

GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station

PROJECT INITIATION

18 December 1967

Project Title: "Printing Research

Project No.: A-1065

Project Director: W. H. Burrows

Sponsor: Hammermill Paper Company

Effective 8 December 1967 Estimated to run until: 7 June 1968

Type Agreement: Standard Industrial Agreement
With Addendum dated 8 December 1967 Amount: \$11,000.*

Reports: As required

Contact Person: Dr. R. W. Brown
Director of Central Research
Hammermill Paper Company
Erie, Penn 16512

* for phase I of total effort, further funding and work to be the subject of review and amendment

Assigned to Chemical Sciences & Materials Division

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GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station

PROJECT TERMINATION

Date September 17, 1969

PROJECT TITLE: Printing Research

PROJECT NO: A-1065

PROJECT DIRECTOR: W. H. Burrows

SPONSOR: Hammermill Paper Company

TERMINATION EFFECTIVE: August 31, 1969

CHARGES SHOULD CLEAR ACCOUNTING BY: September 30, 1969

Final invoice to be issued as soon as
all applicable charges have cleared
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GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION

225 North Avenue, Northwest - Atlanta, Georgia 30332

March 28, 1968

Hammermill Paper Company
Erie
Pennsylvania 16512

Attention: Dr. Richard W. Brown
Director of Research

Subject: Interim Technical Report

Gentlemen:

This report presents the current state of progress on your project, "High Speed Printing Process" (E.E.S. Project No. A-1065), as of March 14, 1965, on which date we reviewed this material for you orally. Major emphasis has been placed upon the generation of a feasible concept for the chemical system of the photosensitive medium for this specific application, rather than upon exploration of a wide spectrum of light sensitive systems.

Areas of Exploration

1. Non-Silver Halide Light-Sensitive Systems

Our proposal mentioned Kosar's Light Sensitive Systems as a source material for this area, and we have given this text further consideration. It has not been a fruitful endeavor, for these systems are generally of low quantum yield and lack the sensitivity required for the high speeds envisioned in this application. Furthermore, contact with some chemical developing medium is required, which would be undesirable, if not impossible, in the present application. Modifications, such as the use of evaporated films to increase sensitivity and response to developing medium, have been considered, but the order of benefication has not been sufficient to be considered encouraging.

Photothermographic materials have been investigated. These materials are sensitized by light and developed by heat. There are few materials in this area, other than the silver organics, which are well covered by patents. All of these materials appear to require relative intense exposures for time periods greatly in excess of those envisioned.



2. Photochemistry

Turro's Photochemistry, Noyes, et al, Advances in Photochemistry, etc. have not been fruitful as possible sources of ideas. Investigations in this area are limited largely to non-thermal organic transformations, and the approach is largely academic, concerned primarily with electron energy states in reference to the phenomena of fluorescence and phosphorescence. There are practical applications, in that photochemistry provides an explanation of observed phenomena (e.g., the nature of the excitation of dyes to higher energy states and subsequent conversion of the polymerization catalysts to an active state in the Hughes photopolymerization mechanism); however, to proceed from theory to application is quite another thing.

It had been hoped that within the rather narrow confines of photochromism we might find theory pointing the way toward application. Such mechanisms as were investigated, however, involved time and energy factors entirely out of the range within which our proposed medium must operate.

3. Spectrum of Literature Studies

The general literature studies were entered by developing a broad list of topics and copying the indexes on these topics for the period 1956-present. As these indexes were surveyed, and as our study of pertinent topics proceeded, it was necessary to abandon some of the original topics and add others. In some instances it became necessary to expand narrow topics into broad categories (e.g., "photochemistry," "photoionization," and "photoconductivity" to "photo-", all topics). From these, the following list has evolved, which is current:

