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F I N A L R E P O R T

on

DEVELOPMENT OF A NEW DRY TYPE FACSIMILE PAPER

to

THE OFFICE OF NAVAL RESEARCH

under

Contract No. N7-onr-330/II

by

THE ENGINEERING EXPERIMENT STATION

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December 18, 1951

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of the

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Summary

When this work was undertaken, there were two general types of facsimile recording paper in use, namely the wet type and the coated type. It was the objective to discover and develop a dry, uncoated paper, not sensitive to light or time and capable of being inscribed by the passage of sparkless current through the sheet itself.

A paper meeting these requirements was developed which will mark under currents ranging from 3 to 45 ma at 40 to 100 volts. It was discovered that the color of the inscription could be controlled to some extent by the choice of metal for the inscribing stylus. The higher the speed of inscription the higher is the required voltage and current.

Experiments with supersonic vibrations, with x-rays and with cathode rays did not yield any significant results in connection with this project. Furthermore, in addition to the chemical compounds which were found to give positive color reaction to the passage of electric current, a list is furnished which did not show any capabilities for use in recording.

A list of all the patents bearing on the subject of facsimile recording indicates the continued and extensive interest in this field.

The Development of a New Dry Type Facsimile Paper

Foreword:-

The need for a dry type electrosensitive recording paper for facsimile and code message reception was first brought to the attention of the writer in 1944 while engaged in studying radio communication problems for the Air Force. At that time there were available four general methods of recording information none of which seemed to meet requirements satisfactorily. The pen-and-ink method was definitely limited as to speed and reliability, the wet electrosensitive paper then available was objected to because it did not provide a clear cut inscription and besides had to be kept moist until inscribed, and the coated papers available were expensive, required an arc to inscribe them and were subject to objectionable smudging. A fourth method involves a photographic process which delays or precludes immediate use of the information. It seemed that there was a definite need for a recording paper which did not possess any of these objections and which among other uses, might also be suitable for use on board aircraft.

During the next three years this subject was frequently discussed with communications personnel in the Armed Forces. In response to a written request a Research Proposal was prepared and submitted to the Office of Naval Research on July 17, 1947, proposing to do certain basic research toward the development of a recording paper better suited to the requirements.

The ensuing contract, N7-onr-330/II based upon this Research Proposal was dated to go into effect January 1, 1948. Final termination of this contract as extended was December 18, 1951.

This report covers the work leading to the discovery and development under the above contract of a new electrochromotropic paper which it is believed will answer many of the objections listed against other available recording papers.

Survey of Data Inscribing Methods

There are at present many methods of recording information on paper. The most commonly used are:

- A. A pen or pencil marking on paper
- B. A stylus scratching a wax coated paper
- C. A light beam marking a photographic film or paper
- D. An electrical stylus marking a moist chemically treated paper
- E. An electrical stylus marking a dry coated paper

This project is concerned with the development of a new paper which is not a coated paper, which does not require shielding from light, does not lose its sensitivity when dry, and which does not require an arc to mark it.

Considering the present state of the art, it was felt that three possible methods of inscribing a new chemically treated paper would merit consideration, namely

- A. A color change induced by applying supersonic energy
- B. An actinic reaction induced by x-ray but not involving photographic film or paper
- C. A color change induced by conducted current through the paper itself

Although three methods of inscribing were listed, and studied, it was considered from the first that the chemical change induced by conducted current would probably offer the greatest promise for success and would therefore merit the most time and work. This proved to be the case.

Specifications for an Ideal Facsimile Paper

After considering the limitations of the various presently available facsimile and recorder papers, a set of specifications was formulated for the proposed new type paper which might be considered ideal. This would outline the desired qualities in such a paper as follows:

- 1. May be stored dry
- 2. May be used dry and does not require further processing after it is inscribed
- 3. Does not require a high voltage arc for inscribing
- 4. Not affected by varying air pressure either in use or in storage
- 5. Not affected by wide changes in temperature
- 6. Not light-sensitive
- 7. Inscription to be black on white or similar high contrast
- 8. Not subject to smudging, blooming, or subsequent change
- 9. Marking is instantaneous during inscription
- 10. Permanent -- that is, for at least 120 days.

Description of the WSC Electrochromotropic Sheet

A record sheet has been produced which is stable as to time, temperature and altitude and which is capable of being inscribed by passing electric current through it. Such a sheet embodies a compound which reacts chemically with another material to produce a change in color. An electrically conductive impregnation is employed which is changed by the passage of current to produce at the point of contact, the other material necessary to effect a color change in the sheet. The color producing compound and the electrically conductive impregnating material is of such a nature that prior to the passage of an activating electric current, they can both be intimately mixed through the body of the record sheet and remain stable under the conditions listed above.

