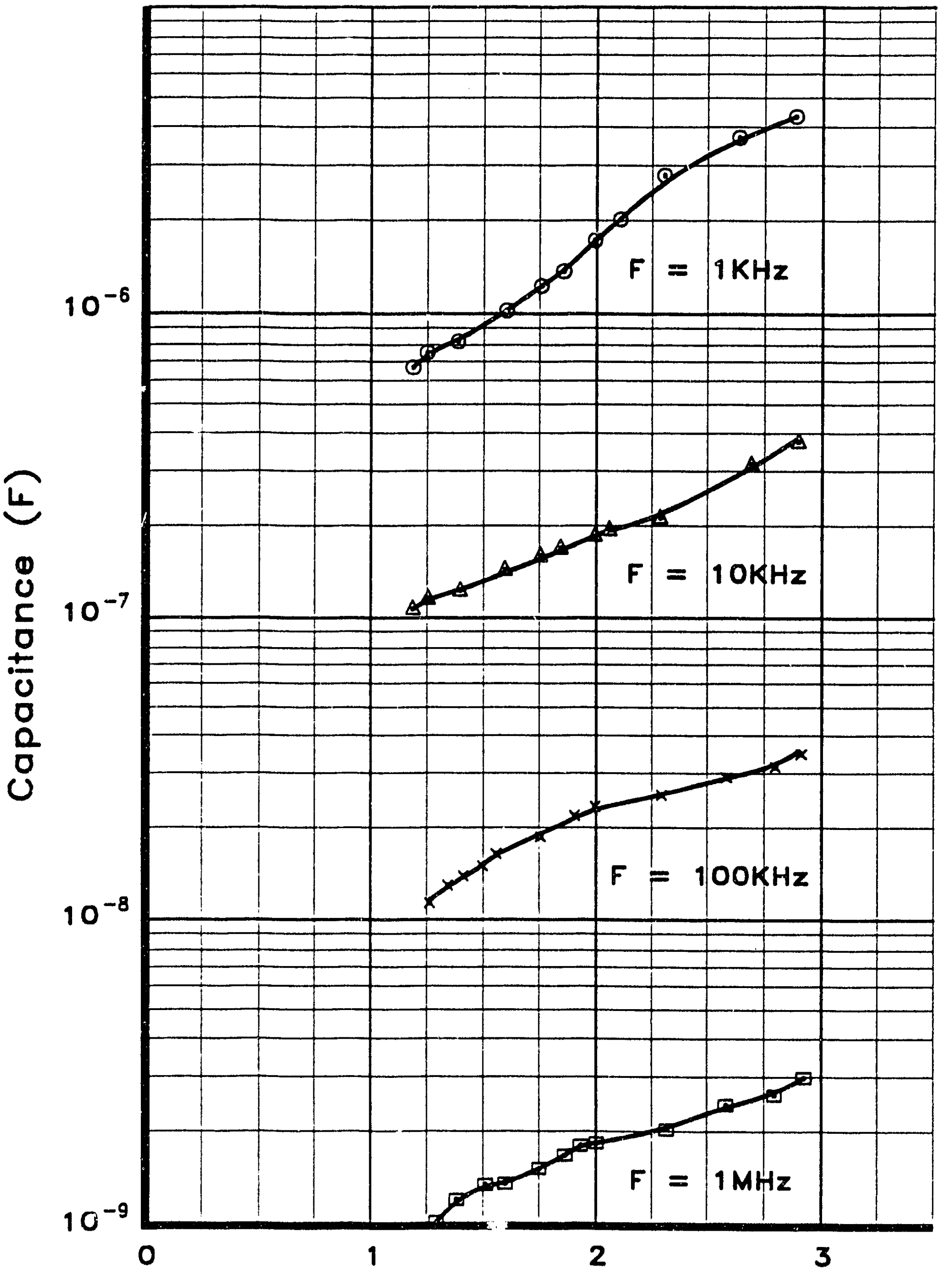


Fig. 29 Capacitance (C) vs Excess Water (dW) with the Frequency (F) as a Parameter

