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**A NEW ELECTROCHEMICAL
RECORDER PAPER.**

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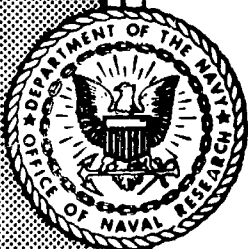
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ABSTRACT

A new electrolytic electrochemical recorder paper utilizing a benzidine marking agent has been developed which has high sensitivity, wide dynamic range, and fine recording definition. The paper is further characterized by good wet strength and stability with respect to shelf-life and to aging of the recorded paper. The recording process is an oxidation reaction which permits the use of chemically inert, noncorrosive metal stylus or printing bar materials. The resultant blue marking provides high optical contrast with the light buff background. Experimental rolls of this recorder paper have been prepared in a continuous process by precipitating benzidine in the paper as the highly insoluble sulfate salt in the first two baths and adding in the third bath the inorganic salts which function as buffering agents and electrolytes to provide electrical conductance. The paper is then adjusted to the proper moisture content and wound into rolls which are sealed in polythene bags and stored in sealed metal containers.

PROBLEM STATUS

→ This is an interim report; the investigation is being continued with emphasis on new types of recording mediums.

AUTHORIZATION

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A NEW ELECTROCHEMICAL RECORDER PAPER

INTRODUCTION

The ECR Recorder Paper, a new electrochemical recorder paper developed at this Laboratory, utilizes benzidine (4,4' - diaminodiphenyl) as the marking agent. In such papers, an electrochemical reaction, induced by an electric current through the paper, is involved in the recording process. The electrical conductivity is ionic in nature and dependent upon moisture and inorganic salts in the paper. The usual types of recorders in which these papers are used employ a moving stylus, or printing bar, as the anode and a metal roll or helix, which supports the paper, as the cathode. Signal currents of varying strength flowing through the paper produce blue marks whose intensities vary with the applied current.

Over-all evaluation of this new recorder paper on the basis of the electrical, physical, and chemical properties reported here is difficult because the characteristics of recorders and the requirements of specific applications vary. These variations must be kept in mind when evaluating this paper for specific application in other recorders.

ELECTRICAL PROPERTIES

The recording electrical properties of the paper were difficult to obtain with any degree of precision due to small errors in readings caused by the relatively uneven surface of the paper resulting in irregular stylus contact and pressure as the stylus moved from one area to another. Irregularities in readings were also attributable to slight variations in the mechanical performance of the stylus driving mechanism and to some extent to the non-uniform distribution of the chemicals within the paper resulting from slight imperfections in the make-up of the paper stock. In order to minimize the effect of these variables the average of a number of readings taken over a three minute period for each voltage level was used.

The electrical measurement system consisted of a CAN-55134-A sonar range recorder with a variable source of dc power connected directly to the stylus because the amplifying system in the recorder was limited to relatively low voltages and currents. The potential across the paper was measured with an RCA VoltOhmyst type WV-97A and the current with a Triplett Volt-Ohm-Mil-Ammeter model 630-A. The platinum-tipped short stylus (Part No. 800385), having a width of 0.015 inches, was the anode, and the steel paper roller bar the cathode. Two stylus speeds were available with this recorder, 1.18 and 2.95 inches per second.

Marking Thresholds

The threshold marking values obtained for the recorder paper were 0.5 volts, 0.01 milliamperes at a stylus speed of 1.18 inches per second and 0.6 v, 0.025 ma at 2.95 in. per sec. The mark produced was faint, but legible.

Dynamic Ranges

The dynamic range will vary from one type of paper to another according to its properties. It also will vary with the particular requirements necessary for a specific use. For example, where very high recording definition is required, the dynamic range will obviously be less than for a use where this is not a primary requirement. Likewise, when the optical range requirement is more important than definition, the dynamic range value may be different. Consequently, it is difficult to cite a value for dynamic range which will be valid for all use requirements and under all conditions of measurement. The dynamic range of a recorder paper, for the purpose of this report, is considered to be the useful recording range with respect to definition and is expressed in decibels. For comparison with other types of recorder papers measured under essentially the same conditions these values may be of some use.

A summary of the dynamic ranges calculated for ECR Recorder Paper are shown in Table 1. The minimum electrical value was arbitrarily chosen as the recording threshold, and the maximum value as the level where appreciable spreading and blooming of the mark occurs.

TABLE 1
Dynamic Ranges Calculated for ECR Recorder Paper

Stylus Speed (in./sec)	Dynamic Ranges (db)	
	Voltage Ratios	Current Ratios
1.18	25	68
2.95	26	67

Resistance and Power Ranges

The resistance of the ECR Recorder Paper was calculated from the observed voltages and currents. The variation in resistance with applied voltage at each recording speed (Figures 1 and 2) shows a real, but as yet unexplainable, "break" in the otherwise reasonably smooth curve. These "breaks" (shown in the insets) occur at 4.0 and 4.5 volts respectively for the recording speeds of 1.18 and 2.95 inches per second.

Curves which illustrate the power-voltage characteristics are shown in Figures 3 and 4.