In this record sheet for electrical inscription, is combined a solution of a substantially colorless basic salt of nitric or nitrous acid in a solvent which will not freeze at low temperatures and which evaporates very slowly; and a Beta naphthyl amine compound which will react chemically with the electrolytic decomposition products of such a salt to form a visible contrast in the sheet.

The Beta naphthyl amine compounds which react chemically as cited above, are best described as electrochromotropic compounds to distinguish them from compounds which may be electrosensitive but do not produce any visible color change in the sheet.

Time must be short in which to effect the necessary electrolytic decomposition and the reaction of the decomposition products with the electrochromotropic compound. Furthermore, if sparking is to be prevented, the conductivity of the sheet must be relatively high, and preferably the sheet itself should be relatively thin and smooth for the same reason. A thinness in the order of .00135" is indicated. The most satisfactory paper found so far is identified as code No. 600 Hi-Wet, furnished by the Patterson Pacific Parchment Co. of 340 Bryant Street, San Francisco. Next in quality for this purpose is designated "bleached transparent bread wrap, specification No. 7050-28 made on program 88-C70" by the Crown-Zellerbach Company of Camas, Washington. Linen cloth of the quality used in tracing cloth, as well as a very fine weave cotton cloth have also been used successfully. While the color of the sheet is not too critical, white is preferred because it will usually afford the highest contrast with the color of the marking made by the passage of electric current through the sheet.

The electrochromotropic compounds are not necessarily conductive. Therefore provision must be made to assure the needed high conductivity, and this process has been found to be rather critical. Conductivity must be substantially uniform throughout the sheet, must remain constant over a long period of time and must not vary appreciably over a temperature range from -35° F to 135° F. The desired conductivity is provided by impregnating an electrolyte into the sheet by means of a particular solvent not subject to freezing or rapid evaporation. Satisfactory solvents must have a low vapor pressure and low freezing points such as polyhydroxy alcohols, derivatives of polyhydroxy alcohols, and polymerized polyhydroxy alcohols. These solvents must remain liquid over the temperature range limitations. Specific examples are: Ethylene glycol $(\text{CH}_2\text{OH})_2$, glycerine $\text{CHOH}(\text{CH}_2\text{OH})_2$, propylene glycol $\text{CH}_3\text{CHOH CH}_2\text{OH}$, diethylene glycol $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$, and triethylene glycol $\text{HOC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OH}$.

The higher molecular weight polyhydroxy alcohols, their esters and polymerized products are not suitable solvents because they do not permit either sufficient solubility or ionization of the electrolytes to provide the necessary conductivity. As examples, the following are not satisfactory solvents: mannitol, sorbitol, carbutoxy-tetra-glycol, dimethoxytetraglycol, ethylene glycol monomethyl ether, polyglycol P-400 and polyglycol P-750.

The solvent in solution contains a stable nitrate salt, at least partially ionized, characterized by absence of color, or at most very low color. When the sheet is impregnated with this solvent and salt it remains conductive even though it appears to be dry in the usual sense.

In general the manufacturing steps of making the sheet conductive are carried out by passing it through a bath of equal parts of water and of glycerine in which a stable nitrate such as ammonium nitrate is dissolved. Excess liquid is removed by passing the sheet between squeegee rolls. Then the sheet is further dried by passing it over heated rolls to remove the excess water, which leaves it dry to the touch and ready to be used or stored. Its electrical resistance, measured as described elsewhere, is in the order of 30 to 100 ohms.

The preferred salt for this purpose is ammonium nitrate, or ammonium nitrite, which of itself does not change color under exposure to light. Such salts are retained in solution by polyhydroxy alcohol solvents throughout the temperature range from -35° F to 135° F. Other salts which are satisfactory are the nitrates and the nitrites of sodium, potassium and zinc, as well as the nitrate of lead. Nitrates of strontium and of barium give good results when dissolved in water and then the glycerine or other softener is added. Nitrate salts of copper and of chromium are not satisfactory because they are highly colored. The essential characteristics of the satisfactory salts are that they are soluble in the solvent, are readily conductive, and of very low color, and that they decompose readily when current is passed through the sheet.