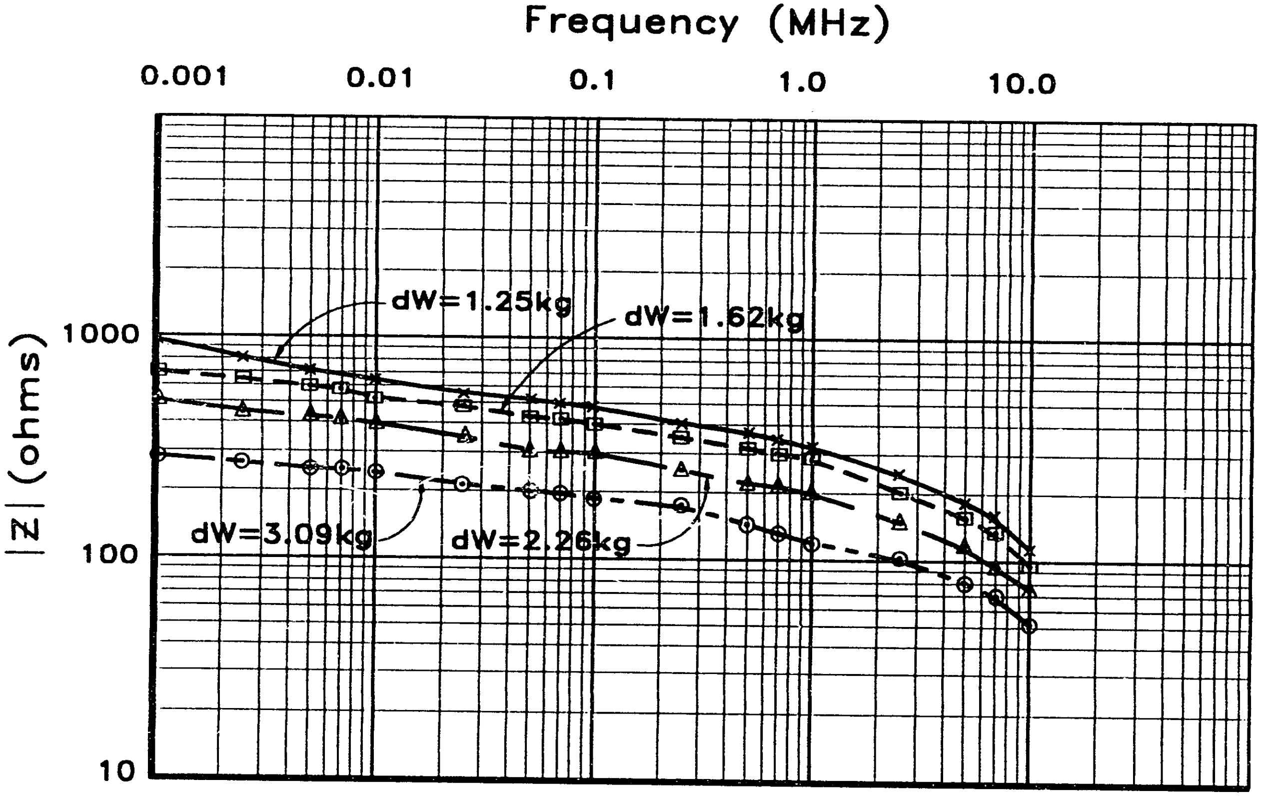


Fig. 30 Magnitude of the Impedance vs Frequency with Excess Water (dW) as a Parameter

### C. C#3 Measurements

Two experiments were conducted with C#3.

1. C#3. C#3 data: height 51 cm, diameter 15 cm, mass (dry) 743 g. C#3 was indented to be used for moisture measurements with instrument I#4, Scale #1. The moisture content of C#3 dry was ≈ 10%. C#3 was filled with sawdust and the mass of the configuration increased to 2268 g., and the moisture content was ≈ 10.2%. Subsequently, the configuration was placed in a moist environment along with C#1 (see above) for several days and its mass was changed to 2346.6 g and the I#4 reading increased to ≈ 13%. In subsequent measurements the excess moisture was gradually reduced with time, but the I#4 reading returned shortly to ≈ 10.2% (dry state). The experiment was abandoned at this stage.