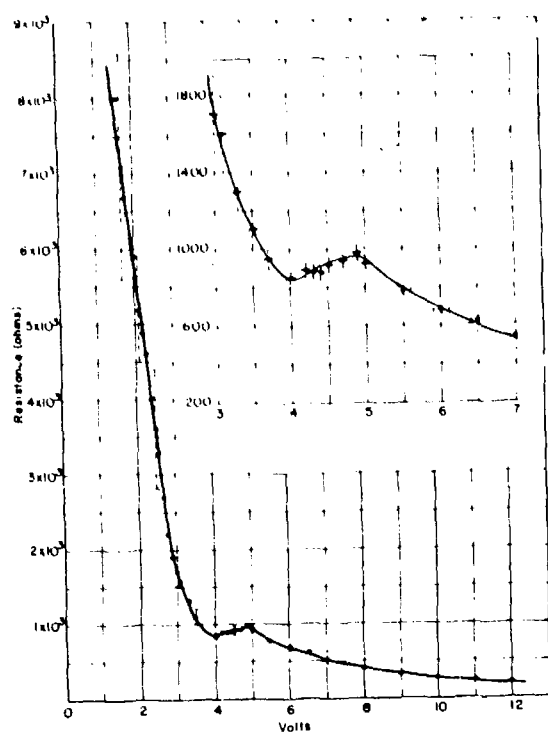


Figure 1 - Resistance-voltage characteristic of ECR Recorder Paper at a stylus speed of 1.18 inches per second and a stylus width of 0.015 inches. Inset shows enlarged plot of "break" in curve.

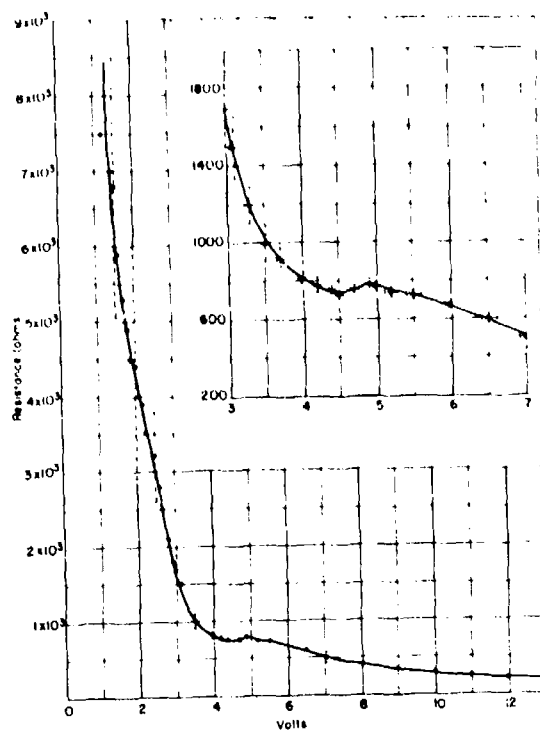


Figure 2 - Resistance-voltage characteristic at a stylus speed of 2.95 inches per second and a stylus width of 0.015 inches. Inset shows enlarged plot of "break" in curve.

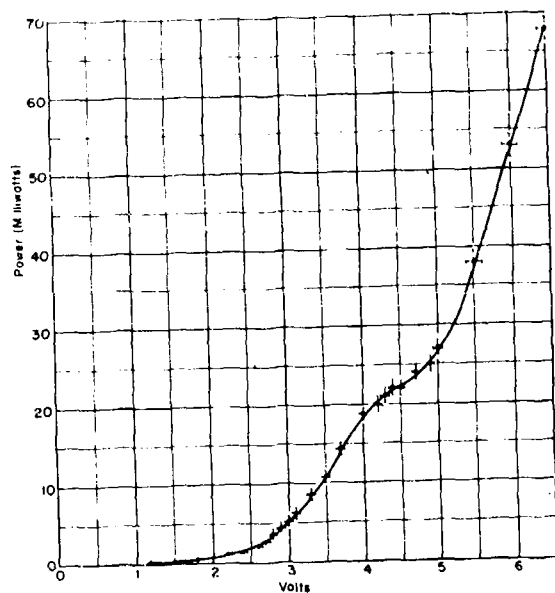


Figure 3 - Power-voltage characteristic at a stylus speed of 1.18 inches per second and a stylus width of 0.015 inches.

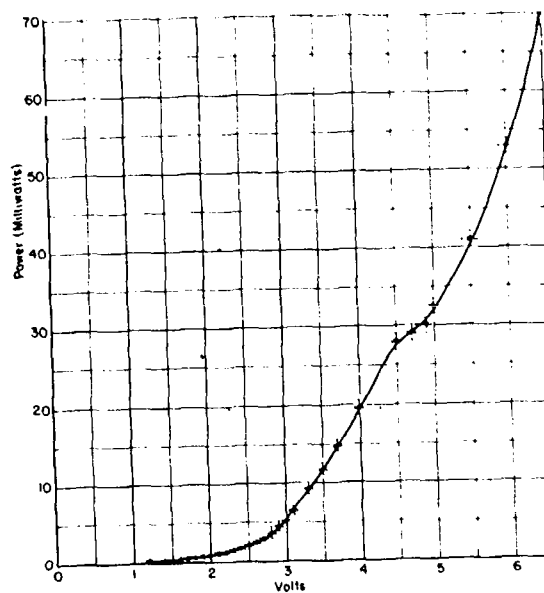


Figure 4 - Power-voltage characteristic at a stylus speed of 2.95 inches per second and a stylus width of 0.015 inches.