- | | |
|------------------------------------|--------------------------------|
| A. Photoconductivity, Theoretical | K. Conductivity; Organic, |
| B. Photoconductivity, Organic | Metal Organics, etc. |
| Materials (excl. of dyes) | L. Photodielectric Effect |
| C. Citations | M. Photoelectric Effect |
| D. Photoconductivity Surface | N. Photoionization, Ionization |
| E. Photoconductivity, ZnO and | O. Thermolysis, Thermochromism |
| Related Compounds | P. Photolysis |
| F. Photoconductivity, Gr. II, | Q. Photochemistry |
| IV Compounds | R. Photochromics |
| G. Photoconductivity, Other | S. Syntheses |
| Inorganics | T. (Unassigned) |
| H. Photoconductivity Solutions | U. Electrophotography |
| I. Photoconductivity Compositions, | (See also, E, F, G) |
| Dyes, etc. | V. Thermography |
| J. (Unassigned) | W. Direct Photocopying |
| | X-Z. Misc. |

The indexes are being reviewed, and those entries that appear to be of interest are being followed up by copying the abstracts. These abstracts are, in turn, reviewed. Those that are pertinent are mounted on 5 x 8 cards for filing, using the letter designations in the preceding list. In many

instances, it is possible to work directly from the abstracts; however, in every instance that indicates the need for further study, the original article is obtained. Our library has extensive holding in the technical literature, and such as it does not have is available by interlibrary loan. So far, we have not had need of special translations, although these can be arranged. Some of these articles are already available in translation from the original.

Evolution of a Concept

Our report of May 4, 1966 to Curtis 1000, Inc. outlined a high speed printing process employing a battery of semiconductor lasers to transfer a matrix of lighted spots to a photosensitive surface. The basic limitations of this system are the following:

1. Short-term illumination (of the order of 10^{-9} seconds)
2. Small area (dot size of the order of 10^{-2} mm²)
3. Triplicate registration (requiring transparency throughout the exposure period.)

In order to meet these limitations, the chemical system that is to record this light pattern must conform to the following:

1. High yield. The amount of chemical change produced must be large by comparison with the amount of energy absorbed from the laser beam during the brief period of exposure. This can be accomplished only through the action of a "trigger" mechanism.

2. "Trigger" mechanism. The energy of the light beam must be used only to activate the molecules from a state in which they are unreceptive to additional energy (e.g., dielectric heat) to a state in which they can receive this additional energy. Then, with the chemical system at an energy level just below "critical," the slight energy of the photons will condition the molecules to a receptive state, and the additional energy they then receive bolt them over the hump into the "critical" region.

3. Pin-point delineation of energy levels will be necessary; e.g., a precise temperature point, such as a melting point, phase transition, membrane rupture pressure, etc. must be used.

Description of a System

We assume the following description of a system and examine the numerical relationships of its parameters as a means of investigating, from a theoretical standpoint, the feasibility of this concept.

March 28, 1968

The photosensitive material will be a photoconductive, colorless organic compound of comparatively high melting point (ca 90-125° C; e.g., phenanthrene, m.p. 100° C). Other substances and other characteristic temperature points may be used, but for simplicity the following description will be limited to phenanthrene and its melting point.

The phenanthrene (or other suitable material) will be deposited as a thin, transparent film on the surface of a suitable sheet material, such as glassine paper or plastic film. As this sheet approaches the laser beam source, it is brought up to a temperature a few degrees below the melting point (or other suitable point) of the material by infrared, convection, or other suitable form of heating.

While at this temperature the sheet is exposed simultaneously to the laser beam of very short ($\sim 10^{-9}$ sec) duration and to high frequency ($\geq 10^8$ cps) dielectric heating for a longer period ($\sim 10^{-6}$ to 10^{-4} sec). The phenanthrene is non-conductive in the absence of light; hence, that portion of the film that remains unexposed to light is not affected. Each spot that is struck by a ray from the laser source, however, is thereby rendered conductive by virtue of the property of photoconductivity.

Under the influence of dielectric heating, each spot that has been rendered conductive increases in temperature by a few degrees. This temperature increase is determined by a combination of factors; the intensity of the photoconductivity effect (quantum yield), the decay rate and period of the photoconductivity, the specific heat of the material, etc. In the system envisioned, the temperature of the phenanthrene will be raised sufficiently that the crystal will melt, at least on the surface.

The melting of the phenanthrene would be accomplished by a color change produced by a suitable mechanism; e.g., dissolution of colored dye particles, liberation of a dye from micro-capsules, or a chemical reaction in the liquid phase. Thus, the spot that had been exposed to the laser beam would become colored, whereas surrounding areas, unless subsequently exposed to a sufficiently high temperature to cause fusion of the phenanthrene (i.e., 100° C or 212° F), would remain uncolored.