2. C#3 Filled with Wet Sawdust. Subsequently, the configuration of C#3 filled with sawdust was flooded with water and was allowed to dry. During drying, the water content was recorded from mass measurements and moisture measurements with instrument I#4. At the start of the measurements the excess water content due to flooding was dW = 3.4 kg, and the I#4, Scale #1 indication was about 19.5%. These measurements were continued for about 5 weeks. During this time the excess water content fell to dW = 1.82 kg, while the I#4, Scale #1 indication remained nearly unchanged from the initial reading. These results suggest that the reading of I#4 depends mainly on the moisture content of the case (surface of the configuration) which apparently has not changed.

## Conclusions and Recommendations

The results of this study indicate that it is feasible to measure moisture in ccc munitions via measurements of their dielectric properties. There is substantial technology available for such measurements in the frequency range from 50 Hz to 1300 MHz. The results show that measurement of capacitance and dissipation factor at frequencies around 1 kHz to 10 kHz should be most suitable. However, if the problem is caused by moisture which has chemically reacted to change the dielectric properties of the materials, the above results may be of no value. Much more information is needed to arrive at specific recommendations.

What is envisioned is a hand-held battery-operated device which could be quickly held to the surface of the cartridge case and provide a reading of the moisture content. Small inexpensive capacitor meters of the type I#2 and I#3 are commercially available and could probably be modified and adapted for this service. If a custom designed capacitance meter is needed, no extensive development is anticipated. This procedure has been apparently incorporated in the TRAMEX Moisture Encounter, I#4. The I#4 appears to be the most suitable instrument for moisture detection in ccc munitions because it is designed as a moisture detection instrument.

The most obvious modification of I#4 for use with ccc munitions is the change of the geometry of its electrodes, from plane to cylindrical, to fit firmly the surface of the cartridge case. Changing the frequency of operation from 12.5 kHz to lower values may enhance the sensitivity of the instrument. An appropriate scale suitable for ccc must be developed. The size and shape of the electrodes should be re-evaluated to match the new application. In addition, modifications such as addition of conducting bands (strips) in the cartridge case itself may be considered for easier access.

It is emphasized that the reading of the instrument I#4 depends strongly on the moisture content of the case wall (near the surface of munitions). Thus, the I#4 is not suitable for measurement of the moisture of the bulk contents of the munitions.

It is feasible that similar electrical measurements could be used to detect the disbonding of skive joints in munitions. If this is successful, the detection of disbonding could be done by the addition of conductive rings (electrodes) on each side of the skive joint. Consideration of this investigation also is recommended.

A continued investigation is recommended, in which the TRAMEX Moisture Encounter is modified and optimized for the rapid determination of moisture in the case wall of ccc munitions. This effort would require both laboratory work at Oak Ridge and interaction with Picatinny Arsenal to test the device on actual munitions. The product of this work would be a prototype device with the modifications and a draft operating protocol.

It is also possible that such measurements could be built into automatic rearm systems to evaluate rounds (and trigger their rejection, if necessary) before they are loaded. That would require the development of a different device from the hand-held meter considered above, and a separate effort.

## PRELIMINARY EVALUATION OF INFRARED SPECTROSCOPY

### Introduction

Infrared spectroscopy is a powerful nondestructive analytical tool which can discern the chemical bonds in a material from its absorption of infrared radiation. To determine whether diffuse-reflectance Fourier transform infrared spectroscopy (DRIFT) measurements could be useful for determination of the moisture content in ccc material, ccc coupon samples were first dried, and then exposed to high humidity for varying periods of time. A series of DRIFT spectra were acquired as a function of exposure time to moisture.

### Experimental

A 1" x 4" sample of ccc coupon was dried by storing in a desiccator with Drierite at room temperature for approximately 120 h. Four smaller samples were then cut from this sample and weighed. One of these smaller samples (Sample 1) was placed back in the desiccator, while the other three (Samples 2-4) were placed in a closed chamber containing an open 40 mL vial of distilled, deionized water. After 24 additional h, the samples were weighed again. Sample 1 and Sample 2 were then cut apart to expose the cellulose nitrate interior, and DRIFT spectra were obtained of the cellulose nitrate faces of each these samples. The samples were returned to the desiccator (Samples 1 and 1a, resulting from cutting Sample 1 apart) or to the humidity chamber (Samples 2 and 2a), and were reweighed at intervals over a period of 21 d. Figure 31 summarizes the weight changes due to moisture uptake by the samples. DRIFT spectra were obtained also over this time period.