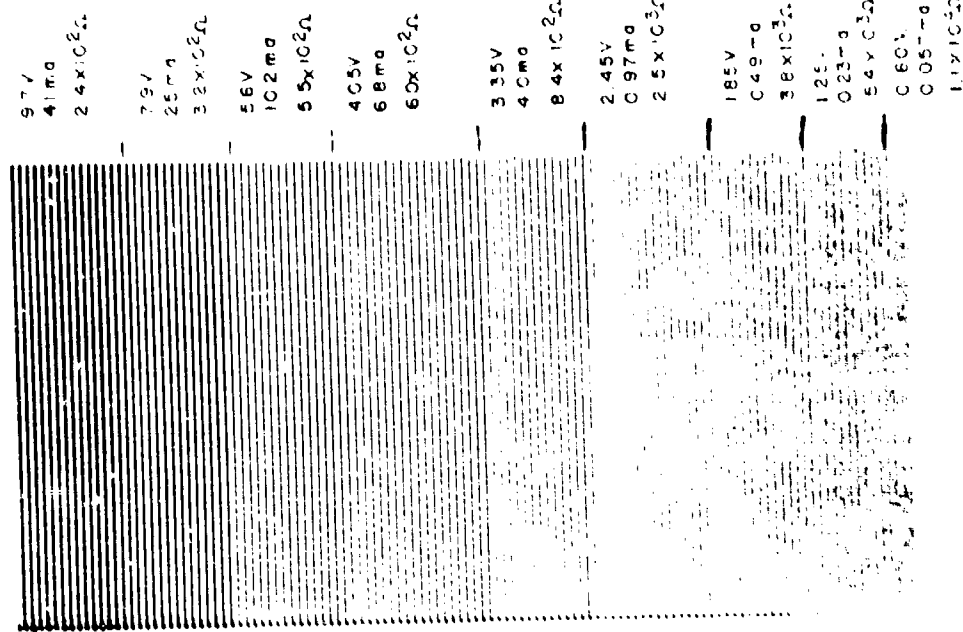


Figure 6 - Typical dc voltage recording on ECR Recorder Paper with a CAN-55134-A sonar range recorder at a stylus speed of 2.05 inches per second and a stylus width of 0.015 inches. Moisture content of paper was 33.5%.

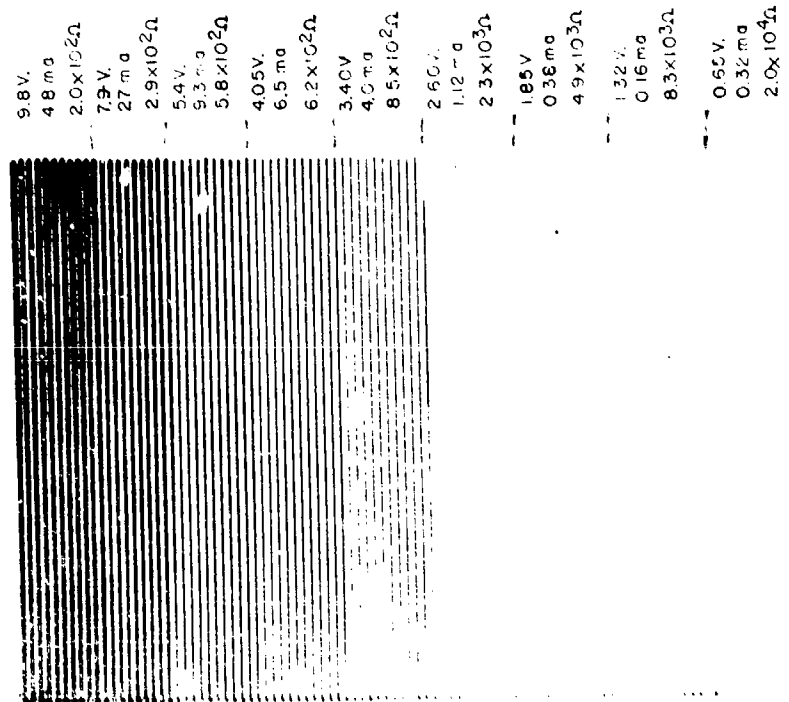


Figure 5 - Typical dc voltage recording on ECR Recorder Paper with a CAN-55134-A sonar range recorder at a stylus speed of 1.18 inches per second and a stylus width of 0.015 inches. Moisture content of paper was 33.5%.

Definition

Recordings made using the ECR Recorder Paper (Figures 5 and 6) illustrate the definition obtained with various recording currents and voltages at the two stylus speeds. Figure 7 shows the manner in which the width of the mark increases with increasing marking current. The stepwise progression at the low currents and voltages (shown in inset) is believed to be associated with definite electrochemical reactions which influence the electrical properties and the formation of the marking pigment. Sufficient experimental evidence has not as yet been obtained to explain fully the nature of these reactions.