A practical sheet is one which is impregnated with a compound which becomes reactive with the electrolyte in solution in the sheet only upon the passage of electric current to produce a visible color change. The compounds having this characteristic are termed electrochromotropic to distinguish them from compounds which are electrosensitive under like conditions without visible change in color. The Beta naphthyl amine compounds are electrochromotropic and do not react with the nitrate salts in the sheet in the absence of electric current. Beta naphthyl derivatives of N-alkyl diamines up to and including hexamethylene diamine have been found to work.

It has been found that all stable Beta naphthyl amine derivatives capable of forming quincid structures by oxidation are considered best. Those derivatives above hexamethylene diamine may be disregarded as the marking value is not satisfactory.

The following particular compounds are illustrative of operative B-naphthyl amine derivatives:

N, N¹ Di-B-Naphthyl-p-phenylene Diamine
Phenyl-B-Naphthyl Amine
Di-2-Naphthyl Amine

N, N¹ Di-B-Naphthyl Benzidine
 N, N¹ Di-B-Naphthyl ethylene diamine
 N, N¹ Di-B-Naphthyl propylene diamine

This class of compounds reacts with electrolytic decomposition products of nitrates or nitrites to form oxidized, nitro or nitroso compounds. Probably all three types of reaction take place during electrochemical reactions at the stylus or wheel contact. Such reaction products are colored, ranging from light gray to black and from light yellow or brown to dark brown, depending upon the amount of current flowing through the sheet. Introduction of a small amount of metal from the stylus, though not essential for color change, will catalyze the reaction and will affect the amount and intensity of color produced. An iron stylus will produce brown colors, one of copper will produce gray or black, and aluminum produces a greenish color. However the erosion of the stylus does not appear to exceed expected normal wear.

B-naphthyl amine compounds in water suspension can be oxidized, nitrated or sulfonated by adding appropriate reagents. Such compounds vary from green to black depending upon the concentration of the oxidizing, nitrating, or sulfonating agent. This proves that the metal of the stylus is not necessary for color formation.

The color produced from such compounds as phenyl-B-naphthyl amine, di-2-naphthyl amine, N, N¹ di-B-naphthyl ethylene diamine and N, N¹ di-B-naphthyl propylene diamine, is light yellow to light brown which results from formation of nitro-, and nitroso-reaction products at the stylus. The dark brown to black color from such compounds as N, N¹ di-B-naphthyl-P-phenylene diamine and N, N¹ di-B-naphthyl-benzidine results from quinoid structure formation by oxidation from reaction products at the stylus.

The above named class of compounds is not water soluble, but is more or less soluble in other types of solvents. Ethyl alcohol, acetone, pyridine, picoline, xylene, morpholine, thio-diglycol and others may be used as solvents. Pyridine and the picolines have been found to serve best for making solutions of the B-naphthyl amines as the solubility is greater in these two specified solvents than in the others named.

Solutions of one half of one percent to the maximum of the solubility of the B-naphthyl amine compound in the solvent have been used to impregnate the sheet, which may be paper or cloth. Excess solution is then removed by passing the treated sheet between compression rubber rolls. By changing the pressure of the rolls the amount of solution left in the sheet can be controlled. After the solvent is evaporated the sheet is treated with a solution of electrolyte solvent and water to make it conductive. Excess conductive solution is removed by passing the sheet between compression rubber rolls, the amount of solution to remain depending upon the pressure of the rolls. The B-naphthyl amines are insoluble in such solutions and therefore these compounds remain distributed in the fibres of the sheet. After further controlled drying, the sheet is ready for use or for storage.

In some cases it may be desirable, though not absolutely essential, to improve the adhesion of the B-naphthyl amine compounds to the fibres of the sheet by a pretreatment by saturating it with a solution of lead acetate

($\text{Pb}(\text{AC})_2$), zinc acetate ($\text{Zn}(\text{AC})_2$), aluminum acetate ($\text{Al}(\text{AC})_3$), or other mordants. Zinc acetate is preferable due to higher solubility than aluminum acetate and to its relatively low toxicity. Sulfonated alcohols or fatty acids may be used in small amounts to lower surface tension and obtain better distribution and adhesion of B-naphthyl amine compounds over the surface of the fibres of the sheet.

Another method for applying the B-naphthyl amines to the fibres of the sheet is to dissolve the electrochromotropic compound in pyridine, morpholine, thio-diglycol or other solvent which is miscible with water, saturate the sheet with the solution, and without driving off or evaporating the solvent, pass the sheet through a water bath. Thereupon, the excess water will precipitate the B-naphthyl amine compound from the solvent upon the fibres of the sheet.