DRIFT spectra were obtained using a Nicolet 20SXC Fourier transform infrared (FTIR) spectrometer equipped with a Spectra-Tech 0030-005 "DRIFTS" cell and mercury cadmium telluride (MCT) detector. The sample chamber of the FTIR spectrometer is purged with dry nitrogen boiloff from a liquid nitrogen Dewar. Fifty scans were averaged for each spectrum acquired. The resolution of the instrument was 2 $cm^{-1}$ (16 K data points).

### Results and Discussion

DRIFT spectra of the "dry" and "wet" samples showed some differences, but these were fairly small and not very reproducible. A background subtraction procedure was used to accentuate the differences in spectra of wet and dry samples. In this procedure, the DRIFT spectrum of a dry sample was subtracted either from that of a wet sample (top trace in Figure 32), or from another dry sample (bottom trace in Figure 32). As Figure 32 shows, there is a fairly noisy peak near 3630 $cm^{-1}$ in the differential spectrum of the "wet" sample (9% water content by weight) that does not appear in the spectrum for the dry sample. The location of this peak in the spectrum agrees reasonably well with transmission IR measurements of moisture in cellulose nitrate (12). This peak was not seen in similar spectra obtained for the same samples two days later, however.

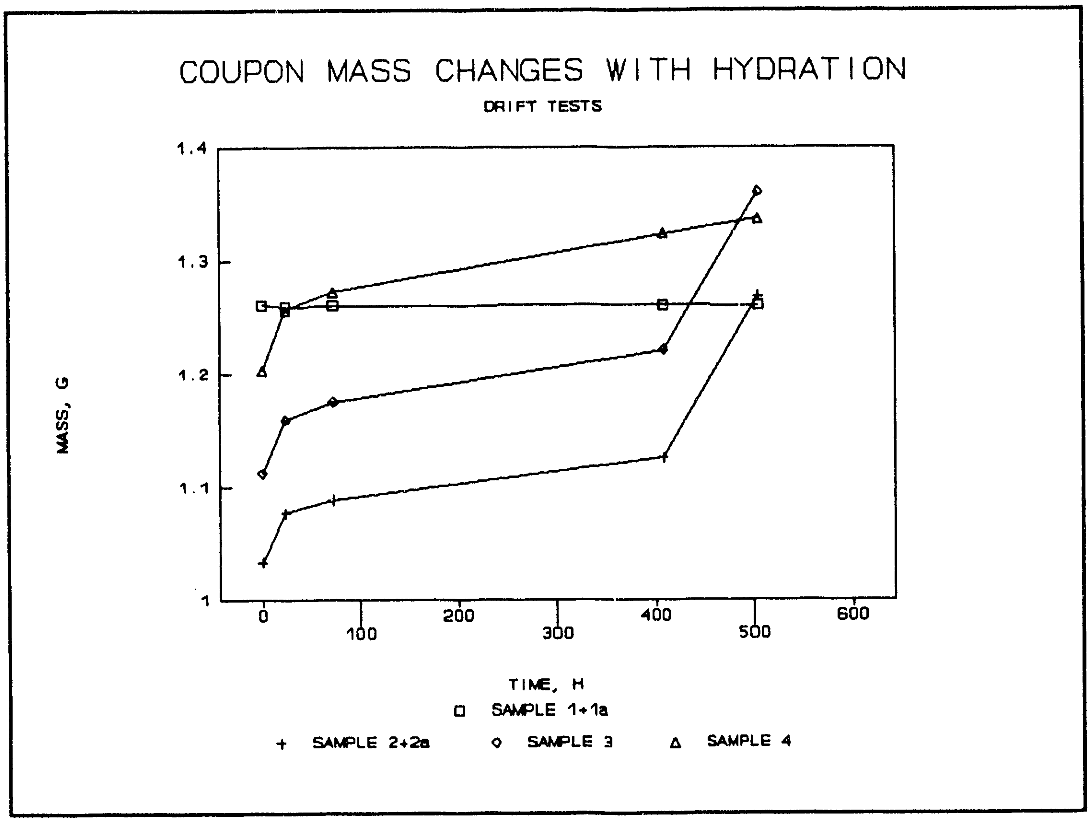


Fig. 31. Mass Changes in CCC Coupons.