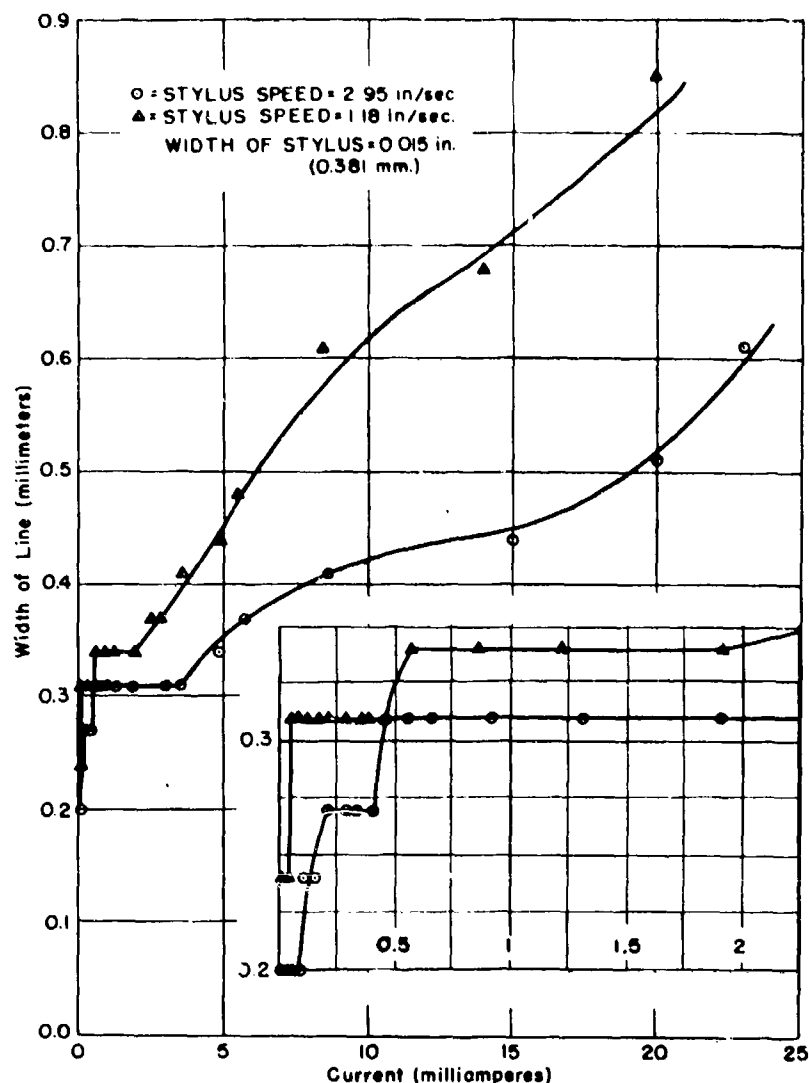


Figure 7 - Variation in width of recorded mark with increasing current. Inset shows stepwise progression at the low currents.

PHYSICAL PROPERTIES

A summary of the physical properties of the recorder paper and the paper stock is given in Table 2. Although no quantitative data is available at the present time, the optical contrast between the light buff recorder paper background and the deep blue recorded mark appears to be high from empirical observations.

TABLE 2
Physical Properties of ECR Recorder Paper and Paper Stock*

	Recorder Paper†	Paper Stock‡
Weight (25 x 40 inches - 500 sheets), pounds	46.0	34.4
(17 x 22 inches - 500 sheets), pounds	16.0	12.9
Thickness, inch	0.0028	0.0020
Bursting strength (Mullen):		
Dry, points	41	44
Wet, points	17	30
Ratio of dry bursting strength to weight (25 x 40 - 500), percent	89	128
Folding endurance: M.I.T. tester (tension 1 kg.):		
Machine direction, double folds	8000	5300
Cross direction, double folds	8000	4900
Tensile properties, (Schopper tester), per 15-mm width:		
Dry, machine direction, kilograms	7.2	8.1
Cross direction, kilograms	4.9	5.1
Wet, machine direction, kilograms	2.7	4.3
Cross direction, kilograms	2.2	2.7
Dry, machine direction, pounds	15.8	17.8
Cross direction, pounds	10.7	11.2
Wet, machine direction, pounds	6.1	9.5
Cross direction, pounds	4.9	5.9
Elongation at rupture, dry:		
Dry, machine direction, percent	6.1	2.6
Cross direction, percent	12.7	6.8
Tearing resistance (Elmendorf):		
Machine direction, grams	54	40
Cross direction, grams	52	42
Opacity (contrast ratio), percent	--†	65
Smoothness (Bekk test), seconds	18	53
Sizing test:		
Indicator method, seconds	22	21
Curl method, seconds	3.5	6.6
Curl (angle), degrees	136	111

* Physical tests made by the Paper Section, Division of Organic and Fibrous Materials, National Bureau of Standards

† Tests made after one month storage. NBS identification, 3690-1; NRL identification, Lot 21 roll 2

‡ NBS identification, 3690-5; NRL identification, Lot 4841-2B

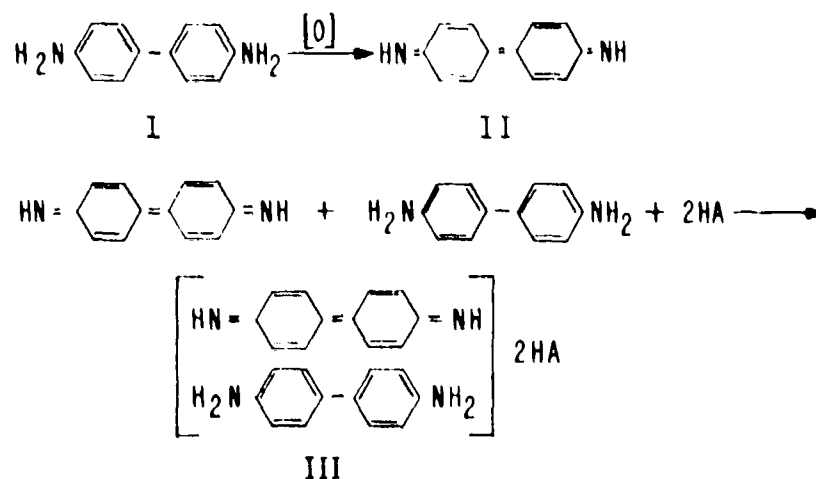
† Opacity not tested because of change in color.

CHEMICAL PROPERTIES

Marking Process

It is believed the recorder paper marking process involves the oxidation of benzidine since the marking takes place at the anode and the characteristic deep blue pigment of "benzidine blue" is obtained. The chemical oxidation of benzidine is described in the literature* as one molecule of benzidine (I) being oxidized to a p-quinonediimine (II) which then unites with a molecule of unchanged benzidine and acid to form a stable merquinoid molecular compound (III) (benzidine blue) according to the following equations:

* W. Schlenk and A. Knorr, Ann. 363: 313-339 (1908)



The over-all electrochemical reaction involved in the recording process which produces the blue marking pigment has not been fully determined in this investigation. The bromide ion of the potassium bromide in the paper is reduced to free bromine when its decomposition potential is exceeded. Bromine is a strong oxidizing agent and undoubtedly figures significantly in the oxidation reaction of benzidine. It has been demonstrated that the blooming (blue shading between recorded lines on the paper) at the higher recording voltages is due almost entirely to the liberation of an excess of free bromine from the paper. More work than is warranted on this type of problem would be required to fully understand the mechanism of the reactions taking place during the recording process in the complex system represented by the recorder paper.