The following five examples describe methods of impregnating a sheet to make it suitable for electrical recording:

- A. Four and one-half ($4\frac{1}{2}$) grams of N, N¹ Di-B-Naphthyl-p-phenylene diamine are dissolved in 66 ml. pyridine. Paper or cloth previously described is immersed in the solution until thoroughly saturated, then passed between rolls which have very light tension. The solvent is permitted to evaporate at room temperature or may be passed over a sheet of aluminum heated by a hot plate. After the solvent is evaporated the paper or cloth is passed through a bath of 11 grams of ammonium nitrate, $17\frac{1}{2}$ grams of glycerine and $17\frac{1}{2}$ grams of water. Excess liquid is removed by very light tension on the rolls. Excess water is removed by passing the paper over heated rolls. The paper is ready for inscription or may be stored for future use.
- B. Paper or cloth may be pretreated by soaking in a water solution of 5% zinc acetate and dried. After drying the paper is then treated in the same steps as used in Example A.
- C. Nine (9) grams of phenyl-B-naphthyl amine are dissolved in 66 ml. pyridine. Unpretreated or pretreated paper is saturated with this solution and excess solution removed by rolls. After the solvent has been evaporated the paper is saturated with a solution of 9 grams of ammonium nitrate, $14\frac{1}{2}$ grams of glycerine and $17\frac{1}{2}$ ml. of water. After removing excess water by drying the paper is ready for inscription.
- D. Picoline is substituted for pyridine in Example A.
- E. Glycol or diethylene glycol is substituted for glycerine in Example A.

The Beta naphthyl amine compounds are insoluble in water and quite stable, and can be incorporated into the sheet in different ways.

- A. They may be dissolved in pyridine, morpholine or thio-diglycol and applied to the sheet, which is then immediately passed through water. Thereupon, the Beta naphthyl amine compounds are

precipitated on the fibres of the sheet and the solvents being themselves soluble in water, are drained out.

A solution of one of the Beta naphthyl amine group in pyridine may be added to the paper pulp beater to precipitate the compound on the pulp fibres at the time the paper is being manufactured. Thus, when the paper is formed, the Beta-naphthyl amine compound precipitate will be in the fibre matrix of the paper.

Sheets treated in accordance with the foregoing disclosure may be inscribed on suitable recording devices, with as low as 40 volts and up to 230 volts without visible sparking. Either alternating or direct current may be used but an anodic stylus will produce the greatest density of color since the color change is most pronounced at the anode surface of the sheet. When alternating current is used, alternate dots on the stylus side of the sheet will be missing or less visible because of the current reversal. Direct or unidirectional current is therefore preferable.

The preferred electrochromotropic compounds is N, N¹ Di-B-naphthyl-p-phenylene diamine.⁽¹⁾ Experiments have shown that it gives the greatest color contrast between the inscription mark and the surface of the sheet being inscribed. When the sheet is impregnated with this compound and with an ammonium nitrate electrolyte the sheet is slightly gray. However the contrast between the inscribed mark and the surface of the sheet is sufficient for blue printing or for retransmission. These sheets are stable as well as the inscribed markings. Sheets are capable of marking after two years of storage and inscriptions are permanent even when the inscribed paper is soaked in water.

Machines for Making Inscribing Tests

In order to prove the relative effectiveness of different chemical formulae for making recording paper electrosensitive it was necessary to set up a standard test procedure. To this end, two Times photo facsimile machines (Army AN/TXC-1A) were set up, one to act as a transmitter and the other as a receiver. On the transmitter was placed a special test copy of perpendicular, parallel, and diagonal lines of varying thickness which could be reproduced on the receiver.

The Times photo facsimile receiving machine consists of a metal drum approximately six inches in diameter and arranged to rotate normally at 1 RPS. At the same time the drum travels axially .01" per revolution thus permitting the stationary stylus to describe a continuous spiral from one end to the other on the paper on the rotating drum. Thus at the speed indicated, the stylus will scan a sheet 18" x 18" in approximately 7½ minutes. For these tests the conventional stylus designed for inscribing on coated paper by means

⁽¹⁾ Di-beta-naphthylparaphenylenediamine is hereafter designated by the abbreviation DNPPD.

of an arc was replaced either with a steel wire contact stylus, or with a small contact wheel.

The amplifier on this machine is designed to deliver the inscribing signal to the stylus in terms of 1800 pulses per second giving a picture density of 10,000 dots per square inch on the inscribed sheet. The amplifier output was modified by adding a power stage to provide a low voltage current to the contact stylus. Arrangements were provided for applying the output signal to the stylus as AC or as plus or minus DC. Output voltage is in the order of 80 to 140 volts. Usually the stylus is the anode.