The manner in which this system might operate is shown in the following example:

Power available for conversion to heat in dielectric material:

$$p = 1.41 V^2 f \times F \frac{A}{d} \times 10^{-15} \text{ kw}$$

where V = applied voltage
 f = frequency
 F = loss factor = E x P.F.

March 28, 1968

E = dielectric constant
P.F. = power factor = $\cos \theta$ (θ = phase lag of i with respect to E)

A = area of material
 d = depth or thickness of material

For a dot $0.1 \text{ mm} \times 0.1 \text{ mm} \times .01 \text{ mm}$ (.25 mils), $\frac{A}{d} = 1$; then, for a specific power source, assume:

$V = 1,000$ (plates closely spaced)
 $f = 10^7 \text{ cps}$
P.F. = .01 to .03
 $E = 2.8$

Then $F = 2.8 \times .02 = 5.6 \times 10^{-2}$ (av.)
 $p = 1.41(10^3)^2 \times 10^7 \times 5.6 \times 10^{-2} \times 10^{-15}$
 $= 7.9 \times 10^{-4} \text{ kw}$
 $= 7.6 \times 239 \times 10^{-4} = 0.19 \text{ cal/sec}$

Suppose that, by photoionization, E is increased by a factor of 5, and P.F. by a factor of 10 to 20, then p becomes

$p' = 0.19 \times 50 \text{ to } 100 = 9.5 \text{ to } 19.0 \text{ cal/sec}$
 $= \Delta H_{\text{photocond.}}$

The heat of fusion of phenanthrene = 24.3 cal/g at 98.2° C ; its density is 1.025 g/mil. ($\Delta H_{t_2-t_1}$ is small by comparison with ΔH_{fusion} .)

For a dot whose dimensions are $0.1 \text{ mm} \times 0.1 \text{ mm} \times .01 \text{ mm}$, ($10^{-4} \text{ mm}^3 = 10^{-7} \text{ cc}$), the heat of fusion is

$$24.3 \times 1.025 \times 10^{-7} = 2.49 \times 10^{-6} \text{ cal}$$

The time required for the heat generated by the dielectric source described above to melt the phenanthrene dot, activated by photoconductivity would be

$$t = \frac{2.49 \times 10^{-6} \text{ sec}}{\Delta H_{\text{photocond.}}}$$

The range of ΔH was calculated to be $9.5 \text{ to } 19.0 \text{ cal/sec}$. If a value of 12.45 cal/sec is taken as median the time becomes

$$t = \frac{2.49 \times 10^{-6}}{12.45} = 2 \times 10^{-7} \text{ sec}$$

The proposed exposure time is only about 10^{-9} sec; however, it has been shown* that the photoconductivity of phenanthrene extends (at a decay rate) over a period of 6 to 8 microseconds, which exceeds the estimated time requirement by a factor of 30 to 40 times.

Record of Invention

Inasmuch as the preceeding analysis indicates the feasibility of this approach, a Record of Invention, dated March 22, 1968, has been filed with our patent attorneys. They will make a preliminary search to determine the advisability of proceeding with an application. When their report is received, it will be forwarded to you. It is our understanding that, should a patent application be in order, it will be handled by an attorney for Hammermill.

The essence of novelty lies in the cooperation of the following factors:

(a) A material (e.g., a mixture of phenanthrene and solid dye particles) is prepared, such that, upon melting, the material will change from clear and transparent (in thin sections) to dark and opaque.

(b) The material is brought to a temperature slightly under its melting point by ordinary heating methods.

(c) The material is exposed to a pattern of light dots from a laser or other suitable source, increasing the conductivity of the material at the lighted points.

(d) The material is subjected to dielectric heating which can now be effective only at the lighted points.

(e) These points are raised in temperature to the melting point, thus bringing about a change of color (darkening) of those points.

(f) The medium remains transparent throughout the exposure to light, darkening only when the dielectric heating has brought it to its melting point; hence, multiple copies may be made with a single exposure.