Reaction with Metals

Prolonged contact of metals with the moist recorder paper may result in discoloration. Copper and alloys containing copper, such as bronze and brass, produce a blue discoloration; zinc causes a bronze discoloration; and iron, steel, and stainless steels corrode and leave rust stains. The paper is not affected, however, by lead, cadmium, silver, nickel, and chromium.

Stylus Materials

Inert noncorrosive metals such as platinum, platinum-iridium alloys, and gold are apparently not affected by the paper and are the best stylus materials. For reasons not yet determined, an iron, steel, or silver stylus does not produce a satisfactory mark on the paper. Copper, bronze, and German silver produce an intense blue-black mark on both sides of the paper. However, these stylus materials are consumed in the marking process.

Effect of Light

The recorder paper is somewhat sensitive to light, the color changing from light buff to a slightly darker shade of buff. The rate of change of color varies with the moisture content of the paper. However, the maximum change so far observed is not great and lessens only slightly the contrast between the background and the record.

Shelf-Life Stability

The stability of the paper with respect to shelf-life appears to be satisfactory as well as can be ascertained from the relatively short time it has been observed and from accelerated aging tests. Rolls stored at room temperature (ca. 22° - 25°C) approximately three months have changed only in color, from the original white to the characteristic light buff. Rolls stored at 45°C for ten days were a slightly darker shade of buff compared to those stored at room temperature. Rolls stored at 75°C for seven days had changed in color to a greenish-yellow. All three samples had the same marking and electrical characteristics with no apparent adverse effects on the initial marking. However, the stability of the mark in atmospheres of high humidity was markedly less on the paper treated at 75°C indicating that, along with the color change, some breakdown had occurred. The paper stored at room temperature and 40°C showed no apparent fading under these conditions.

Laboratory fungicidal assays* indicate that pyridyl mercuric acetate added to the paper in small quantities acts as an effective deterrent to fungus and bacteriological deterioration during storage.

Stability of Recording

The stability of the recorded mark under conditions so far investigated is satisfactory. No fading tendency has been observed under ordinary handling conditions. An earlier paper, while producing a permanent record if dried within a reasonable time, faded markedly in atmospheres of high humidity where the paper remained moist. The recorded mark on the present paper shows no tendency to fade even when stored in atmospheres of 100% relative humidity and 85°F temperature.

THE PREPARATION OF ECR RECORDER PAPER

Benzidine Precipitant

The preparation of ECR Recorder Paper involves an aqueous three-bath impregnation of a paper stock at room temperatures. The solubility of the benzidine marking agent in the form of its dihydrochloride salt, its most soluble derivative, is too low to provide a sufficient concentration in the paper for optimum marking performance when incorporated from a single bath. The proper concentration of this agent has been added to the paper by means of a metathetical rearrangement whereby the paper is impregnated first in a bath containing a salt which reacts with the benzidine dihydrochloride in a second bath to form a highly insoluble salt derivative according to the following equation:



The amount of benzidine removed from the second bath is directly proportional to the concentration of the salt in the first bath. By adjusting the salt concentration of the first bath, the proper quantity of benzidine is precipitated on and into the paper in the second bath. Benzidine is precipitated quantitatively by a number of reagents, such as sulfates, thiosulfates, tungstates, phosphates, and the corresponding acids, but sodium sulfate was found to be the most suitable benzidine precipitant for this process.

The third bath contains a fungicide and those salts necessary for electrical conductivity and buffering action. The low solubility of the benzidine dihydrochloride as well as its

* The fungicidal assays were made by the Biological Deterioration Section, Protective Coatings Branch, Chemistry Division.

incompatibility with some of the chemicals prevented inclusion of these chemicals in the second bath.

Paper Stock

The paper stock used in this process is a high grade 100 percent rag bond containing approximately 2 percent rosin and 2½ percent melamine-formaldehyde resin (Tables 2 and 3). Numerous other less expensive papers have been investigated but so far none has been found which gives comparable over-all results.

TABLE 3
Chemical Analysis of ECR Recorder Paper Stock Lot 4841-2B*

Ash †	0.65%
pH (Hot extraction)	4.8
Nitrogen †	1.04%
Ether soluble †	1.8%
Cellulose	
Alpha §	96.6%
Beta §	1.3%
Gamma §	2.1%
Copper No.	0.5
Pentosans §	0.0%

Note: Paper may contain melamine-formaldehyde resin (MR) as indicated by its appearance on grinding and in the copper number test. The nitrogen content is of the order of that found in a paper containing approximately 2.5% MR.

* Analysis performed by the Paper Section, Division of Organic and Fibrous Materials, National Bureau of Standards

† Moisture-free basis

§ Based on total cellulose

Continuous Impregnation Process

The impregnation apparatus (Figure 8) which has been used successfully for preparing rolls of the recorder paper at this Laboratory, consisted of three tanks with rubber squeeze-rolls mounted on the end of each tank to remove excess solution from the paper. The inside of each tank and the guide-rollers within the tank were coated with an acid resistant paint. Idler rolls were provided after the squeeze-rolls on Tanks 1 and 2 to compensate for slight differences of paper travel speed due to small variations in squeeze-roll diameters. The squeeze-rolls were driven from a common shaft attached to an electric motor. The windup consisted of a drum roller driven by a separate motor. Rolls of uniform width and perpendicular ends were obtained by slitting the paper just prior to the windup. The maximum roll width obtainable on this experimental machine was 6-1/8 inches. The paper speed through the baths was approximately 4 feet per minute.