For high altitude tests a recording unit was constructed to give a paper speed on a small drum of approximately 18" per second, similar to the AN/TXC-1A recorder. This instrument, together with its drive motor is small enough to be placed inside a bell jar which could then be evacuated to simulate any desired altitude. The glass walled jar made it possible to observe the progress of the test as it was being made.

Equipment was also provided for testing electrosensitive papers by the bar-and-helix method of inscribing. A conventional Alden bar-and-helix recorder was secured. In addition a special bar-and-helix unit was constructed for tests in high speed recording. This unit included a smooth plastic platen with multiple helices embedded therein.

Two tape facsimile transceivers-type RC-58-B were obtained from a surplus store in Philadelphia and were used in a series of experiments to compare bar-and-helix inscription methods with the stylus-spiral method used by Times photo machines.

In order to become acquainted with presently used techniques, a receiving station was set up to take weather maps from the Navy transmitter at Guam. For use in this part of the work the Navy loaned a signal shifter. The College provided the necessary beamed antenna and the rest of the receiving equipment, which fed the map signals into one of the Times photo inscribing machines.

Other special pieces of apparatus were improvised from time to time during the progress of the studies. These included a small inscribing unit for high altitude tests, a magneto struction oscillator for inscribing tests, and a device for studying methods of continuous process of impregnating paper.

Measuring Paper Resistance

For the purpose of measuring the relative resistance characteristics of various papers an arbitrary standard was devised and used. It consists of a flat steel plate as a base on which to lay the paper sample and on top of it a piece of 1 3/8" diameter cold rolled shaft, weighing 1270 grams as the weight. Contact area on the paper is 1.477 square inches. Resistance measurements were made through the paper between the base and the weight by means of a General Radio #650A Impedance Bridge.

Raising the Conductivity of Recording Paper

In order to inscribe without sparking at the stylus, it is necessary that the conductivity of the paper be relatively high. Aluminum powder mixed in the paper pulp during manufacture fails to improve conductivity, probably due to the high resistance oxide coating the particles. Graphite mixed with the pulp makes it black or dark gray, which precludes its use as a recording paper in this instance.

A paper impregnated with an eutectic salt mixture and triethelene glycol seems to have sufficient conductivity, but when held at 130° F for several days the conductivity is reduced too low to be useful.

A solution of ammonium nitrate, glycerine and water applied to the paper after it is made electrosensitive, and followed by drying, results in satisfactory conductivity even after a storage period of two years.

Rate of Chemical Reaction Required

The Times photo drum is 6" in diameter and rotates normally at 60 rpm, which gives a paper speed under the stylus of 18" per second. The signal-modulated carrier frequency is 1800 cps, and the signal dots and spaces are approximately equal. Therefore the rate of chemical reaction on this facsimile machine requires 277 micro seconds per dot. Higher speed capabilities have as yet not been explored.

Wringing and Callendarizing

The use of a rubber rolled wringer following the dipping of the paper into the solution improves the uniformity of distribution, and greatly shortens the required drying before immersion in the next solution. Use of a callendar roll at the end of the impregnating cycle serves to lay the paper fibres into a smooth hard surface. This improves the paper for inscribing.

Effects of pH of Treated Paper

In order to determine the effect of relative acidity or alkalinity of the treated paper upon its reaction to an electrical signal, several variations of chemical treatment were tried. Using DNPPD, oxalic and citric acids were added in varying amounts to bring the paper to a pH as low as 3. although the lowered pH did serve somewhat to produce a greater electrochromotropic reaction, the degree of improvement did not seem to warrant the added treatment.

By adding tri-sodium phosphate to the DNPPD treatment a finished paper was produced with a pH as high as 9. Even at this high level of alkalinity, tests with electrical inscription gave good results. This indicates the pH of the paper is not critical and that DNPPD will inscribe satisfactorily over a wide range of acidity or alkalinity.

Patents

The subject of facsimile writing and recording has intrigued inventors for many years. Witness to this fact is the long list of patents which have been issued in this field. Copies have been obtained of 106 U. S. patents and 11 foreign patents, covering machines, recording materials, and methods having to do with facsimile recording in many of its ramifications. Undoubtedly there are also other allied patents not yet discovered.

In no case however, has a practical dry, non-coated recording paper been described in these patents which in any degree would meet the specifications constituting the objective of this contract. Some of the more promising formulas disclosed were tried out, resulting in the discovery in several cases that some objectionable feature or shortcoming was revealed which was not mentioned in the disclosure.