Future Work

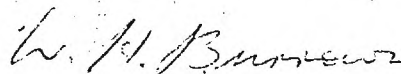
As we have indicated, the concept described and analyzed in the preceeding paragraphs has been derived from our studies of the literature

*Allan Kawada and R. C. Jarnagin, "Delayed Ionization of Excited Phenanthrene and Anthracene in Solution," The Journal of Chemical Physics, Vol. 44, No. 5, (March 1966).

during the course of this project. It does not represent a completed research effort, and this report is only an interim report on our research effort to date. During the remainder of the project we expect to accomplish the following:

1. Completion of the literature survey and preparation of a complete bibliography of the topics for the period included in our study.
2. Compilation of pertinent abstracts and articles.
3. Derivation of a more complete and, possibly, more sophisticated concept of the chemical mechanism of the proposed high-speed printing process.
4. Construction of a mathematical model for the more complete mechanism.

Respectfully submitted,



W. H. Burrows
Project Director

Approved:



Frederick Bellinger, Chief
Chemical Sciences and Materials Division



GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION 225 North Avenue, Northwest · Atlanta, Georgia 30332

A-100

June 17, 1968

HAMMERMILL PAPER COMPANY
Erie, Pennsylvania 16512

Attention: Dr. Richard W. Brown
Director of Research

Subject: Final Technical Report
Project A-1065: Printing Research

Gentlemen:

This report covers the work done in accordance with our proposal of November 15, 1967 and your Purchase Order of December 20, 1967, Requisition No. 9370. This proposal and purchase order covers Phase I of the over-all program of development of a high-speed printing process initially described in our report of May 4, 1966 to Curtis 1000, Inc.

Objectives

The objectives of Phase I were "to provide detailed, documented background information, classification of candidate systems, recommendation for selection of the best candidate system, process steps for utilizing the system (media and high intensity, narrow beam light source), and detailed plans for future research."

During the course of the research we have kept abreast of industrial developments in the field of semiconductor (diode) lasers. We are satisfied that this development is proceeding at a sufficiently rapid pace in several companies and that the materials will be available by the time we reach the point of developing an optical system for this concept. For this reason, and in accordance with our discussions with your research personnel, we have placed our main emphasis upon the theoretical and technical background of the chemical (photosensitive) system that must be developed to meet the illumination and speed requirements of the concept.

Method of Approach

We have made an extensive search of the current literature on the reactions of light with matter, keeping in mind the specific requirements

and limitations imposed by our basic concept. This concept excludes such areas as wet development, contact printing, etc., as the photosensitive material is completely insulated from contact with transient matter.

From a voluminous survey of indexes, we derived a selection of abstracts. Many of these were found to be of no immediate value as background material and were stored without further processing. Those that appeared to be of value were sorted into appropriate categories and mounted on 5 x 8 inch cards as a reference file. Following are the categories included in this file:

- A. Photoconductivity, Theoretical
- B. Photoconductivity, Organic, General
- C. Photoconductivity, Dyes & Pigments
- D. Photoconductivity, Polymers
- E. Photoconductivity, Inorganics
- F. Photoconductivity, Solutions etc.
- G. Conductivity, General
- H. Photoelectric Effect
- I. Photoionization & Ionization
- J. Photolysis
- K. Photochemistry
- L. Photochromics
- M. Syntheses
- N. Electrophotography
- O. Thermophotography
- P. Photocopying, General

A copy of this file has been forwarded to you. We believe that you will find the abstracts more useful than the usual author-title-source bibliography.

An intensive study and review of these abstracts served to generate ideas as to chemical systems that might be applied to our basic printing concept. Those abstracts that appeared to be relevant to these various ideas were followed up by collection and study of the original articles. It is these articles (plus a few books and isolated news items) that make up the Bibliography of this report.

The purpose of the very extensive literature search was (a) to generate ideas from which we might formulate a concept of a novel, high speed, non-mechanical printing system meeting the basic requirements of this project, (b) to provide sufficient theory and supporting data to justify a research program to reduce the concept to practice, (c) to discover any prior art that might be infringed by our concept, and (d) to provide a nucleus of information and literature references to serve as a guide during subsequent research efforts.

