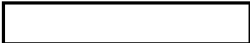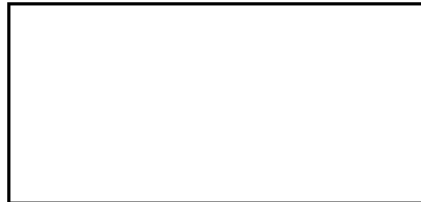# CONFIDENTIAL

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Copy **1** of 3

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25X1   Subject: Contract _____
Task Order No. 93
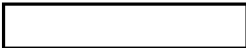
DICK S.

Dear Dick:

Enclosed are four copies of the Final Technical Report on the subject task.   We have forwarded one copy of this report to the Contracting Officer for his file.   This report is the final item to be delivered under Task 93 and completes the technical reporting requirements.

25X1

Enclosures
    Final Report "Black and White Films"
25X1   _____ 30 August 1965 (four copies)

Declass Review by NGA.

GROUP 1

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DECLASSIFICATION

Non-Reversible Color - Study

Progress Report No. <u>8</u>

Financial Status

        Amount Authorized

        Estimated expenditures thru 28 Feb 65

        Funds Committed

        Funds Remaining

25X1

Technical Status

        The engineering progress report for the month of

February 1965 is attached.

25X1

3/8/65

Distribution:
    Technical Representative - two copies
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Progress Report #8
Black and White Films

February 1965

   The effort in the month of February was spread over a variety of
activities. The anthraquinone dyes were studied further with rate and quantum
efficiency results to be described later in this report. The apparatus has been
overhauled and modified with the view towards greater operating efficiency and
accuracy of results. A considerable period of time was spent in reformulation
and reassessment of ideas on the nature of the process, some of which were
incorporated in the proposal for continuance of the project. Finally, some
experiments were run comparing the ASA rating of some of the films with those
obtained on silver halide films of known sensitivity. Previous results, obtained
by use of a laser beam, indicated an ASA equivalent of 0.5 to 0.09. When the
comparison was made using a 500 watt projector as the light source, an ASA
of about 5×10^{-4} was obtained. A more comprehensive comparison of film
speeds is planned for March.

   The remainder of this report will be given over to a review of the
reaction rate experiments performed during the work on this project, a summary
of the quantitative results achieved, and of their significance to the objectives of
the project.

Experimental Apparatus

   The experimental apparatus (MEA) was described in Progress Report #3
for September 1964. In brief, the apparatus functions by moving a slide into and
through a beam of light, which may be monochromatic, or may be white light.
Both before and after exposure, the absorption of monochromatic light at the
wavelength of maximum absorption of the dye is measured as a function of
distance along the slide. This is done by moving the slide past a narrow slit
while monitoring the intensity of transmitted monochromatic light by means of
a photomultiplier. A typical result is shown in Figure 1. The section of curve
marked A corresponds to the portion of the film which was in the light beam at
the start of illumination, and which moved out of the beam as the film
corresponding to section B moved into the beam. Thus, each half of the curve
constitutes a plot of intensity of transmitted light against exposure.

   This technique of obtaining the rate of dye bleaching has several advantages.
It is simple, rapid, and results in a sample in which the effect of variation in
exposure may be visually examined as well as measured intrumentally. The
method is useful, however, only for experiments in which high accuracy is not

-2-

important, because it is difficult to incorporate corrections due to variations in slide thickness in the calculations. When it is necessary to achieve high accuracy, a stationary sample is used. In the stationary sample technique, a small area of the sample is illuminated by the desired light. Simultaneously, the transmitted light is passed through a monochromator if it is not already monochromatic, and monitored by a photomultiplier. A curve obtained by this technique is shown in Figure 2.

Analysis of Data

The data obtained by these two techniques is in the form of plot of percent transmittance against time. Optical density $\underline{D}$ is defined as $\log I_0/I$, where I_0 is the intensity of the incident light, and $\underline{I}$ that of the transmitted light. In the usual run, a full scale deflection (100) is adjusted to correspond to light transmitted by a blank slide. In this case, $\underline{I}$ is percent transmittance. By Beers law, $D = \log I_0/I = \mathcal{E} Cl$, where $\underline{\mathcal{E}}$ is extinction coefficient, $\underline{C}$ concentration and $\underline{l}$ thickness of sample. If the absorption curve of a solution of dye of known concentration is obtained, $\underline{\mathcal{E}}$ can be calculated. Assuming that $\underline{\mathcal{E}}$ is the same in solution as in the film, $\underline{C}$ can be calculated at any time during the run. The analysis of the mathematical relationship between concentration and time is termed the kinetics of the reaction.

For simple, one step reactions in which one molecule of species A reacts with one molecule of species B, we can write $-d(A)/dt = k(A)(B)$, where the parentheses connote concentration. In a rigid medium such as a polymer film, such simple reactions are likely, since diffusion of reactive intermediates towards each other is hindered.

In the experimental investigation of these reaction rates, one may choose conditions of concentration in various ways, to fulfill different objectives. For example, one may work with films of optical density greater than two, less than 0.1, or of intermediate density. For the initial study, we chose to work at intermediate densities, for several reasons. This region is easiest to handle experimentally, much of the equipment was available in the laboratory, and in addition, the color changes in the film are readily produced and readily observed. However, the regions of very high and very low optical density yield quantitative data of greater significance, as will be shown below. For this reason, a new instrument has been purchased and equipment designed and built to make it possible to investigate all regions of optical density, and to compare the results and conclusions derived from each. The new instrument has much greater stability than the photomultiplier used previously, and has accurate range switching capabilities, thus allowing high accuracy independent of optical density.

-3-

We consider next the significance of the results obtained in the extreme regions of optical density.

A.   Initially High Optical Density - When the initial optical density is around two or more, large changes in the concentration will produce only small changes in the number of photons absorbed. Since the extent of reaction is directly proportional to the number of photons absorbed, and the number of photons absorbed remains relatively constant, it follows that the extent of reaction will be independent of the concentration of the dye. The flux of photons is constant, and can be absorbed into the rate constant. Since we are used to thinking of rate constants in terms of concentrations of reactants, we will call the constant for this situation the zero order rate constant k_0. Since very little of the light is transmitted, this is an experimentally difficult region to investigate. To summarize the relationship

$$ -\frac{d(C)}{dt} = k_o = k(C_1)P $$

where C_1 is a limiting concentration and P is the flux of photons per unit area per unit time.

B.   Initially Low Optical Density - When the initial optical density is around 0.1 or less, the changes in photon flux from the front of the film to the back will be relatively small and relatively unaffected by changes in the concentration of the dye. In this case, the rate of loss of dye will be directly proportional to the concentration of the dye. We call this rate constant a first order rate constant, again incorporating the photon flux into the constant.

$$ -\frac{d(C)}{dt} = k_1 (C) = k(C)P $$

For intermediate optical densities in the region of about 0.7 - 0.1, first order kinetics are reasonably well followed, but the interpretation of the results may be more complicated due to the variation of photon flux through the film. Most of the results obtained to date have been in this intermediate region, since the experimental technique is much easier and more accessible. As mentioned above, the new equipment will make it possible to correlate the results in the three density regions. The results which will be discussed below are primarily from the intermediate region of density .07 - .01.

-4-

To obtain the rate constants, the above equations are integrated, resulting in, respectively,

$$C = k_o t + C_o$$

and

$$\ln \frac{C}{C_o} = k_1 t$$

Since $C = D/\varepsilon\, 1$, a plot of D against t will result in a curve with slope $k_o\, \varepsilon\, 1$. If zero order kinetics are followed, this will be a straight line. Such a curve is illustrated in Figure 3. A plot of log D against t will result in a straight line if first order kinetics are followed. The slope will be k_1, all the other constants affecting only the intercept. In practice, one must factor into the calculation the absorption of the reaction products, leading to a somewhat more complex equation. The result of a plot of this equation is illustrated in Figure 4.