Adhesion of the benzidine salt to the paper was facilitated considerably by partial drying of the paper prior to passage through the second and third impregnation baths. Drying

was accomplished by passing the paper between two perforated tubes attached to a hot air blower whereby a stream of air was presented to both surfaces of the paper.

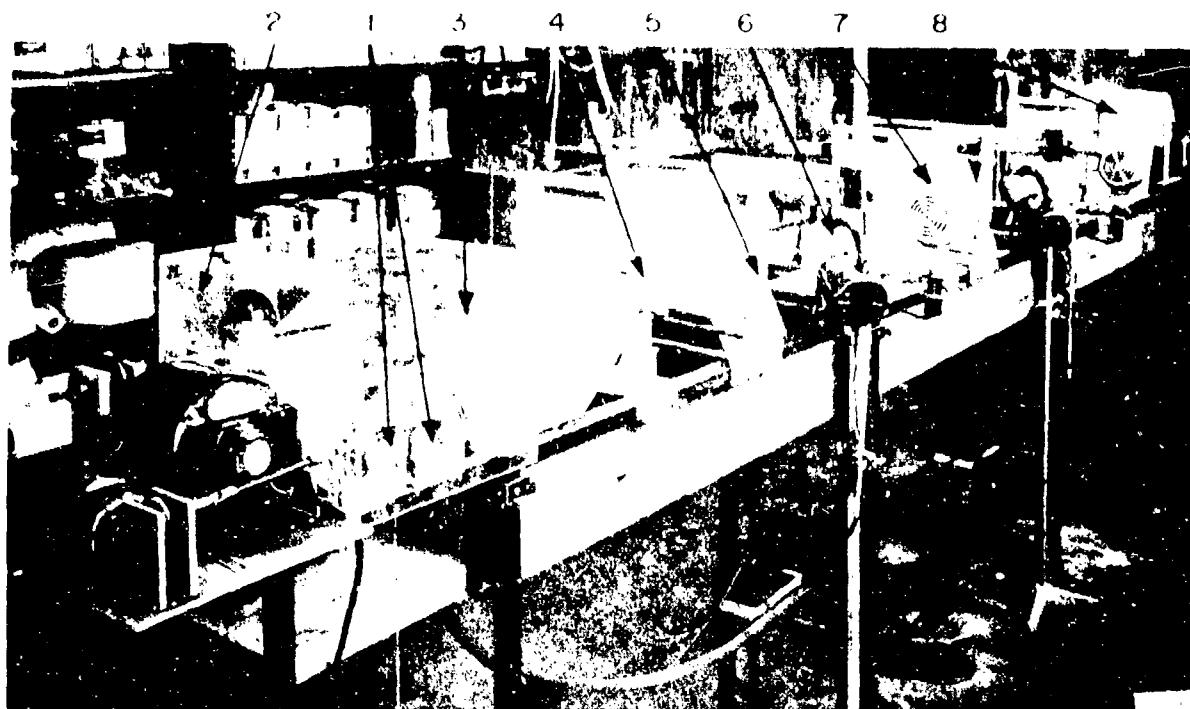


Figure 8 - Experimental paper impregnation machine showing drum windup (1), plastic housing for windup to keep dust from finished roll (2), core holder (3), squeeze-rolls (4), idler rolls (5), stirrer (6), hot air blower and perforated tubes (7), and paper stock feed roll (8).

The proportions of chemicals given in Table 4 have been found to give the best results with respect to both the marking characteristics and the processing of the paper. The molar ratio of sodium sulfate in Bath No. 1 to the benzidine dihydrochloride in Bath No. 2 (approximately 4.5 to 1) is important from the standpoint of adherence of the insoluble benzidine salt to the paper. An appreciable quantity of the insoluble salt is deposited in Bath No. 2 when the concentration of benzidine dihydrochloride falls below 21 grams per liter. To maintain the concentration approximately constant, as determined by the method given in Appendix A, a benzidine dihydrochloride solution was added dropwise during the run. With the concentration kept within the optimum limits, the rate of removal of benzidine dihydrochloride from Bath No. 2 is that shown in Figure 9.

The pH of Bath No. 3 was progressively lowered during a run because of the excess benzidine dihydrochloride and hydrochloric acid carried over from Bath No. 2. Maintenance of the pH at about 6.8 was accomplished by a continuous dropwise addition of a solution of trisodium phosphate and potassium bromide. Since the slight increase in pH of Bath No. 1 during a run apparently does not affect the final paper, no attempt was made to maintain the initial value. The pH of Bath No. 2 was maintained approximately by adding hydrochloric acid in the benzidine addition solution.

A moisture content of 30 - 33%, based on the weight of the wet paper, was found to be satisfactory for optimum recording performance. Because of the relatively low absorption properties of the paper stock, this moisture content was usually the maximum obtained in the continuous impregnation process. The finished rolls of recorder paper were sealed in polythene bags and stored in individual sealed metal containers.