On March 14, 1968 we conferred with Dr. Richard W. Brown and Mr. John DiLuzio, at which time we reviewed our method of procedure and the chemical

system that then appeared to offer a means of meeting the stringent requirements of the printing concept. This review was incorporated in our Interim Report of March 18. On April 24 we conferred with Mr. John Studeny concerning the status of developments to that date.

The following excerpt from our Interim Report describes the concept as it was presented at that time.

Evolution of a Concept

Our report of May 4, 1966 to Curtis 1000, Inc. outlined a high speed printing process employing a battery of semiconductor lasers to transfer a matrix of lighted spots to a photosensitive surface. The basic limitations of this system are the following:

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2. Small area (dot size of the order of 10^{-2} mm²)
3. Triplicate registration (requiring transparency throughout the exposure period.)

In order to meet these limitations, the chemical system that is to record this light pattern must conform to the following:

1. High yield. The amount of chemical change produced must be large by comparison with the amount of energy absorbed from the laser beam during the brief period of exposure. This can be accomplished only through the action of a "trigger" mechanism.

2. "Trigger" mechanism. The energy of the light beam must be used only to activate the molecules from a state in which they are unreceptive to additional energy (e.g., dielectric heat) to a state in which they can receive this additional energy. Then, with the chemical system at an energy level just below "critical," the slight energy of the photons will condition the molecules to a receptive state, and the additional energy they then receive bolt them over the hump into the "critical" region.

3. Pin-point delineation of energy levels will be necessary; e.g., a precise temperature point, such as a melting point, phase transition, membrane rupture pressure, etc., must be used.

Description of a System

In our Interim Report of March 28, 1968, we described a system and examined the numerical relationships of its parameters. The following is taken from that description.

The photosensitive material will be a photoconductive, colorless organic compound of comparatively high melting point (ca 90-125° C; e.g., phenanthrene, m.p. 100° C). Other substances and other characteristic temperature points may be used, but for simplicity the following description will be limited to phenanthrene and its melting point.

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Under the influence of dielectric heating, each spot that has been rendered conductive increases in temperature by a few degrees. This temperature increase is determined by a combination of factors; the intensity of the photoconductivity effect (quantum yield), the decay rate and period of the photoconductivity, the specific heat of the material, etc. In the system envisioned, the temperature of the phenanthrene will be raised sufficiently that the crystal will melt, at least on the surface.

The melting of the phenanthrene would be accomplished by a color change produced by a suitable mechanism; e.g., dissolution of colored dye particles, liberation of a dye from micro-capsules, or a chemical reaction in the liquid phase. Thus, the spot that had been exposed to the laser beam would become colored, whereas surrounding areas, unless subsequently exposed to a sufficiently high temperature to cause fusion of the phenanthrene (i.e., 100° C or 212° F), would remain uncolored.

The manner in which this system might operate is shown in the following example:

Power available for conversion to heat in dielectric material:

$$p = 1.41 V^2 f \times F \frac{A}{d} \times 10^{-15} \text{ kw}$$

where V = applied voltage
 f = frequency
 F = loss factor = E x P.F.

ϵ = dielectric constant
P.F. = power factor = $\cos \theta$ (θ = phase lag of i with respect to E)

A = area of material
 d = depth or thickness of material

For a dot $0.1 \text{ mm} \times 0.1 \text{ mm} \times .01 \text{ mm}$ (.25 mils), $\frac{A}{d} = 1$; then, for a specific power source, assume:

V = 1,000 (plates closely spaced)
 f = 10^7 cps
P.F. = .01 to .03
 E = 2.8

Then $F = 2.8 \times .02 = 5.6 \times 10^{-2}$ (av.)
 $p = 1.41(10^3)^2 \times 10^7 \times 5.6 \times 10^{-2} \times 10^{-15}$
 $= 7.9 \times 10^{-4} \text{ kw}$
 $= 7.6 \times 239 \times 10^{-4} = 0.19 \text{ cal/sec}$

Suppose that, by photoionization, E is increased by a factor of 5, and P.F. by a factor of 10 to 20, then p becomes

$p' = 0.19 \times 50 \text{ to } 100 = 9.5 \text{ to } 19.0 \text{ cal/sec}$
 $= \Delta H_{\text{photocond.}}$

The heat of fusion of phenanthrene = 24.3 cal/g at 98.2° C ; its density is 1.025 g/ml . ($\Delta H_{t_2-t_1}$ is small by comparison with ΔH_{fusion} .)