One criterion of reactivity of great interest is the quantum efficiency. This is defined as the number of molecules which react divided by the number of photons which have been absorbed. That is to say, it is the effectiveness of an absorbed photon in producing a chemical reaction. The photon flux must be known in order to calculate quantum efficiency. Photon flux is arrived at through a calibration of the apparatus with an absolute energy measuring device, the multijunction thermopile. In our case, a twelve junction Eppley thermopile was used to calibrate the irradiation system at each of the many wavelengths. From the energy falling on unit area at the plane in which the sample is kept and from the wavelength of the light, the number of photons per unit time can be calculated. The change in concentration per unit time is given by the first order rate constant times the concentration. This number in units of molecules bleached per minute per cm^2 is divided by the number of photons absorbed per minute per cm^2, obtained by multiplying the photon flux by the initial fraction of light absorbed.
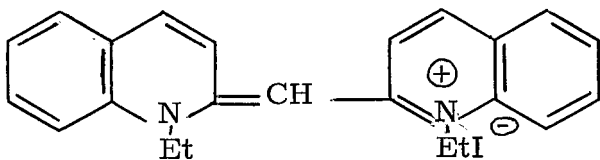
methine dye
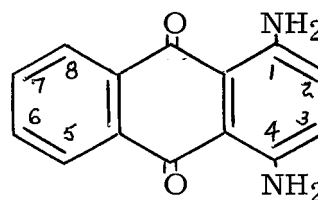
anthraquinone dye

-5-

Tables 1 and 2 give lists of the dyes for which quantum efficiencies have
been measured and information on the structures of the dyes. In Table 1 the
methine dyes are listed. A correlation between the basicity of the heterocyclic
rings in the dye molecules and the quantum efficiency can be shown. This
indicates that the reaction is a reduction reaction since basicity can be considered
to be the tendency to push electrons into the molecule. When there is a high
concentration of electrical charge, or rather of electrons at the reactive points
in the molecule, these sites are more prone to reaction with protons or similar
chemical entities, thus leading to reduction of the double bond and destruction
of the resonance between the heterocyclic rings in the molecule. In the
anthraquinone series shown in Table 2, the quantum efficiency varies over a wide
range. The two compounds which have the highest quantum efficiency, about 2.6,
both have amino groups situated on the anthraquinone molecule and have no other
substituents elsewhere in the molecule. The structure of the one compound,
code no. 139, is not completely known. Some of the amino groups are substituted
with methyl in place of hydrogens, but it is not known which ones or how many.
The other compound has only two amino groups. The contrast between that
compound, no. 181 and no. 95 which has one methyl group substituting for a
hydrogen on one of the two amino groups, and otherwise identical structure, is
very great, a factor of over five in quantum efficiency. In point of fact, the
derived results on quantum efficiency for compounds no. 181 and 139 are very
high and the data for these materials will be rerun to assure precision. If the
quantum efficiencies are actually greater than one, then the process has a built-in
multiplicative factor which, if properly exploited, can lead to high speed films.
It should be noted that these two compounds have relatively low extinction
coefficients. The method of procedure indicated by these results is as follows.
Molecules are to be sought which have the same ability to force electrons into
the conjugated resonance aromatic ring system but which in addition have high
extinction coefficients and thus are more effective in terms of photographic
properties. For example, compounds which may be used to test this hypothesis
are those with amino groups in the one and four positions and methoxy, bromo,
or similar groups in the two position. These compounds are predicted to have
similar reactivity and higher extinction coefficients than the ones with which we
are comparing them.

The foregoing discussion has been designed to describe, clarify and
illustrate the measurements and calculations which are being made on this project,
to indicate the type of conclusions which can be drawn from the measurements,
and to illustrate also the way in which the conclusions drawn direct further attack
and approach to the problems. Thus, the experiments on the anthraquinone dyes
indicate the structural factors of importance to the bleaching process. Dyes are

-6-

then obtained accenting these structural features. If the results agree with the predictions, further improvements in structure can be sought; if not, the theory is revised to accommodate the new data, and the process is repeated. Thus, this repetitive, cyclic process leads to dyes of greater sensitivity in the bleaching process and to a knowledge of which structural factors can be safely modified in attempts at obtaining different initial colors. In addition, when other classes of dyes are investigated, relatively few experiments should determine whether similar factors are operative.

Plans for March

Much of the work for March has been indicated in the above report. Several dyes will be examined for speed values under identical conditions as silver halide films of known ASA rating. Each of several dyes will be investigated in films of low, intermediate and high optical density and the rate constants compared. Dyes predicted to be sensitive will be obtained or prepared and investigated. Dye screening will be continued in classes other than methine and anthraquinone dyes.
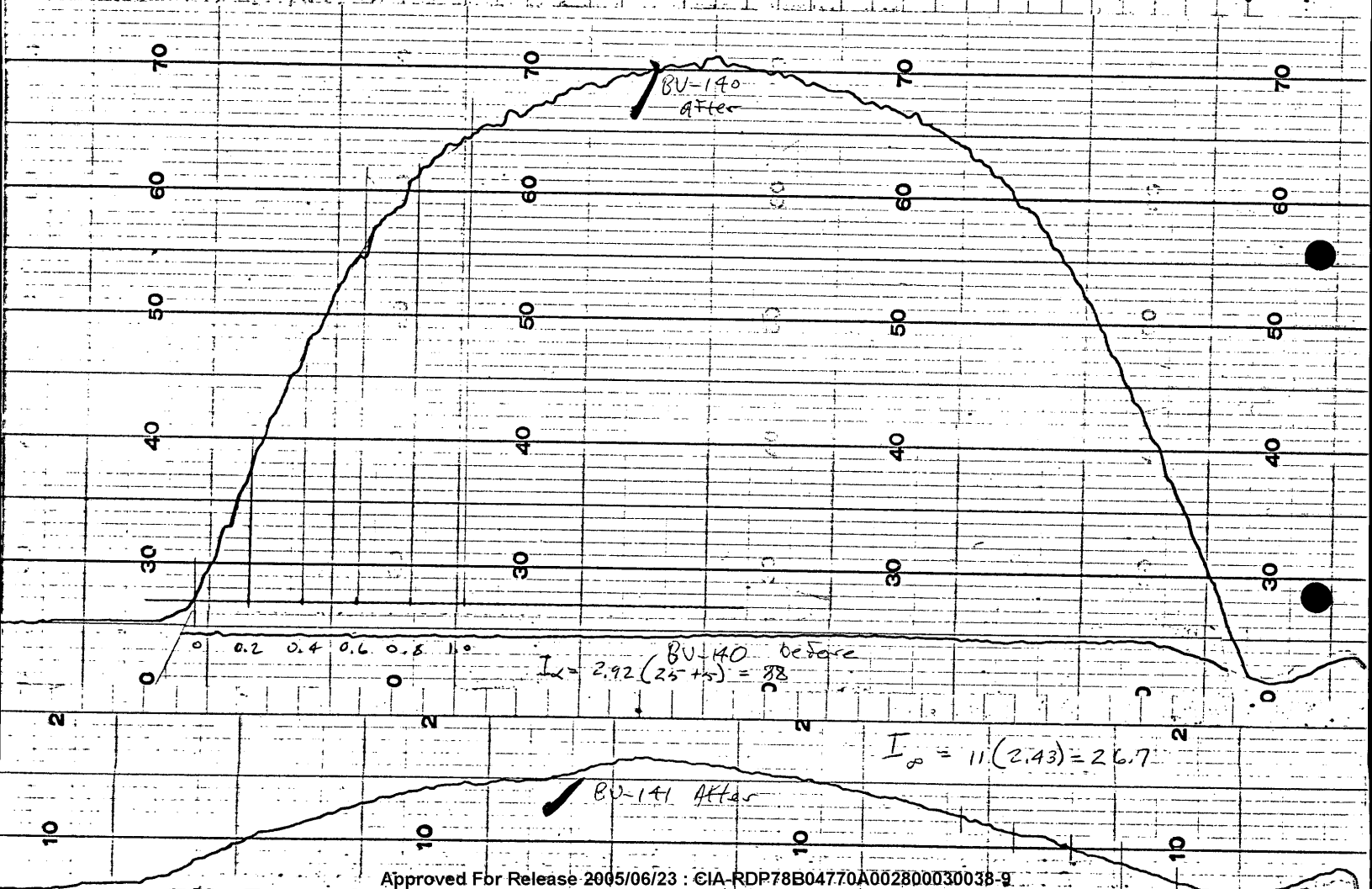
Table I
Quantum Efficiencies of Methine Dyes

No.	Name	Structural Groups	Color	Wavelength	Quantum Efficiency
53	Orthochrome T	N-ethyl 6 methyl quinoline	Violet	570	0.1
81	3, 3'-diethyl-2, 2'selena carbocyanine iodide		Violet	580	0.061
84	3, 3'-diethyl thiocarbocyanine iodide		Green	570	0.042
120	Sevron Brilliant Red 2B	Diethyl aniline 1, 3, 3 trimethylindole	Magenta	550	0.26
143	Genacryl Red 6B	3 Methyl N(2 chloroethyl)ethyl aniline 1, 3, 3 trimethylindole	Magenta	550	0.14