TABLE 4
Composition of Impregnation Baths

Bath No.	pH	Chemicals	Quantity
1	5.2	Sodium sulfate, anhydrous	55 gm
		Antarox A-480* (1%)	0.6 ml
		Water†	1000 ml
2	1.4	Benzidine dihydrochloride, C.P.‡	23 gm
		Hydrochloric acid, sp. gr. 1.190	3 ml
		Antarox A-480 (1%)	0.6 ml
		Water	1000 ml
3	6.8	Potassium bromide, U.S.P. XIII granular	304 gm
		Sodium phosphate dibasic, heptahydrate, C.P.	29.0 gm
		Citric acid, C.P.	1.6 gm
		Antarox A-480 (1%)	0.6 ml
		Pyridylmercuric acetate	0.24 gm
		Water	1000 gm

* Trade name of General Aniline and Film Corporation

† In the experimental work, distilled water was used exclusively. However, it has been shown that water demineralized with ion exchange resins may be substituted without any apparent affect on the properties of the recorder paper.

‡ The C. P. grade (suitable for Occult Blood Tests) manufactured by the Coleman and Bell Company, Norwood, Ohio, was used because it met the requirement that it be substantially free of color. No problem was encountered with respect to the color requirement in obtaining the other chemicals.

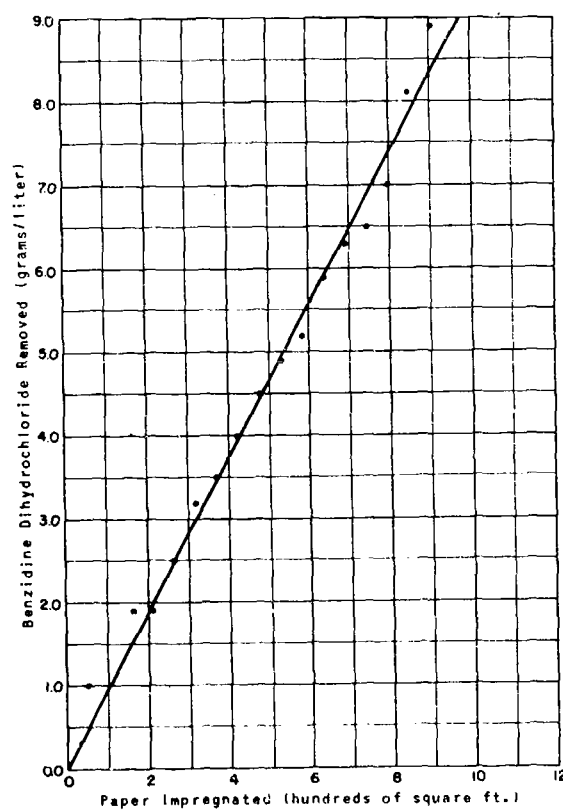


Figure 9 - Rate of removal of benzidine dihydrochloride from Bath No. 2

Stepwise Impregnation Process

One trial run of a stepwise impregnation process for preparing the recorder paper was carried out at the experimental paper mill of the National Bureau of Standards. The paper stock was impregnated in each bath separately, dried, and wound into a roll before processing further in the next bath. At the end of the third bath, the paper was adjusted to the proper moisture content and wound into 100-ft rolls and packaged as described above. Although this method of preparing the recorder paper was not investigated further, the run was sufficiently successful to indicate a possible alternative method for preparing the paper.

CONCLUSIONS

It is believed that the ECR Recorder Paper, with its excellent electrical, physical, and chemical properties, may be used to advantage in present operational electrochemical recorders. This paper should also meet many of the requirements for the design of new types of recorders.

The recorder paper may be used in the standard sonar range recorder CAN-55134-A without modification of the recorder. However, certain precautions are advisable for best performance:

1. Chemically inert stylus materials such as platinum-iridium should be used. A stylus constructed of steel, iron, or silver does not mark this paper satisfactorily.
2. Since metals containing copper, such as bronze or brass, produce discoloration on prolonged contact with the moist paper, the metal parts in contact with the paper should be coated with a clear lacquer, excepting, of course, the cathode and anode.
3. The paper is quite translucent when moist because of its thinness. It is recommended, therefore, that the surface of the recorder over which the paper travels immediately after the recording, be painted white in order to enhance the observed contrast between the record and background.
4. A moist strip of blotting paper should be kept in the bottom of the paper roll tank of the recorder to maintain the proper humidity in the paper during its use.

ACKNOWLEDGMENTS

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* * *

APPENDIX A
Photometric Method of Analysis for the Determination of the
Benzidine Dihydrochloride Concentration in Bath No. 2

A modification of the photometric method for the determination of permanganate using benzidine* was utilized to determine the concentration of benzidine dihydrochloride in Bath No. 2 during a machine run. The procedure is based on the light absorption characteristics of an aliquot sample of the benzidine solution oxidized with potassium permanganate in the presence of nitric acid.

A 0.2-ml sample of Bath No. 2 was pipetted into a 1-liter volumetric flask almost filled with distilled water. Four drops of concentrated nitric acid were added and the sides of the flask were washed down with distilled water. The flask was then swirled to mix the acid and benzidine.