For a dot whose dimensions are $0.1 \text{ mm} \times 0.1 \text{ mm} \times .01 \text{ mm}$, ($10^{-4} \text{ mm}^3 = 10^{-7} \text{ cc}$), the heat of fusion is

$$24.3 \times 1.025 \times 10^{-7} = 2.49 \times 10^{-6} \text{ cal}$$

The time required for the heat generated by the dielectric source described above to melt the phenanthrene dot, activated by photoconductivity would be

$$t = \frac{2.49 \times 10^{-6} \text{ sec}}{\Delta H_{\text{photocond.}}}$$

The range of ΔH was calculated to be $9.5 \text{ to } 19.0 \text{ cal/sec}$. If a value of 12.45 cal/sec is taken as median the time becomes

$$t = \frac{2.49 \times 10^{-6}}{12.45} = 2 \times 10^{-7} \text{ sec}$$

The proposed exposure time is only about 10^{-9} sec; however, it has been shown* that the photoconductivity of phenanthrene extends (at a decay rate) over a period of 6 to 8 microseconds, which exceeds the estimated time requirement by a factor of 30 to 40 times.

Modification of the Proposed System

The color producing mechanism of the proposed system involved melting of the photoconductive material, accompanied by "dissolution of colored dye particles, liberation of a dye from micro-capsules, or a chemical reaction in the liquid phase." Subsequent study has not only supported the feasibility of such mechanisms, but suggested the following modifications, as well:

(1) Utilization of the photoconductive properties of leuco dye bases. Mehl and Wolff (F.2)[†] report the photoconductivity of the leucobase of malachite green in solid solution in various organic media. The conversion of a leucobase to a dye in such a system might be brought about by the addition to the organic medium of a suitable oxidizing agent, such that a thermally initiated reaction would take place between the molecules of oxidizing agent and leucobase. If, in addition, initiation of the reaction is tied to a phase change (e.g., melting of the oxidizing agent leucobase or organic medium) the color development could be made highly sensitive to a slight temperature change within a restricted range. Many dyes, as well as leucobases are photoconductive (C.1 through C.3).

(2) Encapsulation in photoconductive film forming material. A number of synthetic and natural polymers (D.1 through D.9) exhibit photoconductive properties. Such material might be employed as a film for the microencapsulation of one reactant (e.g., a leucobase solution) of a color-producing reaction. The other (e.g., oxidizing agent) might be incorporated in the matrix, which would be a rigid gel. Light would render the capsule wall photoconductive; the wall would then melt or otherwise rupture under dielectric heat, permitting localized reaction to produce the color.

(3) Use of a mixture of thermosensitive dyes and a phosphor. Robillard (O.2) proposes a related system (see below) and suggests the image formation be brought about by use of a phosphor (whose dielectric constant would be changed locally by the incident light) dispersed into a binder together with a "proper addition of thermosensitive dyes," the whole being cast into film form. There is no indication as to what thermosensitive dyes might be used; however, a patent issued to Moncrieff-Yeates in 1957 (O.3) discloses a system closely related to that of Robillard's, and the suggested dye is leuco-rosaniline hydrochloride, which changes from colorless to green when heated to a temperature between 100° and 200° C.

*Allan Kawada and R. C. Jarnagin, "Delayed Ionization of Excited Phenanthrene and Anthracene in Solution," The Journal of Chemical Physics, Vol. 44, No. 5, (March 1966).

[†]The figures in parentheses refer to the attached bibliography.

We think it doubtful that such a reaction would have the temperature sensitivity and pin-point response that is required for our concept. Nevertheless, it would bear investigation.

Related Art

Robillard (0.2) in 1954 proposed a photographic system based on the variation of dielectric constant of a phosphor under illumination, as part of a general article on "New Approaches in Photography." Two items in this article are of particular interest. First is the analysis of photographic systems as to the steps: formation of latent image, development, and image fixation. This analysis leads the author directly to the consideration of a photothermographic system utilizing dielectric heating and, within that system, to a set of premises closely allied to our own. Second is the mathematical description given of the proposed system, which can be of material use to us in the design of equipment for effecting the color registration in our system. We have sent you a copy of Dr. Robillard's article for your file.