Table II
Quantum Efficiencies of Anthraquinone Dyes

No.	Name	Substituents	Color	Wavelength	Quantum Efficiency
88	Waxoline Blue GA	$1\text{-}NHCH_3$, $4\text{-}NH\text{-}C_6H_4\text{-}CH_3$	Blue	600	.065
95	Oracet Violet B	$1\text{-}NH_2$, $4\text{-}NHCH_3$	Blue	620	0.43
139	Palacet Blue 3G	$1, 4, 5, 8\text{-}NH_2$ (methylated)	Blue	640	2.78
140	Celliton Fast Blue FBBN	$1\text{-}NHCH_3$, $4\text{-}NHC_2H_4OH$	Blue	600	0.10
141	Celliton Fast Blue Green BA	$1, 4\text{-}NHC_2H_4OH$, $5, 8\text{-}OH$	Blue	630	0.023
181	Amacel Heliotrope R	$1, 4\text{-}NH_2$	Violet	590	2.64
186	Cibacet Brilliant Violet 3B	$1, 4\text{-}NH_2$, $5\text{-}NO_2$	Blue-violet	570	0.104

FIGURE 1
Representative MEA Data

BU-140
after

BU-140 before

$I_x = 2.92(25 + 5) = 88$

$I_\infty = 11(2.43) = 26.7$

BU-141 After
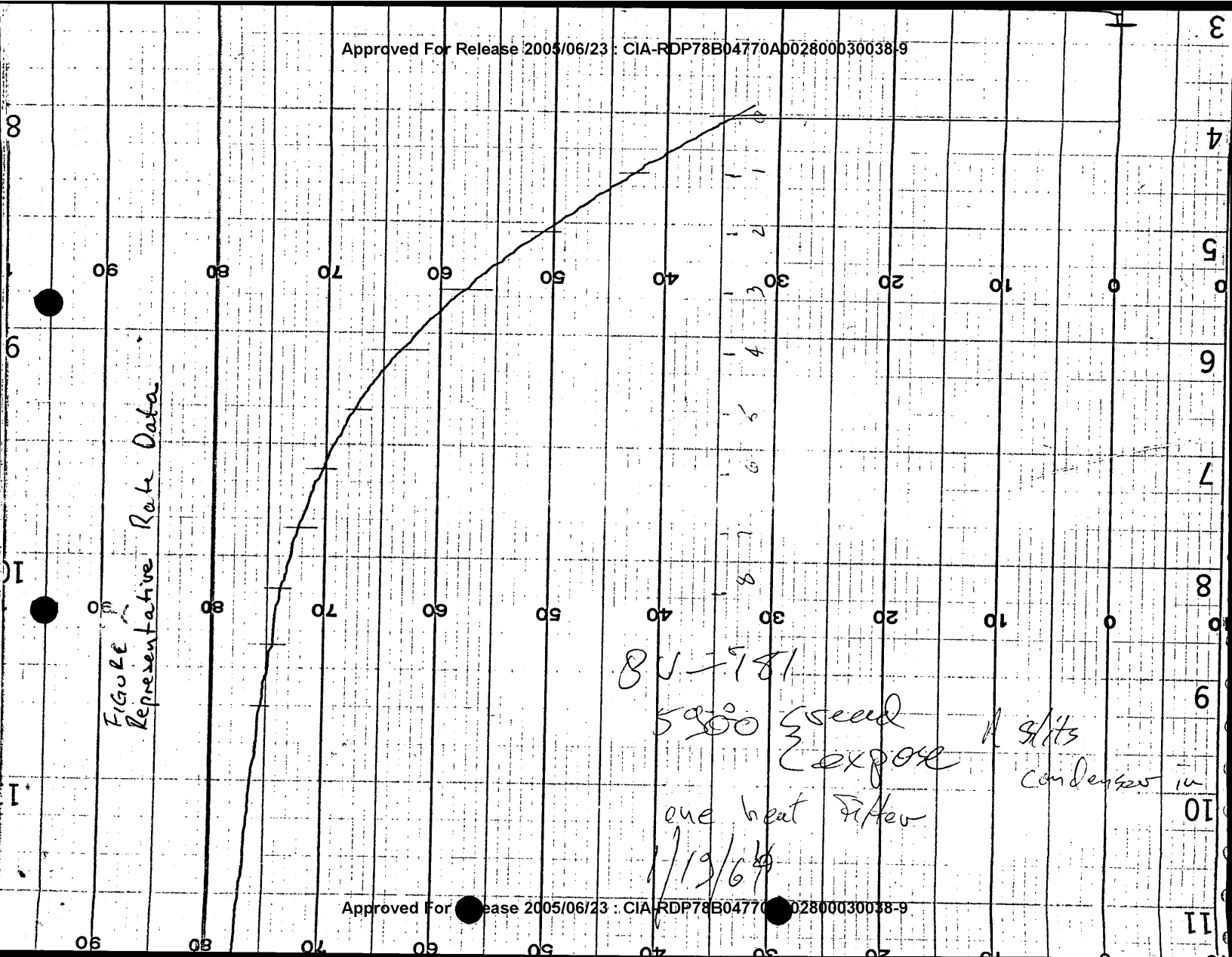
Figure ~
Representative Rate Data

BV-181

5900 speed
Exposi

one heat filter

1/13/67

slits
Condensor in

Figure 3

Zero Order Kinetic Plots

#135 Exposed to O₂ at 300°C Wavelength

λ = 540

λ = 475

λ = 620

Time, min.

Time, min.

Figure 4

First Order Kinetic Plot

$\log \dfrac{I_{(c+n)}}{I_c}$

BV-181 1-19-65
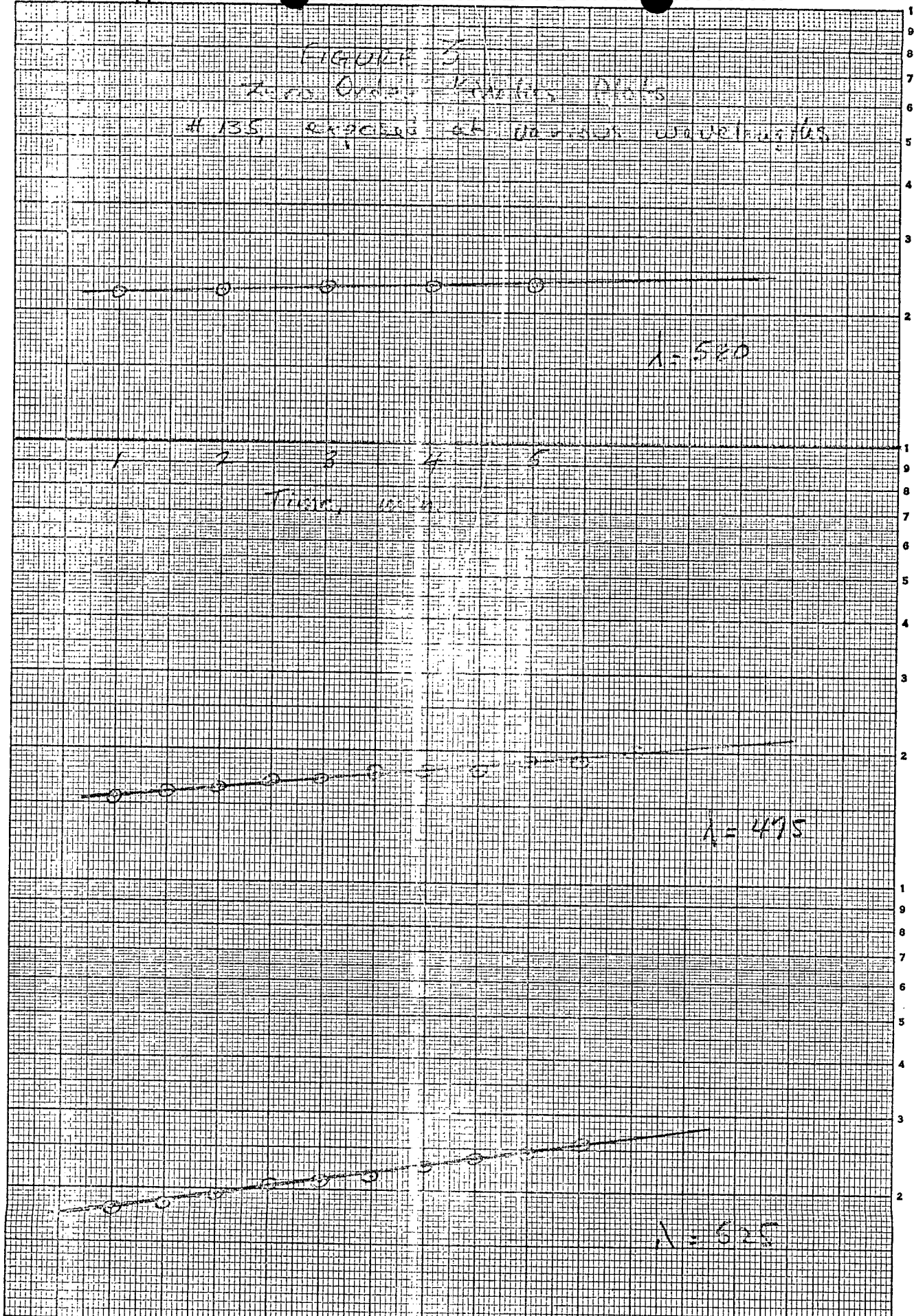
SCHENECTADY, N.Y., U.S.A.