At this point, Sample 2 in the humidity chamber was immersed in water for 24 h, and then removed from the water and allowed to equilibrate in the humidity chamber for 24 h. Sample 2 then had a moisture content of 32%. DRIFT spectra of Sample 2 and Sample 1 (the "dry" sample) were obtained and compared. A large noise content in the DRIFT spectrum of Sample 2 prevented any observation of a contribution from the moisture.

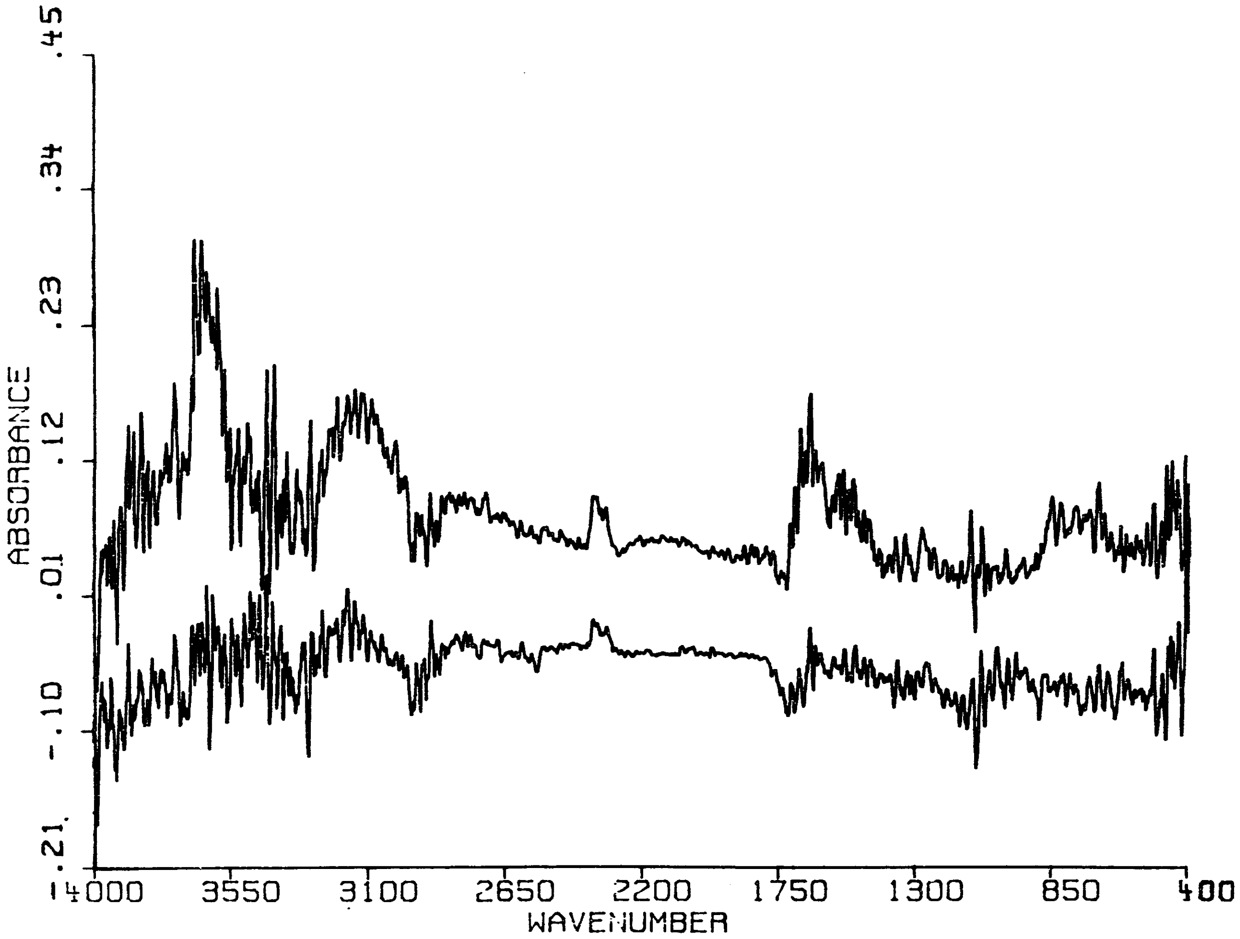


Fig. 32 DRIFT Spectra of Wet (Top) and Dry (Bottom) CCC Coupon.