To the best of our knowledge, Dr. Robillard's concept never proceeded beyond the hypothetical stage. We have tried to contact him to verify this; however, he has not been with the Sanborn Company (Hewlett-Packard Corporation, Sanborn Division) since 1954, and has apparently returned to France to make his residence there. We are continuing our effort to contact him and have written to a Paris address where we think he might be contacted.

That Dr. Robillard's concept does not infringe ours is clearly seen in the following considerations:

1. Ours is an electrodeless system, the heat being generated by induction currents within isolated particles of photoelectric material; his requires two conductor surfaces in contact with the light-sensitive material.
2. Our system employs very brief exposure, with delayed decay of the photoconductivity, during which time the image is developed by a very strong RF field. His purpose is to utilize a low power RF system (portable), hence exposure periods of 10^{-5} seconds are permissible.
3. The thermosensitive dye system proposed by Robillard, as was previously pointed out, probably would not meet the sensitivity requirements of the system we propose. His description does not include alternate color producing mechanisms.

Moncrieff-Yeates obtained patents (0.3) in 1957 (filed 1953) on ideas closely related to Robillard's, except that the source of heat disclosed was ordinary A.C. or D.C. current. Obviously, electrode contact is a

requisite of this system. The same considerations apply here as in the comparison of our concept with Robillard's. Copies of Moncrieff-Yeates' patents have been sent for your file.

It is our opinion that the ideas presented by Robillard and patented by Moncrieff-Yeates serve to strengthen our position that the color registration mechanism proposed by us has substantial merit.

Discussion

Perhaps the most encouraging feature of our proposed concept are the facts that (1) it was generated from our studies of the interactions of light with matter, independently of any knowledge of related art, (2) we were able to draw upon known data to present a mathematical model in support of our concept, (3) we subsequently found through our search a related art supported by a different, but equally valid, mathematical model, and (4) the concept and related art complement, but do not infringe, one another. Either might, in time, have evolved into the other, but, if so, it would have been for entirely different purposes.

It is also encouraging that, by elimination, this concept appears to be the only one that could meet the specified requirements. Photochemical reactions, including photolysis, fall far short of the quantum yield needed for registration. Additional energy must be supplied to fix the image, and--with both electrodes and chemicals eliminated from contact--it is difficult to imagine a means of supplying that energy being provided except as RF energy acting upon photoconductive centers.

Even so, the proposed concept still has a rocky road to travel before being reduced to practice. Present data are not sufficient to provide a mathematical model complete as to all details of materials, time and temperature factors, design of RF system, etc. Much remains to be done by way of interdisciplinary analysis for the purposes of making best use of available theory and data and of specifying needed areas of exploration. An experimental program following such analysis may then be expected to yield maximum returns.

Future Work

As stated, this report covers Phase I of the overall research program for development of a high-speed printing process. Phase I was originally intended for critical review of present and prior art, but has actually proceeded well beyond that point in deriving a basic concept and documenting its feasibility.

Phase 2 should include the following activities:

1. Interdisciplinary Analysis of Concept

By its nature, this research program is involved in various disciplines that are concerned with the generation of radiant energy and

its interactions with matter. The proposed concept involves (a) semiconductor lasers as a source of light, (b) optical systems for directing the laser beams, (c) photoconductive materials to be activated by that light, (d) an RF system to generate thermal currents in the photoconductors, and (e) heat-sensitive materials to react with the thermal currents. For development of this concept, we shall require the assistance of specialists in solid state physics, optics, electronics, and special areas of physical and organic chemistry. Some of these specialists have been consulted from time to time during Phase I with respect to specific items of question, but no full-scale analysis of the concept was possible within the limitations of that phase.

The purposes of such analysis, as stated, would be:

a. Critique of theoretical aspects of the concept. Individual and group discussions would explore the various disciplinary aspects of the concept and the limitations which each might impose upon the other. These discussions would be directed toward such matters as optimum wave length of activating light, from the standpoints of both semiconductor laser design and photoconductive material; relationship of photoconductive and thermally sensitive materials in design of the registering medium; optimum RF frequency, voltage, etc. with respect to registering medium; plus many more specific matters that will lead up to the experimental program.

b. Design of experimental program. The critique will considerably narrow the scope of the experimental program, eliminating useless lines of endeavor and concentrating attention upon those items of information needed for development of the concept. From these discussions will be formed a unified and well oriented experimental program.