This large number of patents on the subject of facsimile indicates a widespread realization of the potential needs in the field of recording of information of all kinds. Furthermore, a study of these patents reveals a glaring lack of coverage in the area of a dry, non-coated, recording medium.

A list of all patents found which bear upon the subject, is shown in Appendix D.

Personnel

The following personnel were employed during the course of work under this contract.

Dr. E. G. Vogt
Dr. R. L. Albrook
James L. Van Meter
Roy Flay
John Mudge
Homer J. Dana, Director of Project

Appendix

- A. Supersonic energy for inscribing
- B. X-Rays for non-photographic inscribing
- C. Cathode Rays, induce reactions
- D. List of Patents
- E. Compounds which didn't work

APPENDIX A

The Attempt to Inscribe by Means of Supersonic Energy

One of the designated objectives of this project was to explore the possibility of inscribing a record by means of supersonic mechanical energy. This was tried without visible success, due in part, it is believed, to the lack of sufficient available focused power.

However, since the publication of a paper on this oscillator in the Proceedings of the National Electronics Conference in 1949, considerable interest has resulted in its construction and operation. For that reason, and because of a by-product result of these tests, it is considered desirable to describe this work somewhat in detail.

It was felt that a practical frequency for the purpose in hand should lie within the general range of 10 to 30 KC, and that a magneto-striction type of oscillator would best lend itself to focusing of the output energy. Under the most favorable conditions the efficiency of conversion of oscillator electrical power into sound energy focused to a point as desired is probably in the order of 1%. On this basis, a 200 watt oscillator theoretically would deliver 2 watts of focused energy.

The Design of the Magneto-Striction Oscillator

A magneto-striction oscillator consists of a suitable nickel alloy rod or tube vibrated parallel to its longitudinal axis. The length of the tube for a desired frequency is determined by the formula:

$$F = \frac{V}{2L}$$

Where F is in cycles per second, V is the velocity of sound in the metal of the tube in cm per second, and L is the physical length of the nickel tube. The velocity of sound in nickel varies somewhat inversely with temperature, and at 32° F is approximately 4973 meters per second. For a natural frequency of 14 KC the length of a 3/8" diameter plain nickel thin walled tube would be 17.75 cm. However the attachment of reflectors to each end of the tube required shortening it to 12.7 cm. First aluminum reflector plugs were pressed into the ends of the nickel tube, but these became very hot, indicating the absorption of a large amount of energy. This was partly overcome by silversoldering a thin spherical reflector shell of nickel to the end of the tube. In order to reduce heating in the walls of the nickel tube caused partly by short circuit currents in the AC field of the oscillator driving coils, the tube was slotted endwise. Since slotting full length produces a wide band of unwanted frequencies outside the fundamental, a compromise was effected by cutting a short longitudinal slot under each coil and leaving the middle and the ends of the tube intact. It still showed considerable heating due to the molecular friction within the metal itself.

The oscillator driver consists of an 805 triode, with a grid coil and a plate coil embracing the nickel tube. The latter is suitably secured and anchored at the center.

When the vibrating element of this type of oscillator is magnetized by an alternating voltage, it will vibrate at twice the applied frequency. This results from the fact that the rod will contract on both the positive and the negative swing of the applied voltage. To make the tube vibrate at the applied frequency, a DC bias is supplied by the current in the plate coil. This bias should exceed the AC induced magnetic field.

It was found that a turns ratio of 1:1 between the grid coil and the plate coil was most satisfactory. These were each wound with 666 turns of #25 SSE wire. Applied plate voltage was 1500 at 250 ma.

Tests showed that the spherical reflectors at the ends of the nickel vibrating tube did not focus enough energy to accomplish the desired purpose. When a hollow cone, resembling a sharpened pencil was attached to the tube, and a .080 hole was drilled axially in the point of the cone, an air blast issued from this hole while the tube was vibrated. This air blast is not a result of air expansion due to rise of temperature of the tube because the tube had two open slots greatly exceeding the area of the hole in the cone. Apparently there is a "pumping" action taking place which causes the tube to expel a jet of air with appreciable force, resulting in a much better focusing of energy than was accomplished with any other type of reflector.

Since time was getting short, and the prospect of success in this method seemed somewhat remote, work was suspended on the use of supersonic energy for inscribing facsimile.

APPENDIX B

Inscription by X-Rays

In a vacuum tube in which an electrical discharge is taking place, the rays projected from the cathode are termed cathode rays. When these rays strike a suitable metal target inside the tube they produce x-rays which have a wavelength in the order of one angstrom unit.