GENERAL ELECTRIC COMPANY.

FN-265-A (8-50)
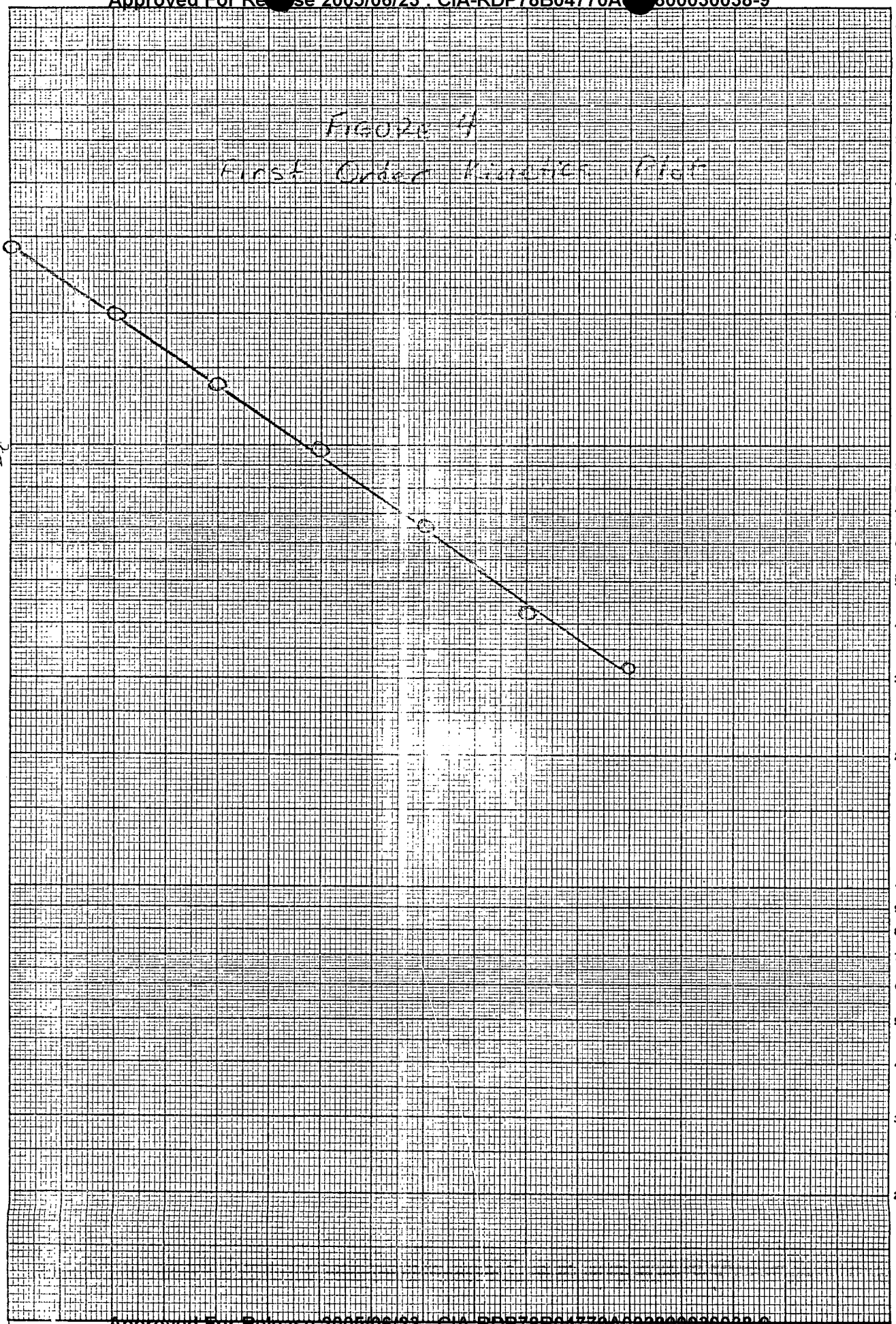
3 cyc. x 170 1mm Divisions

Exposure Time

0   1   2   3   4   5   6
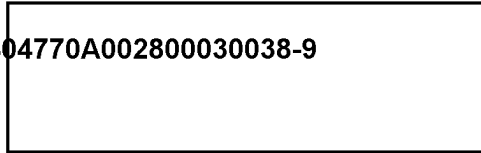
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Non-Reversible Color - Study

Progress Report No. 7

Financial Status

25X1

        Amount Authorized
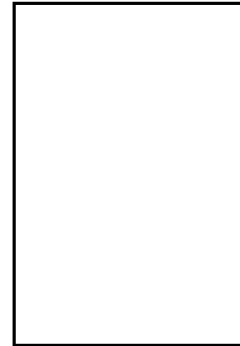
        Estimated expenditures thru 26 Jan 65

        Funds Committed

        Funds Remaining

Technical Status

        The engineering progress report for the month

of January 1965 is attached.

25X1

2/8/65

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Progress Report #7
Black and White Films

January 1965

The criterion, discussed in the previous report, for the comparison of the reactivity of various dyes to light is the quantum efficiency of the photo-bleaching process. That is, it is the probability that an absorbed photon will lead to a reacted molecule. The quantum efficiencies measured for the methine dyes have been correlated with the basicity (the tendency to repel an electron) of the heterocyclic groups of the dye molecules. The correlation is not precise, but is very suggestive of an oxidation or reduction reaction. Polarographic experiments have been started to determine whether a relationship between potentials at which oxidation or reduction takes place, and quantum efficiency, exists.

Further runs have been made on the kinetics of bleaching of anthraquinone dyes. The calculations on these have not been completed. Changes have been made in the apparatus to achieve greater accuracy and sensitivity, and further changes are being planned. Delivery and installation of the necessary components should be complete by the first week in March. Further precise work on quantum efficiency measurements will be resumed when the apparatus has been reassembled.

Four dyes were tested as to the effect of heating after exposure on the extent of bleaching. In one case, bleaching was increased by a factor of about two. In another case, bleaching was considerably decreased. In the other cases, the effect was slight. The significance of these observations is that the heat fixing step may eventually provide a technique for control of gamma or of sensitivity.

Experiments have been carried out to quantitatively determine the efficacy of heating in fixing the films. In these experiments, the rate of bleaching after heat fixing was measured and found to be immeasurably slow. Previous qualitative results, indicating that the dye films were stable to light after heat fixing were corroborated.

The results of a comparison between one of the dye films and two silver halide films of known ASA rating indicate an equivalent speed for the dye of approximately 0.5 to 0.06. This experiment was performed with high intensity monochromatic light produced by a helium-neon laser. It is possible that this type of radiation will produce results which are not representative of the

-2-

materials. Experiments are being set up to accomplish the comparison at a lower intensity, so as to provide results more pertinent to the intended end use of the films.

Plans for February

The apparatus modifications mentioned above are to be completed. Comparison of sensitivity of dye films with silver halide films of known ASA rating is to continue. The results of the polarographic studies will be analyzed to help complete the assignment of the reaction mechanism for the cyanine dyes. Studies of the anthraquinone dyes will be continued.

Non-Reversible Color - Study

Progress Report No. <u>6</u>

Financial Status

  Amount Authorized

  Estimated expenditures thru 31 Dec 64

  Funds Committed

  Funds Remaining

25X1

Technical Status

  The engineering progress report for the month of

December 1964 is attached.

25X1

1/14/65

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Progress Report #6
Black and White Films

December 1964

The observation, noted in the last report, that some dye-iodoform systems are sensitive to light absorbed by the dye, has prompted a reconsideration of the experimental methods to be used to evaluate reactivity. If only light absorbed by the iodoform were active, as is the case for some systems, comparisons of reactivity will be valid as long as a constant light source at a fixed distance is used. In this case, the flux of photochemically effective photons is constant. If, however, photons absorbed by the dye are also active, as is the case in other systems, the flux of photochemically active photons will depend on the absorption characteristics of the dye. For this reason, an action spectrum was measured for one dye. That is, the rate of reaction caused by illumination by nearly monochromatic light was measured at each of several wavelengths. Within experimental error, the rate of reaction of each wavelength was directly proportional to the rate of absorption of photons.