Possible reasons for the lack of reproducibility observed in DRIFT spectra are (a) changes over time in the level of atmospheric moisture in the sample chamber of the spectrometer, and (b) the strong dependence of DRIFT spectra on the light-reflecting properties of the sample surface. Moisture in the sample chamber can be partially compensated for by ensuring equal chamber purge times for wet and dry samples. Problems with sample surface inhomogeneities that adversely affect DRIFT spectra may be eliminated by using other techniques for obtaining infrared spectra. One promising alternative is attenuated total reflectance (ATR), which involves application of modest pressure to bring the sample in contact with a long, thin prism through which the infrared light is passed. Because the sample and prism are pressed together, small irregularities in the sample surface may be smoothed out. Additionally, more of the sample surface will be illuminated by the infrared light in the ATR cell than in the DRIFT cell, yielding a measurement that is averaged over a larger area.

## Conclusions and Recommendations

This preliminary test of one infrared spectroscopy technique for analyzing solid samples was not encouraging in its ability to detect moisture in ccc material. Other infrared surface techniques, such as attenuated total reflectance, should be tested before a final decision is made on the method.

# CONCLUSIONS AND RECOMMENDATIONS

The performance tests using cellulose test squares spiked with NG suggest that nitroester detection in ccc munitions is possible using indicator strips based upon the modified Griess reagent, and that quantitative information can be derived from the color intensity or optical density. Similarly, the pelletized cupric chloride indicator tests suggest that a ccc moisture indicator is possible, although at this stage, the time to color change appears to be the indicator of moisture concentration. At their present stages of development, the performances suggest that the indicators would be most suitable be for temporary, one-time tests of munitions rather than for a permanent installation on the rounds and continuous indication.

It is recommended that development of the nitroester indicator be continued. Further work on the nitroester indicator must address questions of indicator reagent stability and lifetime, means of potentiating the sensitivity over long periods of time, potential sources of interferences from propellant and case wall degradation, adaptation to munitions walls and current manufacturing techniques, and calibration of response with actual munitions. Similar questions also arise in the further development of indicators for moisture.

The commercial meter for moisture determination in building materials by electrical capacitance measurements is very promising in its potential for an inexpensive, rapid, nondestructive, and portable means of measuring moisture in ccc wall. The main work required is to optimize the electrode design(s) for the shapes of munitions, optimization of the measurement frequency, and calibration with munitions. It is strongly recommended that this work be continued, and it appears possible that this device could be brought into use sooner than the indicator strips.