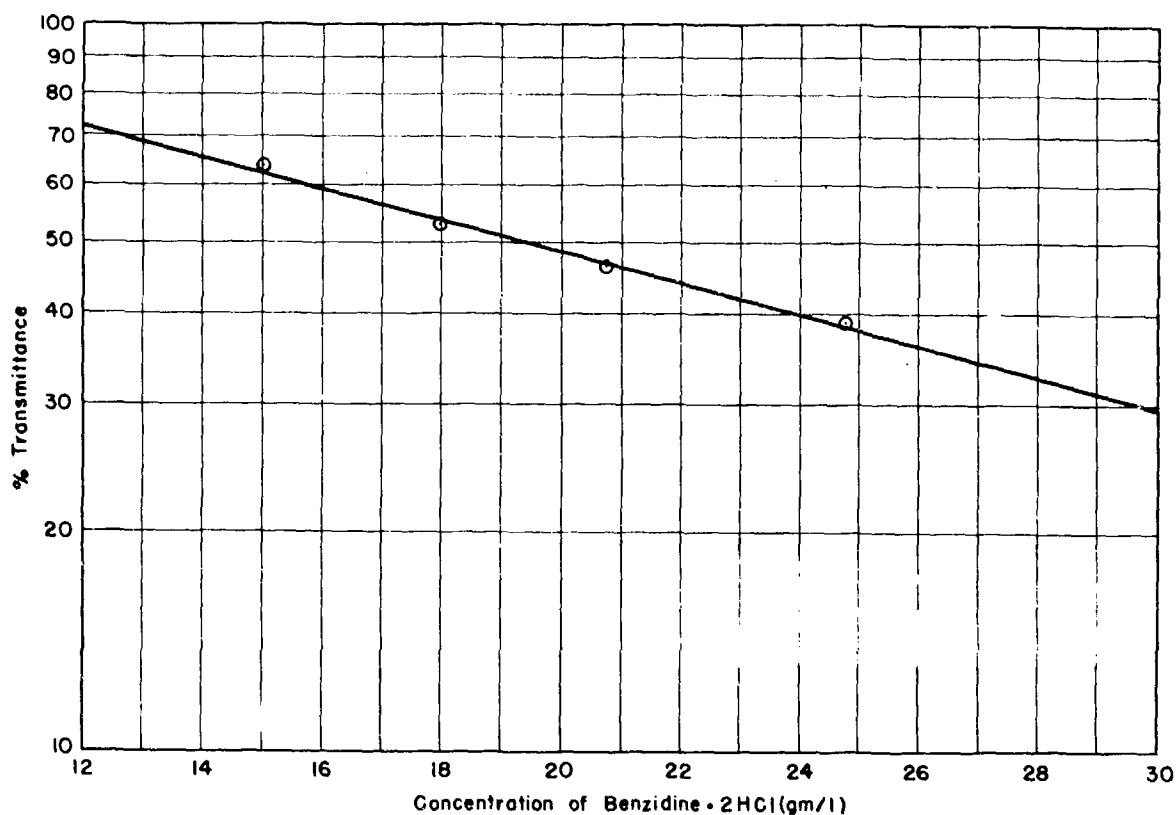


Figure A-1 - Calibration curve for determining concentration of benzidine dihydrochloride in Bath No. 2 from light transmittance data using a Cenco-Sheard-Sanford Photometer with a 410-490 m μ filter.

* F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis*, 3rd. ed., Vol. II, p. 39, New York; D. Van Nostrand Co. (1949)

One ml of a 0.4% potassium permanganate solution† was pipetted into the flask and the sides of the flask again washed down and the flask swirled. The flask was then filled to the mark with distilled water and the contents mixed well. A 1-centimeter absorption cell was filled with the yellow-green solution from the flask and placed in a Cenco-Sheard-Sanford Photometer using a 410-490 m μ filter.‡ Exactly eight minutes after addition of the permanganate solution the percent light transmittance of the solution was read against the light transmittance of distilled water to obtain the relative percent light transmittance. The concentration in grams per liter of benzidine dihydrochloride was read directly from a calibration curve (Figure A1) prepared from a series of solutions of benzidine dihydrochloride of known concentration and containing the other components of Bath No. 2. This method was checked during a machine run against gravimetric methods of analysis and found to be accurate within 1-2%, which was of an order sufficient for maintenance of the concentration of benzidine dihydrochloride within the optimum limits.

† Prepared according to F. A. Fales and F. Kenny, "Inorganic Quantitative Analysis" New Edition, p. 408, New York: D. Appleton Century Company (1939)

‡ The cell should be cleaned frequently with cleaning solution. Otherwise a film of benzidine, which is not removed by rinsing with water, forms on the glass and significantly changes the light transmittance.

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Naval Research Laboratory. Report 4001.
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by E. J. Kohn, D. L. Venezky, R. G. Rice, F. J. Ross,
and G. F. Asbury, Sr. 14 pp. & figs., July 11, 1952.

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(Over)
UNCLASSIFIED1. Recording paper -
Development

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- II. Venezky, D. L.
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memorandum

7103/110

DATE: 17 October 1996

FROM: Burton G. Hurdle (Code 7103)
Robert Pellenbarg (Code 6101)

SUBJECT: REVIEW OF REF. (a) FOR DECLASSIFICATION

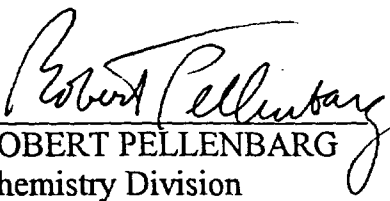
TO: Code 1221.1

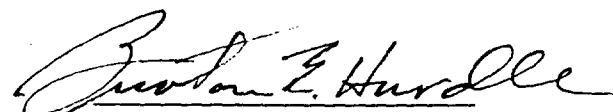
VIA: Code 6100
Code 7100REF: (a) NRL Secret Report #4313, March 1954 (U)
(b) NRL Report #4001 ✓
(c) Declassified from Secret to Confidential, 1570-476/55, E. Bliss,
Code 2027

AD-036791

AD-495964 ✓

1. Reference (a) is a report on the development and testing of a chemical recorder to record (reference (b)) the phase versus time of sonar graphic indicator signals. The recorder included both electronic and mechanical units.
2. Both the concept and design of the recorder and sonar graphic indicator have long been technically and operationally superseded.
3. Reference (a) was reduced to Confidential by reference (c).
4. Based on the above, it is recommended that reference (a) be declassified with no restrictions.


ROBERT PELLENBARG
Chemistry Division


BURTON G. HURDLE
Acoustics Division