Records indicate that ever since Roentgen discovered x-rays on November 5, 1895, studies have been made of chemical reaction to these rays. Since Roentgen's discovery results of tests on about a hundred chemical compounds have been published. As a result the use of chemicals photographically sensitive to x-rays is now widespread. However these are also more or less light sensitive.

In order for x-rays to effect a chemical change, there must be a transfer of energy to the chemical causing a rearrangement or a recombination of the basic constituents resulting in a display of chromotropic properties.

Attempt was made under this contract to prepare a chemical treatment for paper which will not be sensitive to ordinary day light, but will experience

a color change under an exposure to x-rays.

Three samples were prepared, the first with DNPPD dissolved in methoxy ethyl alcohol, another with DNPPD dissolved in thiodiglycol, and the third was treated with a solution of silver chloride dissolved in thiodiglycol. All three were exposed three days to daylight without any apparent change taking place.

The first paper described was placed 9" from the target of an x-ray tube and exposed 90 seconds at 60 KV and $1\frac{1}{2}$ ma. No immediate change was noted, but two days later the paper had turned a greyish blue all over, and six weeks later had remained the same. Unexposed samples of the same paper remained a greyish white without noticeable change.

The second and third papers either exposed or not exposed did not show any color change during the same period.

The mechanism of the activation of chemical reactions by x-rays is not well understood, although there are several significant known reactions which can be produced by x-rays. Included amongst these are the production of ozone from oxygen, the production of hydrogen peroxide with oxygen dissolved in water, the liberation of iodide from potassium iodide, and the liberation of metallic mercury from alpha acetoxymercuri-beta-methoxy hydroxy cinnamic ethyl ester.

A number of chemicals, which it was thought, might react to x-rays, were exposed for five minutes to x-rays at 30 KV and 20 ma. This list follows, together with notation as to the reactions observed.

TABLE I

Test No.	Chemical	Color Change	Character of X-ray		Exposure Time
1	2-Amino Pyridine	none	30 KV	20 Ma	5 min.
2	m-Amino Phenol	Slight bleaching	"	"	"
3	5-benzal-2-thiohydantion	none	"	"	"
4	8-Amino quinoline	none	"	"	"
5	alpha-benzildioxime	none	"	"	"
6	Benzhydrol	none	"	"	"
7	Nigrosine (oil Sol.)	none	"	"	"
8	Nigrosine (H ₂ O Sol.)	none	"	"	"
9	Potassium iodide-Starch	White to yellow	"	"	"
	Sodium Thiosulfate	White to bluish when wet	"	"	"
10	Dinitroso DNPPD	Slight bleaching	"	"	"

TABLE I (continued)

Test No.	Chemical	Color Change	Character of X-ray		Exposure Time
11	Para Phenylenediamine	White to pink after several days	30 KV	20 Ma	5 min
12	Methylene blue	none	"	"	"
13	Lead iodide	none	"	"	"
14	Silver iodide	none ?	"	"	"
15	Diazotype Paper	none	"	"	"
16	Para-Amino phenol	none	"	"	"
17	Benzenesulfonic acid	none	"	"	"
18	Amino diphenylamine HCl	none (slight loss in chemical activity)	"	"	"
19	Acetyl thiourea	none	"	"	"
20	1-Amino anthraquinone	none	"	"	"
21	2-Amino anthraquinone	none	"	"	"
22	2-Amino benzothiazole	none	"	"	"
23	2-Amino fluorene	slightly bleached	"	"	"
24	1-Amino-2-Naphthol-4-sulfonic acid	none	"	"	"
25	1-Amino-8-Naphthol-4-sulfonic acid	none	"	"	"
26	2-Amino phthalhydrazide	none ?	"	"	"
27	1-Amino-8-Naphthol-2,4-Disulfonic Acid	none	"	"	"
28	Para-Amino Diphenyl	slight increase in chemical activity	"	"	"
29	Benzotriazole	none	"	"	"
30	Catechol	none	"	"	"
31	Diaminodiphenylamine	none	"	"	"
32	2,4 Diaminotoluene	none ?	"	"	"

TABLE I (continued)

Test No.	Chemical	Color Change	Character of X-ray	Exposure Time
33	P,P' Diaminodiphenylmethane	White to tan (shows most activity of organic compound)	30 KV 20 Ma	12 min.
34	Diphenylamine	none	"	5 min.
35	4,4' dihydroxybenzophenone	none	"	"
36	4,4' diaminodiphenylamine 2-Sulfonic Acid	none	"	"
37	2,5 diaminotoluene HCl	slight loss in activity	"	"

(none ? = any action so slight as to be doubtful.)