The criterion for comparison of reactivity of dyes is the relative probability of bleaching of the dye-iodoform complexes on the absorption of a photon. Therefore, to obtain meaningful interpretation of data from exposure to white light, we must go through a complex procedure involving multiplication of the number of available photons at each wavelength by the fraction absorbed at that wavelength, and a numerical integration of the resulting curve. As an alternative to this procedure, we have adopted the technique of irradiating the samples with nearly monochromatic light. The wavelength range is about 100 Angstroms, and is centered on the absorption peak of the dye. For slow systems, the wavelength range can be increased to 200 Angstroms. While this technique adds experimental complications, it enormously simplifies the calculations.

Using this technique, rate constants and quantum efficiencies were measured for all of the available methine dyes which showed bleaching, and several of the anthraquinone dyes. Quantum efficiencies measured to date lie in the range of 0.01 to 0.25. An attempt at correlation of these results with the structural features of the dyes is in progress.

Further experiments included comparison of quantum efficiency of light absorbed by a dye with that for light absorbed by iodoform. For the dye studied, the ratio was about 6:1, with the iodoform absorption the more efficient. A measurement of the effect of intensity on rate of bleaching showed the expected effect, that is, that rate is approximately linear with intensity.

-2-

The work on determination of changes in infrared spectra caused by the bleaching reaction has continued. Several techniques of sample preparation have been tried. Of these, a technique for obtaining infrared reflection spectra shows promise. The standard methods of solution spectroscopy and KBr pellet spectroscopy are not applicable since the reactions which take place in these media differ from the bleaching reaction in the polymer film.

Plans for January

Work in the areas described above is to be continued: kinetic measurements on anthraquinone dyes, structure-reactivity correlations, and infrared spectra. Some modification of experimental procedure is planned, to reduce experimental error and to increase efficiency.

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3005

Non-Reversible Color - Study

Progress Report No. <u>5</u>

Financial Status

    Amount Authorized

    Estimated expenditures
      thru 27 November 1964
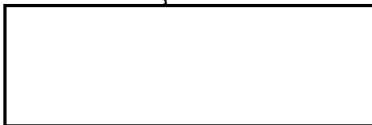
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Progress Report #5
Black and White Films

November 1964

The effort during November has continued to be concentrated on the quantitative evaluation of dyes as described in previous reports. Formulas have been derived expressing the rate constant for dye bleaching in terms of experimentally observed quantities. A punched card system for storing dye data has been developed. This system simplifies the collation of data and the ordering of structural information. One hundred sixty-four dyes have been recorded on the cards, of which 92 have known formulas. Absorption spectra have been obtained for 73 dyes, before and after illumination, some under a variety of conditions and 28 of these have been evaluated on the MEA.

It has been found that some of the dye-iodoform systems are sensitive to light absorbed by the dye as well as that absorbed by the iodoform. Thus, for a given light source, many more photons are available to participate in the reaction, and the film will be faster. In addition, this observation means that in order to calculate a meaningful rate constant for dye bleaching, it will be necessary to make a careful determination of the action spectrum of several of the dyes and to determine the relationship of the action spectrum to the absorption spectrum. (The action spectrum is the relation between the wavelength of incident light and the extent of reaction.) If there is a simple relationship between these spectra, a knowledge of the absorption curve will suffice for the calculation of rate constants. Otherwise, action spectra may have to be determined for many of the dyes. Apparatus has been ordered to permit determination of action spectra. If it proves necessary to determine action spectra for most dyes, it seems feasible to modify the instrumentation so that it can be used in conjunction with the MEA to obtain action spectra automatically.

A start has been made on the problem of determination of infrared spectra of dye systems. Several experiments have been planned, and project personnel have learned the operation of the available infrared spectrophotometer.

Plans for December

The measurement of rate of bleaching of all the dyes of known formula which have been obtained thus far is to be completed. The correlation of reactivity with structure is to be continued. It may be necessary to procure additional dyes to augment the data, and to fill in gaps on the correlation.

Further work is planned on the action spectra of the dyes late in the month. The investigation of feasibility of infrared spectra will be continued.

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27 Nov. 64
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Non-Reversible Color - Study

Contract No.

Progress Report No. **4**

Financial Status

  Amount Authorized

  Estimated expenditures
   thru 30 October 1964

  Funds Committed

  Funds Remaining

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Technical Status

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month of October 1964 is attached.

11/5/64

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Progress Report #4
Black and White Films

October 1964

The effort in October has been concentrated on the quantitative evaluation of a series of dyes, some of which had been previously examined qualitatively. The MEA (materials evaluation apparatus) described in the previous report is proving useful and versatile in these evaluations.

A routine screening process has been put into operation. This process includes three steps. In the first step, a slide of the material to be evaluated is run through the exposure step in the MEA. If a color bleaching is observed, spectrophotometric curves are obtained of a sample before and after illumination. A fresh slide of the material is then run through the MEA. The wavelength of maximum decrease of absorption, as shown by the spectrophotometric curves, is used in the evaluation or readout step of the procedure.

Twenty-seven dyes have been examined by this procedure during October, in one or both of two media, to be described below. Of these, eleven were processed through the three steps of the cycle. These showed a variety of responses to illumination, ranging from fast to slow, and from large changes in optical density to small changes.

Two media have been chosen for the more polar dyes. These are Carboset resins, dissolved in tetrahydrofuran (THF), or in a mixture of THF and ethyl alcohol. We have shown that the solvent has a large effect on the photosensitivity of the dye, even though the solvent is evaporated before the illumination of the dye. Of the solvents which have been evaluated, THF has proven the best, and a THF-ethyl alcohol mixture almost as effective. At the other extreme, methyl alcohol seems to inhibit photosensitivity. These results are strictly applicable only to the dye systems used in the solvent evaluation. If the interaction is between solvent and iodoform, as seems possible, the relationship will hold for all dyes. This, however, will have to be checked with several additional dyes of various dye classes.

Plans for November

Screening of dyes is to be continued.as is the correlation of structure with photosensitivity. Further tests of the effect of solvent on photosensitivity will be made. An investigation of the feasibility of obtaining infrared spectra of the dye systems which can be useful in the elucidation of the reaction mechanisms will be started.

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Non-Reversible Color - Study

Contract No.

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Progress Report No. <u>3</u>

Financial Status

    Amount Authorized

    Estimated expenditures
       thru 9/25/64

    Funds Committed

    Funds Remaining

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Technical Status

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Progress Report #3
Black and White Films

September 1964

During September, the effort has been concentrated on exploration of the experimental parameters affecting the photoprocess, and on making operational the new materials evaluation apparatus (MEA) constructed in the previous month. The operation of the apparatus will be described in some detail, with examples of results obtained. Following this, the parametric studies will be described briefly.

1. Apparatus. The apparatus designed for the evaluation of materials (MEA) is shown in Figures 1 and 2. Figure 1 is a photograph of the apparatus as it is set up, and Figure 2 an exploded view. The apparatus is used to expose a slide to light from the projector, and then to evaluate the results of the illumination.

In exposure, a 1" x 3" microscope slide, coated with a sample to be evaluated, is inserted in the slide holder. The slide initially is shielded from illumination. It is then caused to move into the field of illumination at a constant rate. When the leading edge of the slide has traversed an appropriate distance, the light is shut off by means of a microswitch activated by the slide carriage. The slide then has had an exposure which varies linearly from the total time of exposure at one end of the exposed area to zero at the other. If we wish to investigate the effect of illumination by light of a particular wavelength region, we can insert an appropriate filter combination in the space provided, as shown in Figure 2.

For evaluation of the results of illumination, a thin slit is interposed between slide and projector. A monochromator, set at the wavelength of maximum absorption of the dye, monitors the transmitted light, which is then picked up by a photomultiplier. The output of the photomultiplier is recorded by a potentiometric recorder. For precise quantitative work, it is necessary to run a similar curve on the sample before exposure in order to get a base line, which reflects variations in thickness of the sample. This is illustrated by the lower curves in Figures 4 and 5.

Figures 3 and 4 illustrate the results obtainable with this apparatus. Figure 3 is reproduced from the first progress report in this series. It shows the absorption spectrum of Brilliant Oil Blue with iodoform in polystyrene after various exposures to a tungsten source. From the curve, it is seen that the

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wavelength of maximum absorption of the dye is at 6500 A. Illumination causes a maximum change in absorption of the dye at this wavelength. When a slide of the same dye, made up in the same way, is run through the MEA, with the monochromator set at 6500 A, the curves of Figure 4 are obtained. The lower curve shows the absorption of the slide before illumination, the upper curve after illumination. The time of traverse of the slide was 107 seconds. Illumination was by a Prado 500 watt projector, set up as shown in Figure 1.

To determine the evenness of illumination across the slide, a slide of Sudan Blue with CHI_3 was illuminated while stationary, in the position it would normally occupy at the end of a run. The slide was then evaluated in the way described above, with the results shown in Figure 5. As is evident from the figure, the distribution of intensity is highest in the center of the field, falling off seriously at the ends. To overcome this problem, the central portion of the field only will be used, corresponding to the horizontal line marked A on the figure, which subtends a space of 0.5 inch. The variation of intensity in this area is +3% of the average intensity.