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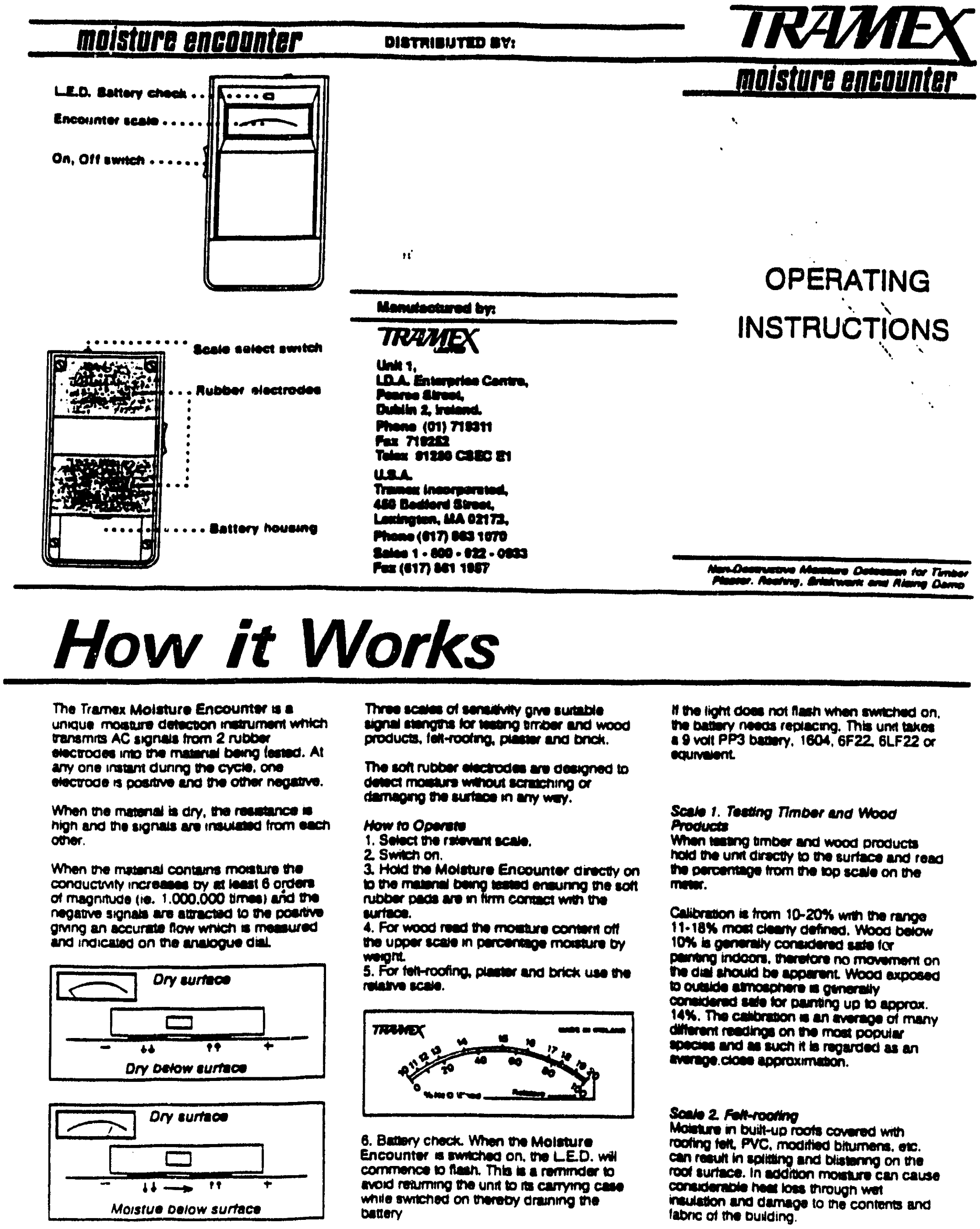
# APPENDIX

## Instruction Manual for TRAMEX Moisture Encounter Model MF-1



moisture encounter

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*Non-Destructive Moisture Detection for Timber Plaster, Roofing, Brickwork and Rising Damp*

# *How it Works*

The Tramex **Moisture Encounter** is a unique moisture detection instrument which transmits AC signals from 2 rubber electrodes into the material being tested. At any one instant during the cycle, one electrode is positive and the other negative.

When the material is dry, the resistance is high and the signals are insulated from each other.

When the material contains moisture the conductivity increases by at least 6 orders of magnitude (ie. 1.000.000 times) and the negative signals are attracted to the positive giving an accurate flow which is measured and indicated on the analogue dial.

Three scales of sensitivity give suitable signal stengths for testing timber and wood products, felt-roofing, plaster and brick.

The soft rubber electrodes are designed to detect moisture without scratching or damaging the surface in any way.

*How to Operate*
1. Select the relevant scale.
2. Switch on.
3. Hold the **Moisture Encounter** directly on to the material being tested ensuring the soft rubber pads are in firm contact with the surface.
4. For wood read the moisture content off the upper scale in percentage moisture by weight.
5. For felt-roofing, plaster and brick use the relative scale.

6. Battery check. When the **Moisture Encounter** is switched on, the L.E.D. will commence to flash. This is a reminder to avoid returning the unit to its carrying case while switched on thereby draining the battery

If the light does not flash when switched on, the battery needs replacing. This unit takes a 9 volt PP3 battery, 1604, 6F22, 6LF22 or equivalent.