2. Preliminary Experimental and Informational Program

Initially, as indicated, it will be necessary to fill in the informational gaps left by our Phase I survey and needed to make decisions as to optimum materials selection and equipment design. Some of this information might be obtained through further library research; for this purpose the extensive file of indexes and abstracts developed in Phase I should be useful as a starting point. However, additional information will need to come from experimental work in any or all of the involved disciplines.

3. Development Program, Chemical System

The physical aspects of the concept are comparatively well defined; following the aforementioned critique it is not expected that further work will be done in that area until development of a workable chemical system nears completion; the greatest effort of Phase 2 would be devoted to that development.

We anticipate that the critique will provide us with clearly defined areas for exploration; that a choice will have been made as to which type

of photoconductive material (crystal, polymer, dye, etc.) and which type of thermally sensitive material (crystal, microcapsule, leucobase, etc.) might be expected to produce best, next best, etc., registration. The experimental program will be designed for an orderly exploration of these avenues with a broad selection of candidate materials.

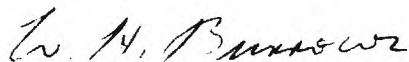
Initially, candidate materials will be screened as to type and sharpness of response. Those that appear to offer promise for this application will be subjected to more rigorous testing, separately, then in the form of mock-up registering medium. The testing program would include light activation, effects of sensitizing agents, response to RF heat, and effect of ambient heat over a normal range.

The outcome of the Phase 2 program would be a well-defined high-speed printing system with one or more experimentally proven chemical registering systems. Subsequent phases would deal with development of the physical and mechanical concept into an operational unit, together with such improvements or modifications of the registering medium as might be dictated by the latter development.

Conclusions

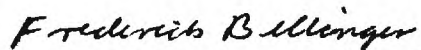
1. An extensive review of the literature has explored both the prior art and the general background material related to development of a high speed printing system.
2. A concept has been derived, analysed as to theoretical background, and compared with prior art.
3. A program is outlined for research and development of the chemical and interdisciplinary aspects of this concept.

Respectfully submitted,



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Project Director

Approved:



Frederick Bellinger, Chief
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(Abstracts, only)

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An imaginative discussion of reproduction processes reduced to 3 essential steps: (1) a triggering step or formation of a latent image, (2) an amplification step, utilizing external energy, (3) a fixing step. A concept closely allied with ours is outlined under the heading, "System based on the variation of dielectric constant of a phosphor under illumination."
- O.3a Alexander J. Moncrieff-Yeates, "Photoconductive Thermography," U.S. Patent 2,798,959 (July 9, 1957) assigned to Radio Corporation of America
Patent disclosing an art that anticipated in part the concept proposed by Robillard (O.2). It is not known that this art was ever practiced commercially.
- O.3b Alexander J. Moncrieff-Yeates, "Photoconductive Thermography," U. S. Patent 2,798,960 (July 9, 1957) assigned to Radio Corporation of America
Patent disclosing an art that anticipates in part the concept proposed by Robillard (O.2). It is not known that this art was ever practiced commercially.

BOOKS

Electronic Properties of Materials--A Guide to the Literature, Vol. 1 (ed by H. Thayne Johnson), Vol. 2 (ed by D. L. Grigsby, D. H. Johnson, M. Neuberger and S. J. Welles), New York: Plenum Publishing Corp.

These two volumes comprise an extensive and intensive directory to the recent literature with which we are concerned (independently of our own literature search). In addition, the Glossary contains excellent resumes of various topics (photoconductivity, etc.)

Albert Rose, Concepts in Photoconductivity and Allied Problems, New York: Interscience Publishers, 1963, 1-69.

Photochemistry and Reaction Kinetics, ed by P. G. Ashmore, F. S. Dainton, and T. M. Sugden, Cambridge: At the University Press, 1967, 378 pp.

Progress in Semiconductors, Vol. 1, ed by Alan F. Gibson, New York: John Wiley & Sons, Inc., 1956, 220 pp.