APPENDIX C

Cathode Rays

It is known that cathode rays, in some instances, cause more chemical activity than do x-rays. However it is difficult to project cathode rays outside the envelope of a vacuum tube, and for that reason not much work has been done with them. For this project a cathode ray tube was provided with a flanged cover to replace the screen end. After releasing the vacuum, the end plate can be removed and the chemical sample introduced, after which the tube must be closed and pumped down again for the test.

Some study was given to providing a window of some material which would pass the cathode rays to the exterior for easier testing. Beryllium foil 008" thick proved opaque to the rays, as did cellophane plastic 003" thick, using an anode voltage of 10 KV. The few tests which time permitted to be made on a cathode ray emitter all proved negative.

Unexpected Results

A sample of lead iodide was placed in the cathode ray tube and the latter evacuated. When the tungsten filament was heated and without any electrical charge on the anode the sample turned from yellow to black. A sample of bismuth chloride likewise turned from white to black.

This indicates that a very definite chemical activity results from the thermionic effect of the tungsten filament, and should prove an interesting field for fundamental research.

APPENDIX DFacsimile Patents

The following is a list of all the patents discovered which bear upon the subject of facsimile and facsimile recording, both in the U.S. and in foreign countries. This list indicates the continued interest in this field and the persistent effort being devoted to improving the art.

U.S. Patents

6-420	1-333-700	2-008-966	2-306-471
129-841	1-457-255	2-030-973	2-309-492
130-810	1-457-581	2-035-474	2-310-946
132-455	1-550-018	2-038-486	2-316-340
141-774	1-588-482	2-063-992	2-318-013
160-402	1-633-324	2-075-022	2-319-765
160-403	1-646-296	2-080-209	2-328-198
160-404	1-666-329	2-108-852	2-339-267
160-580	1-697-932	2-112-864	2-346-670
166-859	1-765-448	2-118-910	2-358-839
166-860	1-770-493	2-154-918	2-367-113
166-861	1-770-494	2-173-141	2-372-829
168-465	1-796-584	2-181-533	2-374-214
168-466	1-803-532	2-186-732	2-400-544
168-467	1-844-190	2-186-850	2-419-296
366-078	1-844-199	2-192-127	2-421-367
423-970	1-851-298	2-214-559	2-425-742
440-953	1-857-230	2-217-478	2-450-254
655-970	1-880-449	2-225-247	2-453-632
670-510	1-885-355	2-229-091	2-435-700
761-310	1-886-480	2-244-147	2-437-708
	1-892-099	2-251-742	2-440-526
	1-893-074	2-263-616	2-442-596
	1-916-947	2-281-013	2-451-331
	1-918-492	2-283-220	2-453-430
	1-939-232	2-283-558	2-459-521
	1-965-635	2-294-146	2-461-892
	1-970-539	2-294-149	2-471-607
		2-294-150	2-677-651 ⁽¹⁾

(1) Patent issued and assigned to State College of Washington under this ONR contract.

Foreign Patents

British

318-203
329-258
537-593
551-856
661-856

German

81-241
86-826
388-724
523-258
543-635

French

36-297

TABLE I (continued)

Test No.	Chemical	Color Change	Character of X-ray	Exposure Time
11	Para Phenylenediamine	White to pink after several days	30 KV 20 Ma	5 min
12	Methylene blue	none	"	"
13	Lead iodide	none	"	"
14	Silver iodide	none ?	"	"
15	Diazotype Paper	none	"	"
16	Para-Amino phenol	none	"	"
17	Benzenesulfonic acid	none	"	"
18	Amino diphenylamine HCl	none (slight loss in chemical activity)	"	"
19	Acetyl thiourea	none	"	"
20	1-Amino anthraquinone	none	"	"
21	2-Amino anthraquinone	none	"	"
22	2-Amino benzothiazole	none	"	"
23	2-Amino fluorene	slightly bleached	"	"
24	1-Amino-2-Naphthol-4-sulfonic acid	none	"	"
25	1-Amino-8-Naphthol-4-sulfonic acid	none	"	"
26	2-Amino phthalhydrazide	none ?	"	"
27	1-Amino-8-Naphthol-2,4-Disulfonic Acid	none	"	"
28	Para-Amino Diphenyl	slight increase in chemical activity	"	"
29	Benzotriazole	none	"	"
30	Catechol	none	"	"
31	Diaminodiphenylamine	none	"	"
32	2,4 Diaminotoluene	none ?	"	"

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