*Scale 1. Testing Timber and Wood Products*
When testing timber and wood products hold the unit directly to the surface and read the percentage from the top scale on the meter.

Calibration is from 10-20% with the range 11-18% most clearly defined. Wood below 10% is generally considered safe for painting indoors, therefore no movement on the dial should be apparent. Wood exposed to outside atmosphere is generally considered safe for painting up to approx. 14%. The calibration is an average of many different readings on the most popular species and as such it is regarded as an average.close approximation.

*Scale 2. Felt-roofing*
Moisture in built-up roofs covered with roofing felt, PVC, modified bitumens, etc. can result in splitting and blistering on the roof surface. In addition moisture can cause considerable heat loss through wet insulation and damage to the contents and fabric of the building.

The Moisture Encounter can be used to confirm a new roof has been installed dry and to trace leaks in an old roof.

As there are many different types of membrane and insulations it is not possible to calibrate to give a percentage moisture measurement. The Relative Scale is used for checking the difference between wet and dry.

A leak in a built-up roof may enter the building a long distance from where the moisture enters the roof. Take the Moisture Encounter to the area above the leak. Place it on the roof so that the signals penetrate the felt and indicate if moisture is present. By checking across the roof, the outline of the "Moisture Profile" can be marked with spray paint or chalk. By this method the entire wet area can be outlined thereby leading to the defect which allows water entry.

If gravel surfacing is present it needs to be removed by scratching with a claw hammer or similar to ensure close contact with the surface.

No cutting of the membrane is necessary in order to detect moisture. However, it is always recommended that a core be cut to determine the depth and density of water before deciding to carry out repairs.

### *Scale 3. Plaster, Brickwork*

When testing plaster, the readings are taken on the relative scale. When the reading is in the green area the plaster is considered safe for the application of paint. When in the red it is considered wet. Please note. The presence of salts on the surface could give a high reading.

Masonry walls which have been placed on soil which becomes wet or saturated or those that have defective or non-existant moisture barrier, often have moisture migration into them. Because of the high cost of remedial work it is essential that the extent of the dampness be identified. Sliding the Moisture Encounter across the wall surface, with the electronic pads in contact, will show the difference between wet and dry even if it is not visible.

Fire damage. Quite often a lot of water damage is caused during the fighting of a fire. The Moisture Encounter can be used to check walls, furniture, carpets, drapes etc. and is extremely useful in the maintenance and renovation of all types of buildings.

### *Limitations*

On dense concrete mid scale readings may be obtained even if the material is dry. When moisture is present a higher reading will be obtained so a comparison can be made. If a more accurate reading is required contact Tramex for details of the Tramex Concrete Scanner.

The Moisture Encounter will not detect moisture through certain rubber roof membranes due to the presence of carbon black filler. These include EPDM's and Butyl's. If this is the case, contact Tramex for details of the Tramex C.R. Scanner which has been specifically developed for these materials.

### *Guarantee*

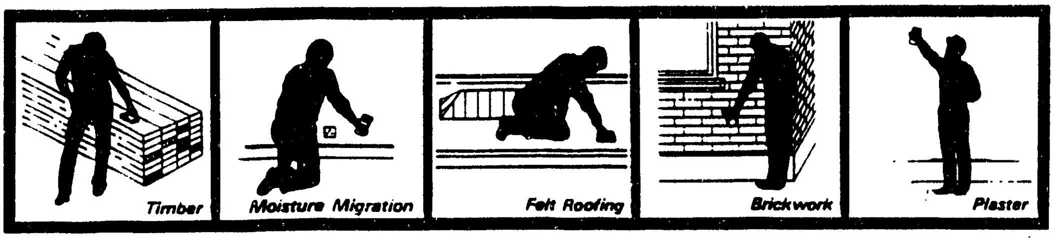
Limited guarantee covers repair required resulting from defects in materials or workmanship for a period of one year from date of purchase. Proof of purchase is necessary.

Tramex Limited accept no responsibility for costs incurred due to information given by this instrument.

### *Testing*

All Tramex instruments are rigorously tested to ensure long life under rough conditions. New batteries will need to be occasionally installed and replacements should be kept in reserve and installed once battery check light (LED) is not constantly lit.

Moisture Encounter. Patent Pending.



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