2. Parametric Study. In order to make meaningful comparisons of dyes, and correlations between dye structure and reactivity in the photoprocess, it is essential that the experiments be carried out under as nearly identical conditions as possible. If this is not done, extraneous factors, such as interactions between photosensitive reagent and solvent or binder, may invalidate the comparisons. To obviate the effect of such extraneous factors on the dye itself, experiments should be done, if possible, in more than one solvent-binder system. For non-polar dyes, a good system is available, that is, polystyrene in benzene. Here, interactions are at a minimum, and the photosensitive reagent currently in use, iodoform, is sufficiently soluble. For more polar dyes, the situation is not as favorable. We have been experimenting with the Carbosets, a family of acrylic resins, in a variety of solvents. We have not as yet chosen a standard reference solvent-binder system, since none of the combinations we have tried is completely satisfactory. Work in this area is continuing. We hope to standardize on a pair of solvent-binder systems for polar dyes in the near future.

Other parameters which have been under study are the temperature to be used in the film drying step, and in the heat=locking step, and the concentrations of dye and iodoform that are most effective. In the study of dye to iodoform ratio, good results were achieved at a dye/CHI_3 ratio of 1:2, but the system gets faster, in the photographic sense, as the ratio goes to 1:5, at

-3-

the expense of a deepening of the yellow iodoform background color in the exposed areas. The temperature at which the films are dried is found to be important. A drying routine of 10 minutes at 100°C is found to be sufficient to deactivate the films. A temperature of 75° gives good results, and has been adopted as routine. Heat locking of the exposed films can be accomplished in about five minutes at a temperature of 140°. The discrepancy between the conditions for film casting and for heat locking is undoubtedly due to the higher mobility of the iodoform in the liquid, so that it is more readily evaporated in the film casting process.

The effect of delaying the casting of slides after preparation of the solution on slide quality and sensitivity was also investigated. Adverse effects were noted when the solution was stored overnight before casting.

3. Plans for Future Work. The apparatus will be modified as described in Section 1. It will then be calibrated, and a routine procedure developed. This will result in consistent and meaningful quantitative data.

The testing of solvent-binder systems for polar dyes is continuing, and selection of standard systems will be made. When this has been done, continuation of the dye screening work, and review of some of the dyes already screened in the light of the improved solvent-binder systems is scheduled. When sufficient data are available for meaningful correlations to be made, a comprehensive review will be written and included in the appropriate progress report. The present target date for this review is Progress Report #6, the half-year report.

MATERIALS EVALUATION APPARATUS

EXPOSURE

PRADO PROJECTOR

FILTER

FILM

NON-REFLECTING
BACK PLATE

PRADO PROJECTOR

SLIT

FILM

MONOCHROMATOR

PHOTOMULTIPLIER
TUBE

READOUT

figure 2

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Figure 3

Brilliant Oil Blue
Toluidine
in Polystyrene
exposures made
with 500w tungsten

FIGURE 4
MEA EVALUATION
Brilliant Oil Blue - CHI₃ · PS2

Transmittance at 6500 A
arbitrary units

Exposure, Seconds →

Unexposed

FIGURE 5

DISTRIBUTION OF LIGHT INTENSITY
ALONG SAMPLE SLIDE

Sudan Blue GA
CHI$_B$ - PS2
exposure - 1' 47"

A

exposed

Transmittance at 6500 A, arbitrary units

Distance along slide, inches →

unexposed
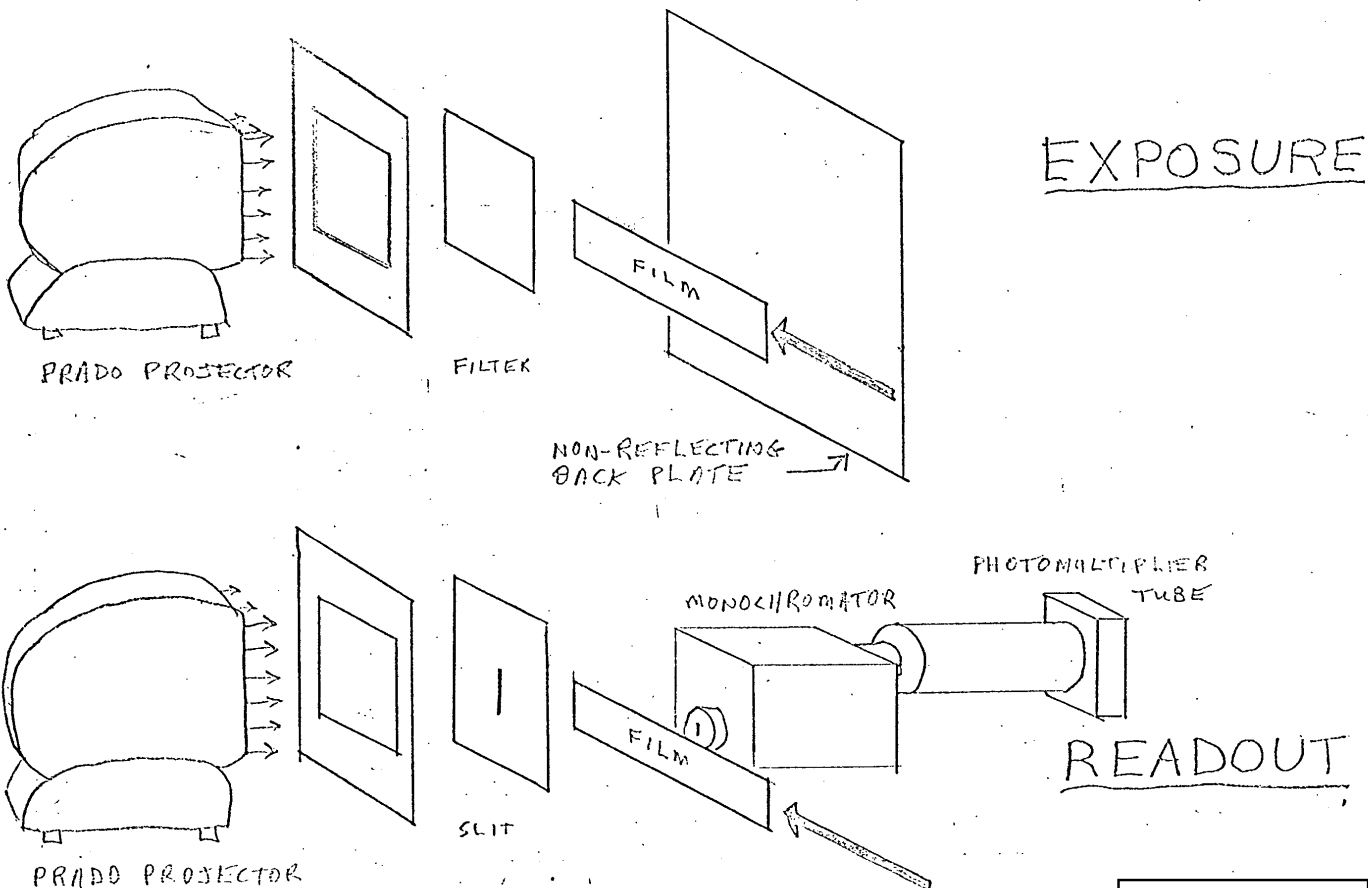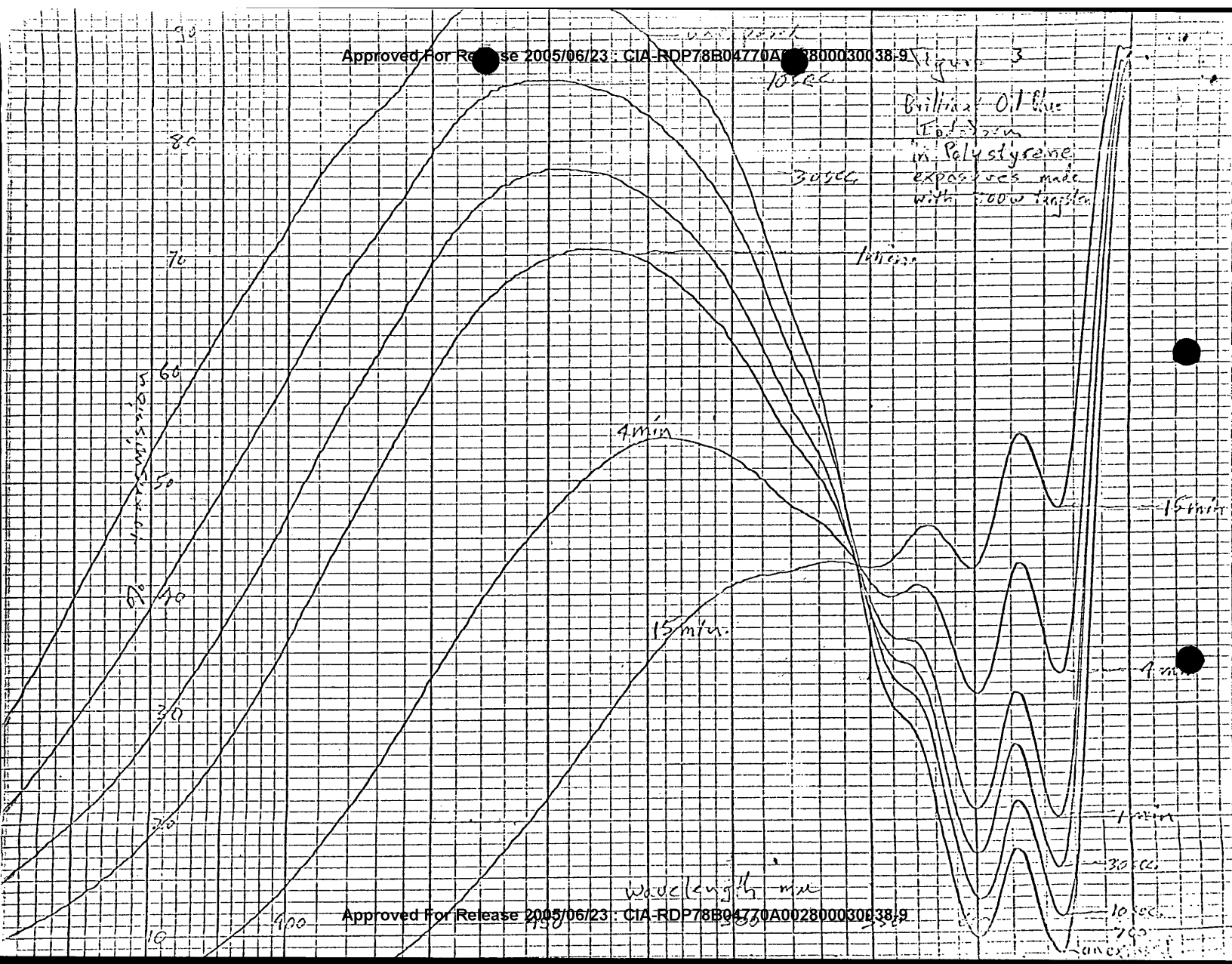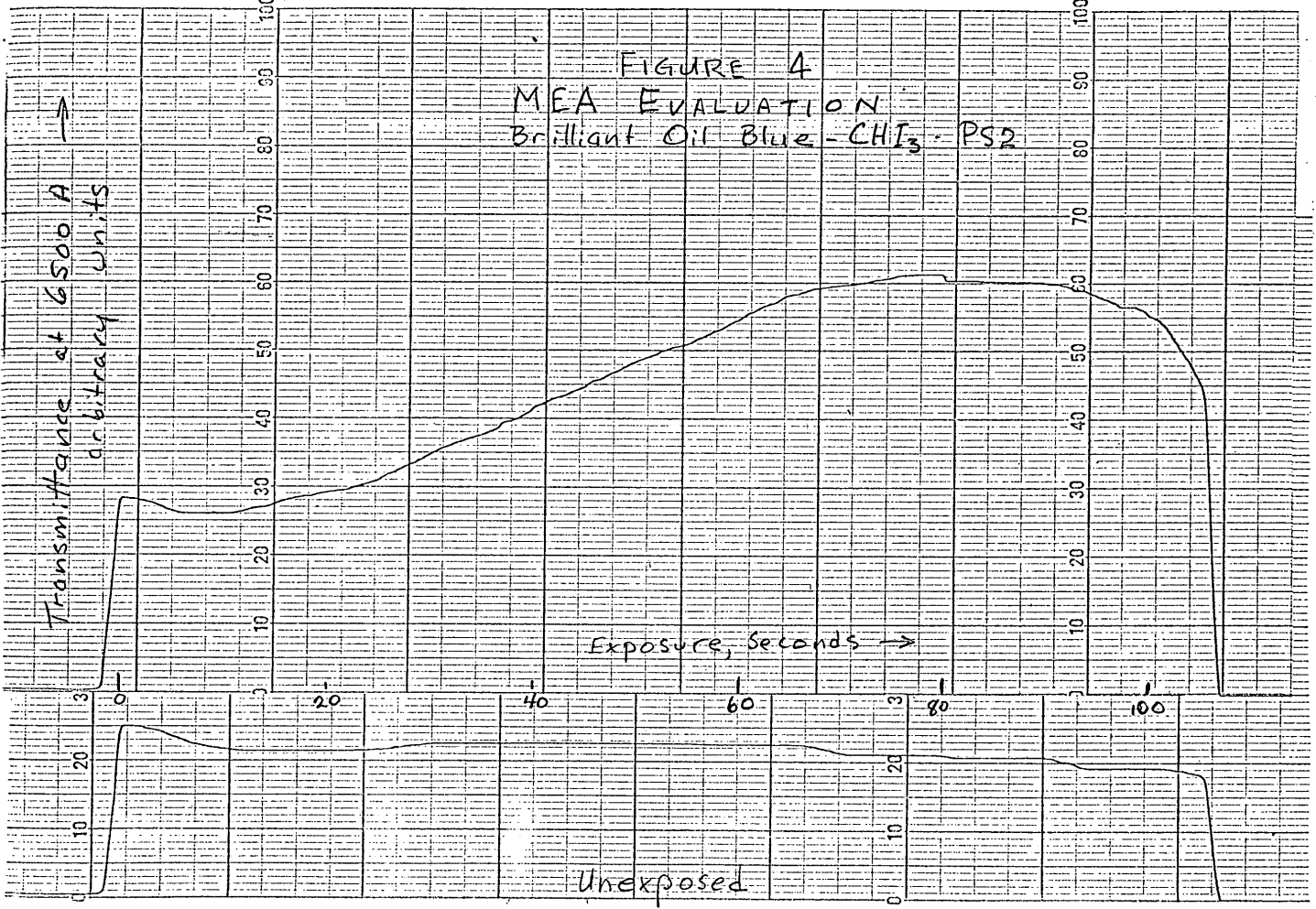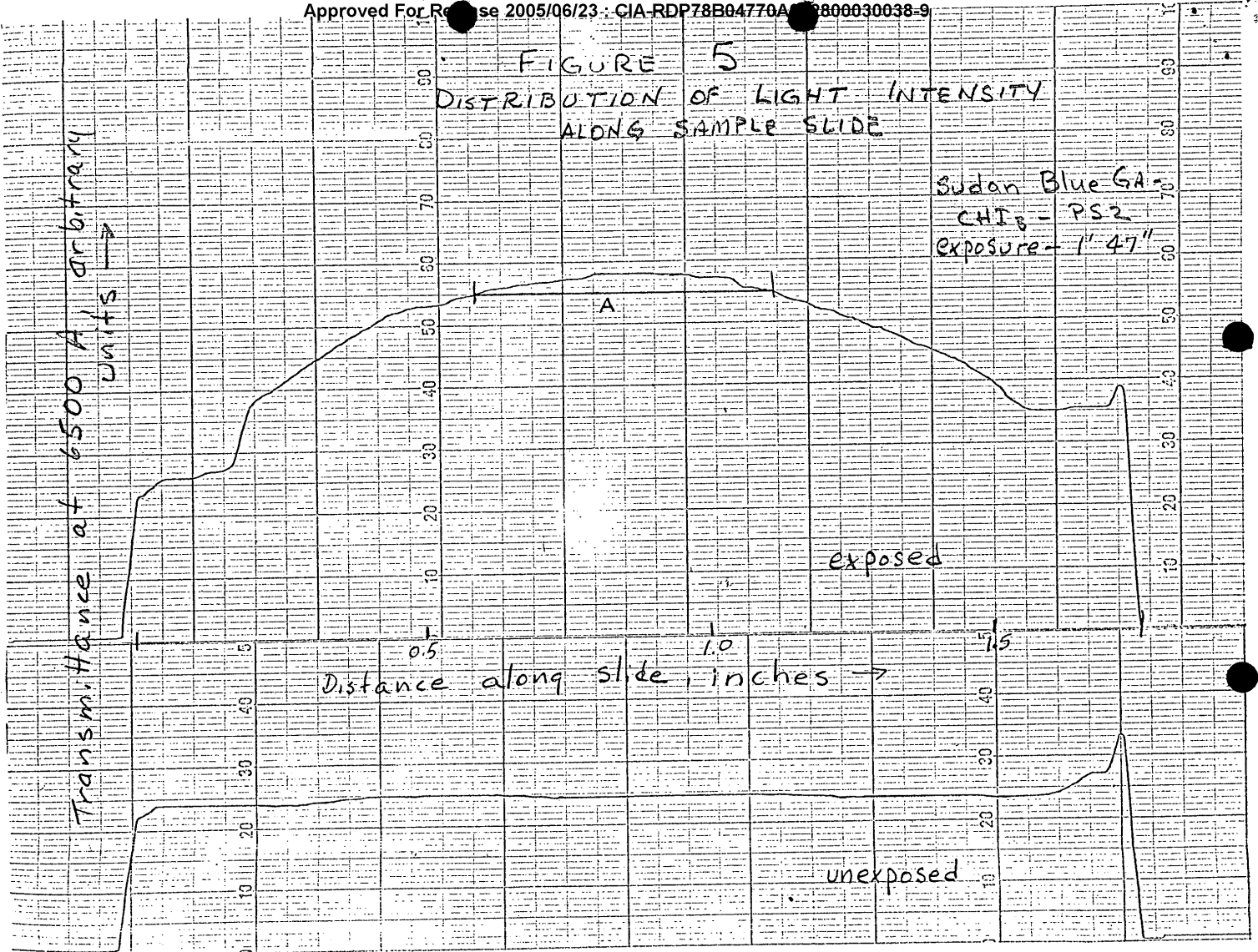
Non-Reversible Color - Study

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Contract [   ]

Progress Report No. **2**

ll.X.
9-22-64
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Financial Status

    Amount Authorized

    Estimated expenditures thru 8/28/64

    Funds Committed

    Funds Remaining

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Technical Status

    The engineering progress report for the month

of August 1964 is attached.

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GROUP 1

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Progress Report
Black and White Films

August 1964

During the subject period, work has continued on the three areas previously described, that is, screening of materials, mechanism studies, and equipment design and construction. In addition, a new process has been discovered and investigated.

1. Screening of Materials. The screening of dyes and pigments has continued, with about fifty dye-binder combinations being tested. Of these, three dyes showed good color changes, and were also heat locked. Twenty samples showed good color changes, but did not heat lock (i. e. were not made immune to further photoreaction by heating). Some of these, in fact, reversed the color change on heating. Twenty-seven samples showed no color change or only slight color change on illumination.

Comparison of a series of binders was started. Carbosets 511, 514, and 525, all of which are acrylic resins, were compared using a series of dyes. In most cases the results were similar in all three binders, but in some cases the same dye behaved differently in the different Carboset resins. The conditions for heat locking the Carboset formulations seem to be the same as for polystyrene, that is, heating for 30 minutes at $120^{\circ}C$.

An attempt was made to produce an opaque film by loading with TiO_2. When sufficient TiO_2 was used to render the film opaque, it caused a grainy appearance and also decreased the speed of the films.

2. New Process. A process was discovered which utilizes a film consisting of a complex between pyrene, dichlorodicyanobenzoquinone (DDQ) and iodoform in polystyrene. When this film is irradiated with light, it turns black in the irradiated areas. This process seems to be somewhat slower than the dye decolorizing process, but gives excellent contrast and definition. The effect of changes in concentration of the various components was investigated, and an optimum combination determined. There seems to be no way to render the images permanent as yet. However, if the images are protected by a yellow filter, such as Kodak Wratten #15, excellent protection is obtained. The slides protected in this way can be projected in the 500 watt projector for over ten minutes with no trace of deterioration of the image.

I saw the black image produced by the DDQ above. ~~It~~ From a visual viewpoint it was very interesting indeed. It was however very slow. SPX, 9-22-64

-2-

3. <u>Mechanism Studies.</u> Several spectra of the type described previously have been obtained. These will be compared with the spectra produced when the dyes are caused to undergo chemical reactions, to see if the effects of the photoreaction can be duplicated.

4. <u>Equipment.</u> The slide carrier has been completed and is being checked out and calibrated. A scanning monochromator with a photomultiplier readout is being used with the slide carrier to monitor the data.

5. <u>Plans for September.</u> The optical set-up for the slide carrier will be improved. The illumination of the active area of the slide carrier is not sufficiently uniform, and will have to be improved. The output of the photomultiplier is not sufficiently linear, so some trouble-shooting and perhaps some electronic equipment construction will be required. When this has been completed, quantitative studies on the rates of the photoreactions will be started.

Concurrently, work will proceed on the screening program, with emphasis on the role of the binder, so as to find an optimum binder-solvent system for the more polar dyes. Sufficient data is being accumulated so that the correlation of reactivity and structure will be commenced.

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Non-Reversible Color - Study

25X1

Contract No.

Progress Report No. 1

Financial Status   25X1

     Amount Authorized

     Estimated expenditures
          thru 7/31/64

     Funds Committed

     Funds Remaining

Technical Status

     The engineering progress report for the month

of July 1964 is attached.

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8/6/64

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Progress Report
Non-Reversible Color

July 1964

Work on this project was commenced on July 8, upon receipt of authorization. This report covers the period July 8 - July 31, and each subsequent report will cover a calendar month.

During the subject period, effort has been expended on 1) screening of materials, including dyes, photosensitive materials and binders, 2) initiation of mechanism studies, and 3) calibration and design of equipment.

1.   <u>Screening of Materials</u>. Twelve pigments were obtained from General Aniline and Film and from Allied Chemical Corp. These pigments are in the oil-soluble and spirit-soluble classes, in black, blue or brown. Films of the dyes were made up in each of three binders: polystyrene, saran and Carboset 511. The Carboset is a more polar material than the other two and should act as a vehicle for dyes too polar to remain in solution in polystyrene. It also forms smoother films than we have been able to obtain with saran. The photosensitive material for the first series of tests was iodoform. Four of the dyes gave usable color changes in 30 seconds of exposure to a 500 watt projector, when dissolved in polystyrene or in saran. In Carboset, three of the same dyes gave similar results.

A comparison was made between iodoform as the photosensitive agent, and trichloromethyl-sulfonylchloride (TCSC). The four dyes giving positive results with iodoform, as well as two others and the previously studied indophenol blue were tested. Of these seven dyes, two gave positive results with TCSC. When this comparison was repeated in Carboset, none of the dyes gave positive results with TCSC. The successful use of TCSC in polystyrene indicates that the reaction can occur with reagents quite different than iodoform. The end product of the use of TCSC is usually a pink color, rather than the yellow of iodoform. One of the objectives of the project is to find a reagent whose end product is colorless.

A series of tests were run to determine the heating conditions to be used after exposure of the film needed to protect the film from further photo-bleaching in the projector. Thirty minutes of heating at 120° or fifteen at 130° gave excellent protection to dyes in combination with iodoform in a polystyrene film, 5% iodoform by weight.

Several other dyes have been ordered, and will be similarly tested when received. As the work progresses, correlations between the structures of the dyes and their reactivity (or non-reactivity) will be made.

2.   Mechanism Studies.   The initial mechanism studies consist of the determination of the changes in the absorption spectrum of the dye due to the photoreaction.   A typical set of spectra is shown in the figure.   The increase in transmission at long wavelengths corresponds to bleaching of the dye, while the decrease at short wavelengths is due to the darkening of the iodoform.   We plan to obtain similar curves for all reactive dyes, and to compare the effects of various photosensitive agents.   We then plan to react the dyes with various reagents, such as oxidizing and reducing agents, to see if the photoreacted spectra can be duplicated.

3.   Equipment.   Light sources used on the project include 500 watt and 300 watt tungsten sources, a 100 watt mercury lamp, and a 150 watt xenon lamp.   The 500 watt tungsten source is used routinely, with the other types to be used to evaluate the effectiveness of the low wavelength end of the spectrum. The 500 watt tungsten lamp has been calibrated to give the total energy per unit area incident on the plane of exposure.   The wavelength distribution of this source is approximately known from previous work.

A slide carrier is being designed to provide a continuous smooth motion of the slide in the exposure plane, so as to provide a continuous variation in time of exposure across the slide.   This will provide more accurate rate of color change data than is available by the present method of discrete exposures.

4.   Plans for August.   Work is to be continued in all of the areas outlined above.   Several more dyes will be screened, new photosensitive agents will be tried, and new binders will also be evaluated.   Mechanism studies will be continued as discussed in Section 2.   The slide carrier will be completed, and its use compared with present techniques.   No unexpected problems have been encountered as yet.

Brilliant Oil Blue
Iodoform
in Polystyrene
exposures made
with 300w tungsten

unexposed
10 sec.
30 sec.
10 min.
4 min
15 min.

wavelength mu

15 min
4 min
1 min
30 sec.
10 sec.
700
unexposed

90
80
70
60
50
40
30
20
10
900